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# Indium phthalocyanines and naphthalocyanines for optical limiting

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Dedicated to Professor A.B.P. Lever on the occasion of his 65th birthday

## Contents

## Abstract

In this work, an overview of optical limiting processes in phthalocyanines is given. The synthesis and the linear and nonlinear optical properties of a series of highly soluble axially substituted indium(III) phthalocyanines and the analogous series of naphthalocyanines are

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described. Several techniques, such as transient absorption, Z-scan, and degenerate four-wave mixing (DFWM), were used for assessing the optical properties and optical limiting performance of the indium phthalo- and naphthalocyanines. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The phthalocyanines, naphthalocyanines and their metal complexes have been the subject of many investigations over the years. These materials are important industrial dyes. More recently, they have been found to have useful optical and electrical properties and have also become important functional materials for several different applications [1]. Recently, we have been investigating the nonlinear optical applications of these complexes.

There is a considerable interest in nonlinear optical (NLO) materials to manipulate optical signals in optical communication and optical signal processing applications. New materials are needed for high speed electro-optical and all-optical switches and modulators. Organic nonlinear optical materials can be used for high density data storage, phase conjugation, holography, and spatial light modulation. Organic materials, like the phthalocyanines, can have picosecond response times, large non-linearities, low losses, and small dielectric constants. They also have the potential to be processed and fabricated into wave guides and integrated optical devices more easily and economically than inorganic materials.

Among the nonlinear optical applications of phthalocyanines, optical limiting has been particularly promising. Phthalocyanine optical limiting materials have been reviewed [2]. A lead tetrakis(cumylphenoxy)phthalocyanine [(CP)$_4$PcPb], described by Shirk et al. [3] and a tetra-*tert*-butyl substituted Chloroindium(III) phthalocyanine described by Perry et al. [4] are known to be very good materials for optical limiting. Recently, our groups have made new approaches [5,6] to optimizing indium phthalocyanines for optical limiting using different axial and peripheral substituents and expanding the ring to naphthalocyanines. We will review here the synthesis of different peripheral and axially substituted Indium phthalo- and naphthalocyanines, and describe how the resulting changes in the steric and electronic properties alter their linear and nonlinear optical properties.

## 2. Optical limiters

Optical limiters have a transmission that varies with the incident intensity of light. The transmission is high at normal light intensities and low for intense beams. Ideally, this intensity dependent transmission can limit the transmitted light intensity so that it is always below some maximum value, hence the name. This is useful

to protect elements that are sensitive to sudden high-intensity light, such as optical elements, sensors and the human eye. All-optical devices possess an enormous advantage over mechanical or electro-optical devices since they can provide the response speeds that are required for such applications. A device with a slow response time would be useless for protecting optical elements because the reduction of transmission would occur after the device is damaged. Thus the better optical limiting materials usually rely on a third-order or pseudo-third-order response, such as nonlinear absorption or refraction. A nonlinear absorption where the material's absorbency increases with the intensity of the incident light is obviously useful for optical limiting.

One mechanism that has been especially effective at producing large nonlinear absorption is a sequential two-photon absorption. A simple energy level diagram where this process can occur is shown in Fig. 1.

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 $\sigma_{ex}$ that is larger than the ground state cross section $\sigma_0$, 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 [7]. Thus, 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. This sequential two-photon absorption process has also been called reverse saturable absorption (RSA) or excited state absorption [2,8–10].

Some criteria necessary for a large, positive nonlinear absorption are apparent including a large excited state cross section $\sigma_{ex}$ and a large difference between the ground and excited state absorption cross sections ($\sigma_{ex} - \sigma_0$). A variety of organic and organometallic materials have been found to fulfil these conditions. Materials known to possess a positive nonlinear absorption in the visible besides phthalocyanines [2,3,11–14] include porphyrins [10,15–17], organometallic cluster compounds [18–23], and other materials [24–33].
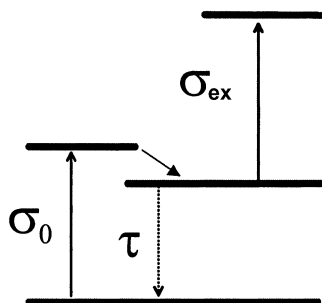


Fig. 1. Lowest energy levels of a simple nonlinear absorber.

The condition that $\sigma_{ex}$ is greater than $\sigma_0$ is necessary, but it is not sufficient for a useful optical limiting material. 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 non-linearity 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 is highly soluble in common organic solvents, or it is a pure liquid or a solid film that can be prepared with good optical quality.

Many of the dyes used as nonlinear absorbers tend to aggregate at high concentration. The intermolecular interactions caused by aggregation are often deleterious. Extensive aggregation needs to be suppressed by modification of the molecular shape and electronic effects to suppress the van der Waals interaction between the large $\pi$-systems. In addition, the material must possess a high linear transmission and a large nonlinear absorption over a broad spectral bandwidth as well as a high threshold for damage. Furthermore, the nonlinear absorption must appear with a sub-nanosecond response time. Meeting all these criteria is a significant chemical challenge in synthesis. Among the large number of nonlinear absorbers that have been identified, a lead phthalocyanine (PcPb), ($\beta$-cumylphenoxy)$_4$PbPc [3,34], the chloro-indium phthalocyanines (PcInCl), ($t$-Bu)$_4$PcInCl [4] (see Fig. 2) and some substituted porphyrins [10,15] have been used to construct optical limiters that approached the characteristics necessary for a practical device.

lead-phthalocyanine

chloro-indium phthalocyanine

tetra-($\beta$-cumylphenoxy) lead-phthalocyanine

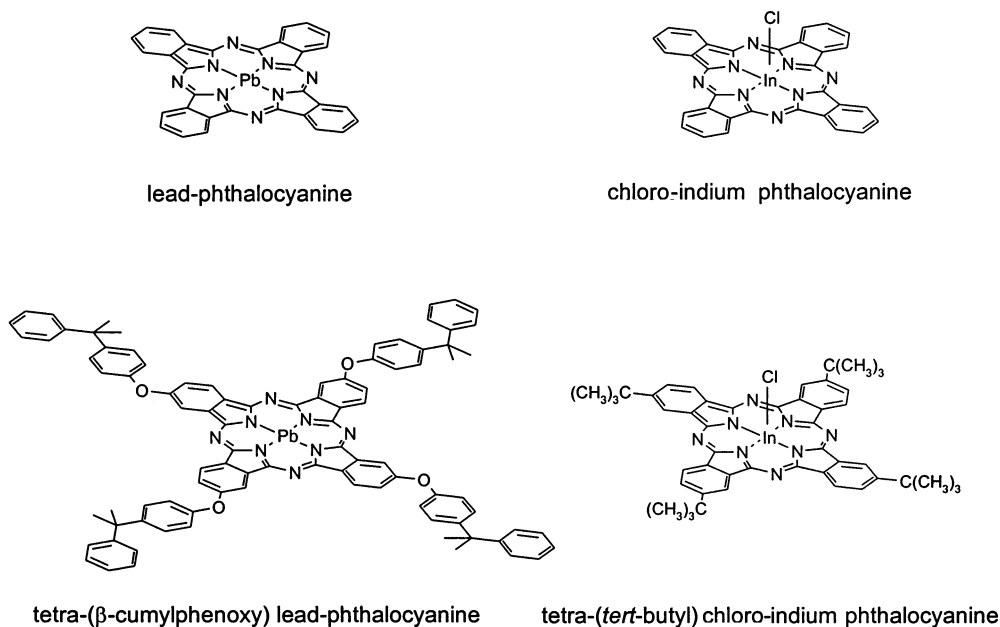tetra-($tert$-butyl) chloro-indium phthalocyanine

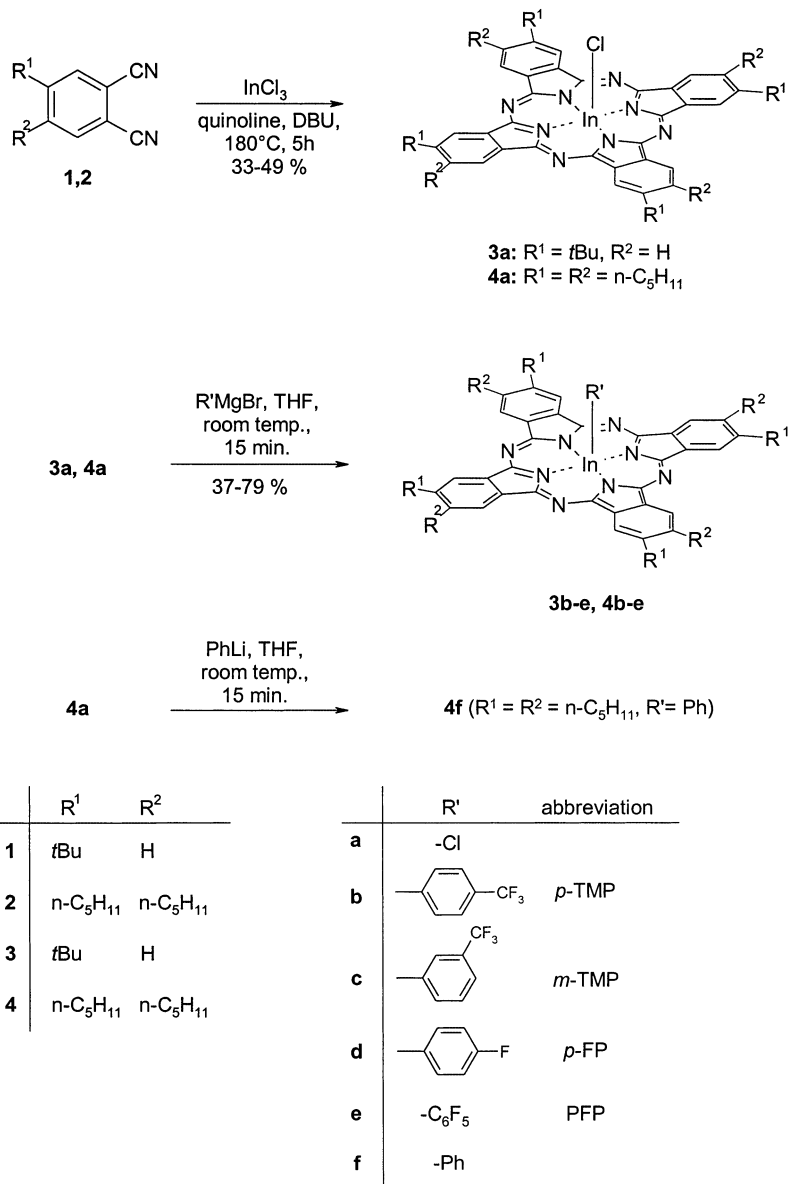Fig. 2. Metallophthalocyanines for optical limiting.

Modifying a strong nonlinear absorber like these phthalocyanines should result in interesting new optical limiting materials. The heavy metals are most promising as the central metals because they enhance the intersystem crossing rates. This is desirable since triplet lifetimes are usually orders of magnitude longer than singlet lifetimes and the triplet-triplet transition can be more strongly absorbing than the corresponding singlet-singlet transition [41]. Indium is useful as a central metal because in the normal oxidation state, it can be axially substituted.

## 3. Indium phthalocyanines for optical limiting

The diversity of the structural features [35] of phthalocyanines means that tuning of the optical properties can be achieved by synthetic variations. For example, about 70 different elements have been incorporated into the phthalocyanine core, some of them with different oxidation states. In addition there are, depending upon the oxidation state of the central metal, one or two sites which can coordinate a variety of axial ligands. The introduction of different peripheral substituents, and there are many possibilities to alter the substitution pattern, can influence [36–38] the electronic absorption spectra and potentially the optical non-linearities. The substitution pattern can also alter other factors, which may affect optical non-linearities, such as the crystal structure, and the thin film fabrication techniques [2].

We systematically synthesized different indium phthalocyanines and studied the effect of axial substitution on the nonlinear optical properties and specifically on the optical limiting behavior of the complexes. Axial substitution can have several effects. It can alter the electronic structure of the phthalocyanine, it can introduce a dipole moment perpendicular to the macrocycle, and, via steric effects, it can also alter the spatial relationships between neighboring molecules and thus the magnitude of the intermolecular interactions. Large axial substituents can alter the packing of the molecules in the solid state and the tendency to aggregate in solution. Each of these effects can influence the NLO properties. A correlation between the magnitude of the third-order non-linear optical susceptibility tensor $\chi^{(3)}$ for third harmonic generation (THG) experiments [2] and axial substitution has been noted. It has been suggested that this effect may be associated with the variation in the permanent dipole moment in these materials. The effect of a varying dipole moment on an excited state absorption in these phthalocyanines has not been previously studied.

In 1998, we prepared for the first time highly soluble axially substituted alkyl- and arylphthalocyaninatoindium compounds [5]. Later, a variety of soluble naphthalocyaninato-indium compounds were synthesized [42]. This allowed us to study the effects of different axial substituent patterns on the optical properties of these materials. Among the soluble, axially substituted phthalocyanines we investigated, the phthalocyaninato indium(III) complexes bearing different peripheral alkyl substituents (see Scheme 1) were found to have large positive non-linear absorption coefficients.

**3a:** $R^1$ = *t*Bu, $R^2$ = H
**4a:** $R^1$ = $R^2$ = n-$C_5H_{11}$

**3b-e, 4b-e**

**4f** ($R^1$ = $R^2$ = n-$C_5H_{11}$, R'= Ph)

|   | $R^1$ | $R^2$ |
|---|-------|-------|
| **1** | *t*Bu | H |
| **2** | n-$C_5H_{11}$ | n-$C_5H_{11}$ |
| **3** | *t*Bu | H |
| **4** | n-$C_5H_{11}$ | n-$C_5H_{11}$ |

|   | R' | abbreviation |
|---|-----|-------------|
| **a** | -Cl | |
| **b** | —⟨⟩—$CF_3$ | *p*-TMP |
| **c** | —⟨⟩ $CF_3$ | *m*-TMP |
| **d** | —⟨⟩—F | *p*-FP |
| **e** | -$C_6F_5$ | PFP |
| **f** | -Ph | |

Scheme 1. Synthesis of the chloro- and aryl(phthalocyaninato)indium(III) complexes.

Later Heckmann [5,39] synthesized the corresponding axially substituted bromo and iodo phthalocyanines. The aim was to investigate if there is an enhancement of the intersystem crossing rate by substituting the axial chlorine atom by the heavier iodine. As expected they only showed slightly different absorption characteristics at normal light intensities. However, in transient absorption studies, we found that the

intersystem crossing rate of the iodo compound was nearly twice as fast as the chloro compound and the high quantum yield for triplet formation was maintained. Some axially substituted alkyl indium phthalocyanines were also synthesized, but they were unstable when exposed to daylight [39].

The aryl substituted indium phthalocyanines were prepared from the soluble chlorophthalocyaninatoindium(III) complexes **3a** and **4a** given in Scheme 1 by reacting them with R-MgBr as also shown in Scheme 1 [5]. The resulting compounds are the stable σ-bonded arylphthalocyaninatoindium(III) complexes **3b**–**e** and **4b**–**e**. The high solubility of the complexes **3a**–**e** and **4a**–**f** besides the influence of the peripheral substituents, is considered to be derived from the large dipole moments present, which are due to the strongly electron withdrawing axially ligands and from the lower tendency of axially substituted phthalocyaninato complexes to form aggregates. The dipole moments of the compounds **3a** and **3b** have been measured. They are quite large, between 10 and 15 Debye [43]. The axially $p$-(trifluoromethyl)phenyl ($p$-TMP, **3b**) and pentafluorophenyl (PFP, **3e**) substituted ($t$-Bu)$_4$PcIn complexes were found to exhibit a higher solubility than their chloro analogue and to have higher non-linear absorption coefficients, lower limiting thresholds and a lower transmission at high fluences.

## 3.1. Linear optical properties

We published a comparative study of the optical properties of ($t$-Bu)$_4$PcInCl (**3a**) with several axially aryl substituted analogues [6]. Compared with the chloro ligand, the larger aryl substituents, $p$-TMP (**3b**) and PFP (**3e**), can reduce the intermolecular interaction in the solid state and inhibit the tendency to aggregate in solution. Variations in the electron withdrawing properties of the substituted aryl ligands should lead to variations in the electronic properties including the ground state dipole moment. The UV–vis spectra of ($t$-Bu)$_4$PcInCl (**3a**) and $p$-(trifluoromethyl)phenyl-indium(III) tetra-$tert$-butyl-phthalocyanine [($t$-Bu)$_4$PcIn($p$-TMP), **3b**] are shown in Fig. 3. In dilute solution **3a** and **3b** are characterized by the strong Q band near 697 nm and the strong B band near 340 nm that are typical of metal phthalocyanines. There is less than a 1 nm shift in the position of the Q-band between **3a** and **3b**. The region of interest for optical limiting is in the high transmission region between 420 and 600 nm, between the intense Q and B bands. The nonlinear optical experiments were performed on quite concentrated samples; the concentrations were between 22 and 45 mmol l$^{-1}$ in CHCl$_3$.

In Fig. 3 we compare the electronic spectra of the chloro compound ($t$-Bu)$_4$PcInCl (**3a**) and the axially ($p$-trifluoromethyl)phenyl substituted derivative **3b** in diluted and the more highly concentrated chloroform solutions.

Aggregation in the phthalocyanines usually results in spectral shifts and changes in the band shapes [40]. The observed band shapes change only a little over a concentration range from about 10$^{-5}$ to greater than 10 mmol l$^{-1}$ in each material. This was most prominent in the concentrated ($t$-Bu)$_4$PcInCl (**3a**) sample and less so in the aryl substituted compounds. Qualitatively, this is spectral evidence that the aggregation is less extensive in these axially substituted materials than in, for
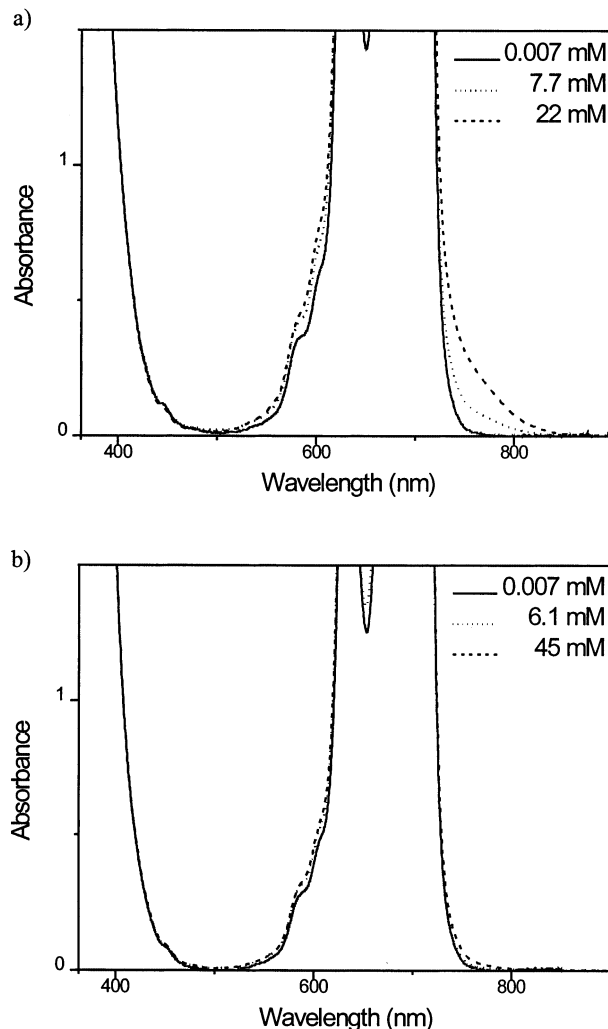
Fig. 3. Normalized absorption spectra of (a) $(t\text{-Bu})_4\text{PcInCl}$ (**3a**) and (b) $(t\text{-Bu})_4\text{PcIn}(p\text{TMP})$ (**3b**) at different concentrations in $\text{CHCl}_3$.

example the tetra(cumylphenoxy) substituted phthalocyanines. The latter showed more pronounced spectral changes over this range of concentrations [40]. We conclude that the intermolecular interactions are weaker in the aryl substituted compounds compared with the chloro compound.

The spectra of the aryl substituted complexes **3a**, **3b** and **3e** in the region of interest for limiting, 450–620 nm, are shown on an expanded scale in Fig. 4. Each of these materials has a high transmission near 500 nm. $(t\text{-Bu})_4\text{PcInCl}$ (**3a**) has an absorption cross section of less than $2 \times 10^{-18}$ cm$^2$, corresponding to a molar extinction coefficient of less than 500 l/(mol × cm), over the range 460–533 nm,
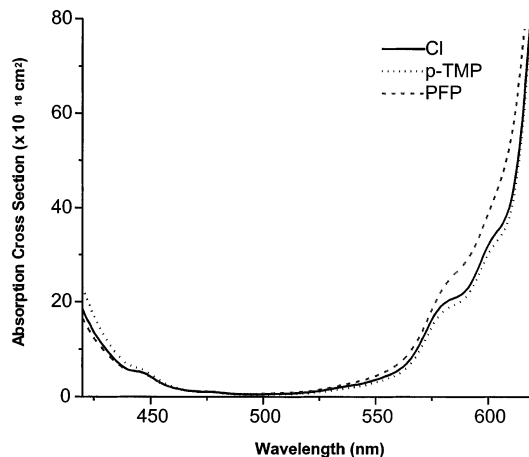
Fig. 4. Ground state absorption cross sections for $(t\text{-Bu})_4\text{PcInCl}$ (**3a**), $(t\text{-Bu})_4\text{PcIn}(p\text{-TMP})$ (**3b**), and $(t\text{-Bu})_4\text{PcIn}(\text{PFP})$ (**3e**) in the region where each has a large nonlinear absorption.

even in concentrated solutions. The measured absorption coefficients of the aryl substituted materials vary by less than $\pm 30\%$ from that found in $(t\text{-Bu})_4\text{PcInCl}$ over the range 430–610 nm. In the range 500–610 nm where the nonlinear optical studies were performed, $(t\text{-Bu})_4\text{PcIn}(\text{PFP})$ (**3e**) had a systematically larger absorption coefficient and $(t\text{-Bu})_4\text{PcIn}(p\text{-TMP})$ (**3b**) had a slightly smaller ground state absorption than the $(t\text{-Bu})_4\text{PcInCl}$ (**3a**) solution.

## 3.2. Nonlinear optical properties

The photophysical processes and their dynamics in the different axially substituted materials have been determined from transient absorption spectra, DFWM measurements with co- and cross-polarized beams, Z-scan experiments, nanosecond nonlinear transmission and f/5 optical limiting experiments. The latter two experiments are similar. In nonlinear transmission experiments, all the transmitted light is collected whereas in the optical limiter experiments an f/5 exit aperture is used [6]. The latter are usually carried to higher input energies.

For each of the compounds $(t\text{-Bu})_4\text{PcInCl}$ (**3a**), $(t\text{-Bu})_4\text{PcIn}(p\text{-TMP})$ (**3b**) and $(t\text{-Bu})_4\text{PcIn}(\text{PFP})$ (**3e**), transient absorption studies showed that excitation in the visible gave an initially excited singlet state that evolved into a triplet state with a quantum yield near one and an intersystem crossing time of about 300 ps. With the relatively fast intersystem crossing rate, the triplet absorption spectrum will dominate the nanosecond nonlinear response. The triplet state lifetime was found to be long compared to 5 ns. In both the triplet and singlet state, the excited state cross section is larger than that of the ground state. The triplet excited state absorption spectrum, measured in a transient absorption study is shown in Fig. 5 and compared with the ground state absorption spectrum. The material is a reverse saturable absorber over the range between 420 and about 620 nm.
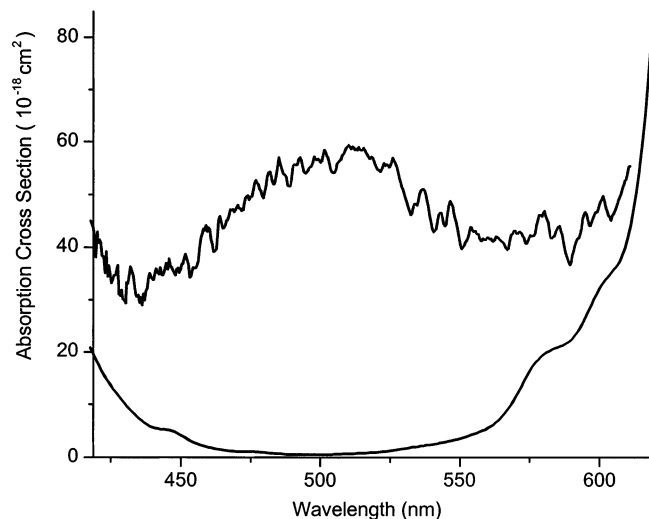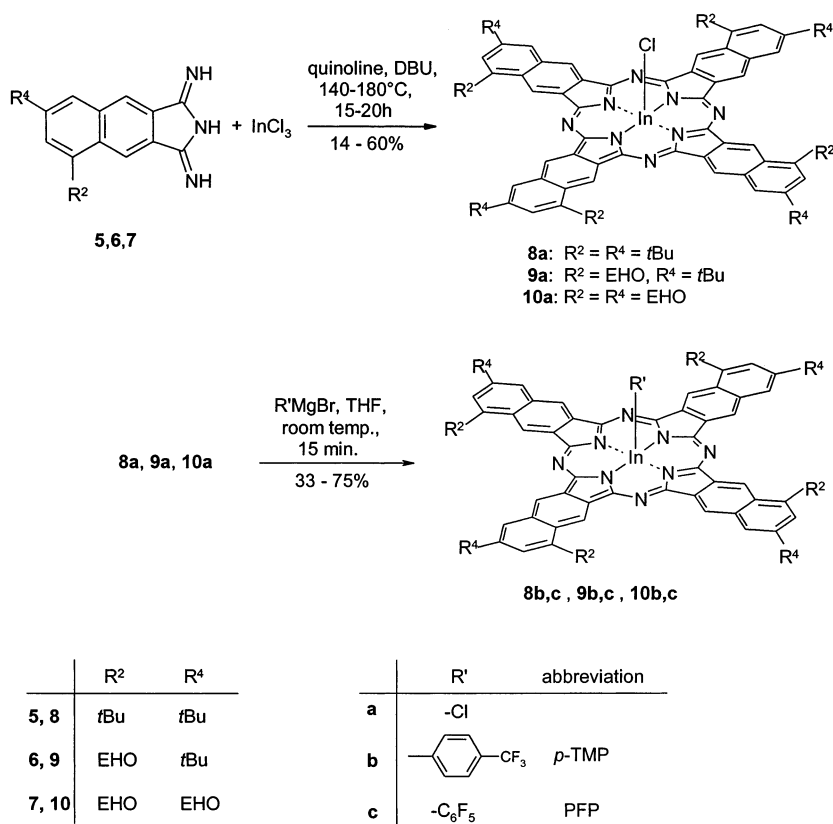
Fig. 5. The ground and excited triplet state absorption spectra of $(t\text{-Bu})_4$PcInCl (**3a**).

Z-Scan measurements at 532 nm revealed that the complexes $(t\text{-Bu})_4$PcInCl (**3a**), $(t\text{-Bu})_4$PcIn($p$-TMP) (**3b**) and $(t\text{-Bu})_4$PcIn(PFP) (**3e**) are reverse saturable absorbers at this wavelength. The Z-Scan measurements [6] also showed that there are both a negative (thermal) and a positive (excited state) contribution to the nonlinear refractive response of these materials. The nonlinear absorption coefficients, $\alpha_{\text{NL}}$, were derived from measurements of the nanosecond nonlinear transmission between 500 and 620 nm. The values of $\alpha_{\text{NL}}$ were large for all of the complexes, but those for the aryl substituted phthalocyanines were larger over much of this range. These larger $\alpha_{\text{NL}}$ resulted in lower thresholds for optical limiting in the aryl substituted materials. The threshold is defined as the input energy required to achieve $T_{(F)} = 0.5 \times T_{(F=0)}$; it is measured as a function of the wavelength of the incident light. The higher thresholds observed in the range 500 to about 530 nm were traced to a small ground state absorption cross section, $\sigma_0$. It was less than $2 \times 10^{-18}$ cm$^2$ in this range.

Optical limiting experiments were conducted using f/5 optics. For samples that had a transmission of 0.81 at 532 nm, the $(t\text{-Bu})_4$PcIn($p$-TMP) (**3b**) material had a lower threshold for optical limiting than did $(t\text{-Bu})_4$PcInCl (**3a**), by about a factor of 2. At intermediate fluences, the transmission was substantially less than that of the chloro substituted material. Experimentally, the $(t\text{-Bu})_4$PcIn($p$-TMP) (**3b**) showed a lower transmission than $(t\text{-Bu})_4$PcInCl (**3a**) at all fluences above the threshold except at very high fluences where the difference between the materials decreased. The PFP substituted material, $(t\text{-Bu})_4$PcIn(PFP) (**3e**), also had a lower transmission at any given fluence than $(t\text{-Bu})_4$PcInCl, so it was a better limiter material. However, it was susceptible to photochemical degradation at high fluences.

## 4. Indium naphthalocyanines for optical limiting

The axially substituted indium(III) phthalocyanines described above represent one of the more promising classes of materials for practical optical limiters. However, in some applications, the strong absorption in the red, due to the Q-band absorption of these phthalocyanines is undesirable. It would be useful to have a limiting material that has a high transmission in the red and yellow region of the spectrum. Actually, it would be best to have a material that is nearly transparent across the visible but, until this is achieved, it is useful to have materials with alternative transmission windows. In order to obtain materials that have different transmission windows, we investigated the linear benzannellated species, the indium-(III) 2,3-naphthalocyanines. These materials have their Q-band absorption shifted to the near IR and have transmission windows in the yellow and red (530 to 650 nm) region of the spectrum. The extended $\pi$-electron system in naphthalocyanines is an effective means to shift the Q-band absorption to the red. There are a larger number of substitutable positions on the periphery of the naphthalocyanine core, so



| | $R^2$ | $R^4$ | | | R' | abbreviation |
|---|---|---|---|---|---|---|
| **5, 8** | *t*Bu | *t*Bu | **a** | | -Cl | |
| **6, 9** | EHO | *t*Bu | **b** | | —CF$_3$ | *p*-TMP |
| **7, 10** | EHO | EHO | **c** | | -C$_6$F$_5$ | PFP |

Scheme 2. Synthesis of the chloro- and aryl(naphthalocyaninato)indium(III) complexes.

the variety of peripherally substituted naphthalocyanines is in potentially quite large. Unfortunately, these larger ring systems are in general less stable and less soluble than their phthalocyanine analogues. This could be partly due to steric effects of the substituents on the stability of the complexes, especially when the substituent is adjacent to the naphthalocyanine core. In any case, the number of soluble naphthalocyanines actually synthesized is small compared to the phthalocyanines [45].

We synthesized a variety of peripheral unsymmetrically substituted indium(III) naphthalocyanines (see Scheme 2) [42]. The goal was to see if these materials possessed both a red shifted Q-band and the nonlinear absorption properties and the good stability and solubility of substituted phthalocyanines. Electron donating substituents like *tert*-butyl (*t*-Bu) and 2-ethylhexyloxy (EHO) groups were used to enhance the solubility of the complexes and the red shift of the Q-band absorption. As we shall discuss below, in the naphthalocyanines we synthesized, the red shift of the Q-band is sufficiently large so that it is no longer in the visible. The hue of these naphthalocyanines is determined by the B-band absorption in the blue region of the spectrum. To the eye, the color of dilute solutions of these dyes is a greenish-yellow to orange.

The general scheme for their synthesis is depicted in Scheme 2; it is analogous to the phthalocyanine synthesis shown in Scheme 1. However, the precursors for ring formation are the more reactive diiminoisoindolines **5**–**7** derived from the corresponding dinitriles via catalytic addition of ammonia [42].

The resulting chloro indium(III)-2,4-octa-(*tert*-butyl)-naphthalocyanine [(*t*-Bu)$_8$NcInCl (**8a**)], chloro indium(III)-4-tetra-(*tert*-butyl)-2-tetra-(2-ethylhexyloxy)-naphthalocyanine [(*t*-Bu)$_4$(EHO)$_4$NcInCl (**9a**)] and chloro indium(III)-2,4-octa-(2-ethylhexyloxy)-naphthalocyanine [(EHO)$_8$NcInCl (**10a**)] are much more soluble in organic solvents like chloroform and toluene than, e.g. the tetra-(*tert*-
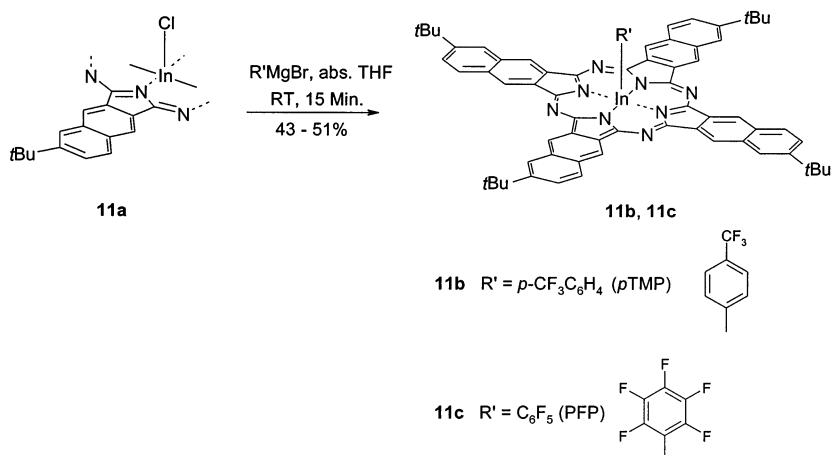


Scheme 3. Synthesis of axially fluoroaryl substituted indium naphthalocyanines **11b** and **11c**.

butyl) substituted chloroindium(III)-naphthalocyanine **11a** due to steric crowding of eight bulky substituents.

Each of these octasubstituted chloro complexes are reacted with the appropriate Grignard reagent to give the axially (*p*-trifluoromethyl)phenyl (*p*-TMP; **8b**, **9b**, **10b**) and perfluoro-phenyl (PFP; **8c**, **9c**, **10c**) substituted compound, as described in the second part of Scheme 2. These fluoroaryl groups were chosen because of the good performance of the corresponding indium phthalocyanines described above. The syntheses of the unsymmetrical isoindoline precursors **5**, **6** and **7** will be published elsewhere [42].

In addition to the indium naphthalocyanines described above we also investigated the tetra-*tert*-butyl substituted indium complexes **11a**–**c**. The synthesis of these compounds is given in Scheme 3 [44]. Again the chloro precursor **11a** is reacted with the appropriate Grignard reagent to give **11b** and **11c**.

## 4.1. Linear optical properties

The absorption spectrum of a dilute solution of $(t\text{-Bu})_8\text{NcInCl}$ (**9a**) in chloroform is shown in Fig. 6. It is typical of these naphthalocyanines. The principal features are the Q-band at 823 nm with some satellite bands. The red shift of the Q-band is sufficiently large so that it does not absorb in the visible region. The visible absorption is due to a wing of the B-band encroaching from the blue. There is a good window of transparency between about 480 and 660 nm.

In order to be useful in an optical limiter, a material must be soluble at concentrations of at least 10 to 50 mM without deleterious aggregation. The initial screening of materials consisted of a qualitative study of the spectra as a function
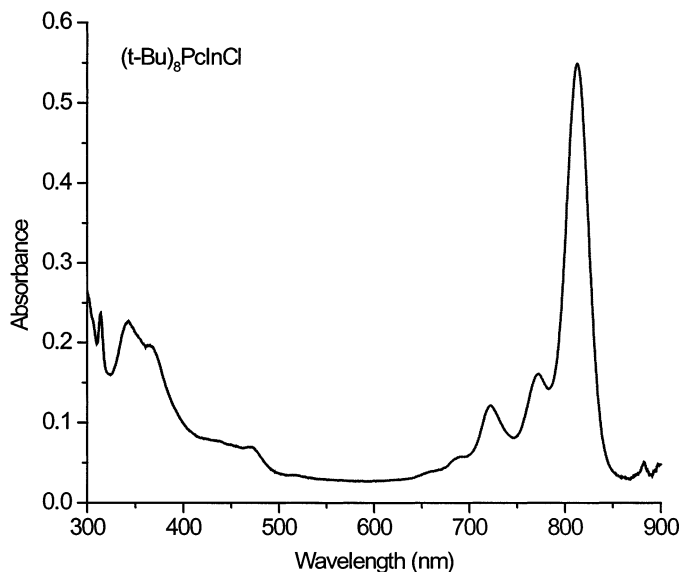


Fig. 6. Absorption spectra of a dilute solution of $(t\text{-Bu})_8\text{NcInCl}$ (**9a**) in CHCl$_3$.

of concentration. The spectra, described below, were quite useful in outlining how the propensity to aggregate in solution varied with the different axial and peripheral substituents.

Fig. 7 shows the absorption spectra of different concentrations of ($t$-Bu)$_4$(EHO)$_4$NcInCl (**9a**), and ($t$-Bu)$_4$(EHO)$_4$NcIn($p$-TMP) (**9b**) in chloroform. The path length for these spectra varies from 200 μm for the low concentrations to 32 μm for the spectra above 10 mM. With these high concentrations, the maxima of the Q- and B-bands are off scale.
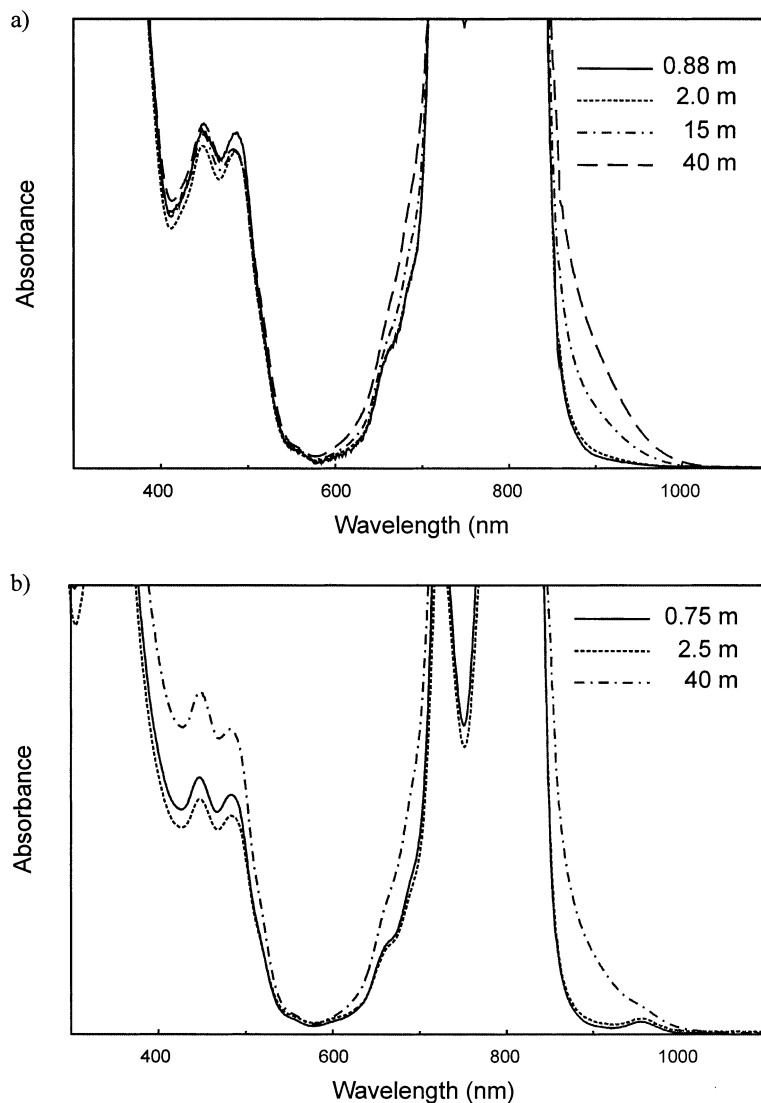
a)

| | |
|---|---|
| —————— | 0.88 m |
| ·············· | 2.0 m |
| —·—·—·— | 15 m |
| — — — — | 40 m |

Absorbance

Wavelength (nm

b)

| | |
|---|---|
| —————— | 0.75 m |
| ·············· | 2.5 m |
| —·—·—·— | 40 m |

Absorbance

Wavelength (nm)

Fig. 7. Normalized absorption spectra of (a, top) ($t$-Bu)$_4$(EHO)$_4$NcInCl (**9a**) and (b, bottom) ($t$-Bu)$_4$(EHO)$_4$NcIn($p$-TMP) (**9b**) at different concentrations in CHCl$_3$.

The spectrum of the *p*-TMP substituted **9b** is similar to the spectrum of the chloro compound **9a** in both the band shape and the peak positions. The Q-bands are slightly shifted to the blue from 823 nm for the chloro compound **9a** to 820 nm for the *p*-TMP substituted **9b**. The influence of changing the axial ligands on the spectra of the more dilute solutions is minimal. As with the analogous phthalocyanines, one can observe the change in band shape with increasing concentration of the solutions. Aggregation can be seen by a change of the band shape near the Q-band maximum including a change with the appearance of a shoulder around 900 nm and a broadening of the Q-band with increasing concentration seen in Fig. 7b). The transparent window in the UV–vis spectrum is slightly smaller for **9b** in comparison to **9a**.

The spectra in Fig. 7 were recorded on freshly prepared solutions. Initially, even in solutions as concentrated as 40 mM, the spectra of **9a** and **9b** are similar. However, the spectrum of the chloro substituted material evolved with time. In solutions of the chloro compound, **9a**, an increasing shoulder near 900 nm was observed after 2 days. In contrast, the solution of the *p*-TMP substituted **9b** remained unchanged, even after two months. Apparently, in concentrated solutions of the chloro compound **9a**, a slow aggregation occurs with time. This is suppressed in the *p*-TMP substituted naphthalocyanine.

The spectrum of a concentrated liquid and a pure solid film of ($t$-Bu)$_4$(EHO)$_4$NcIn($p$-TMP) (**9b**) are compared to a diluted solution (0.006 mmol l$^{-1}$) in Fig. 8. The liquid film was prepared from a highly concentrated (or saturated) solution of the naphthalocyanine and a highly viscous solvent, usually a polyglycol. It was sheared on a slide to form a thin film. In the very concentrated materials, the absorption bands are broadened and shifted slightly as expected, but the spectrum still shows a Q band near that of the monomer.
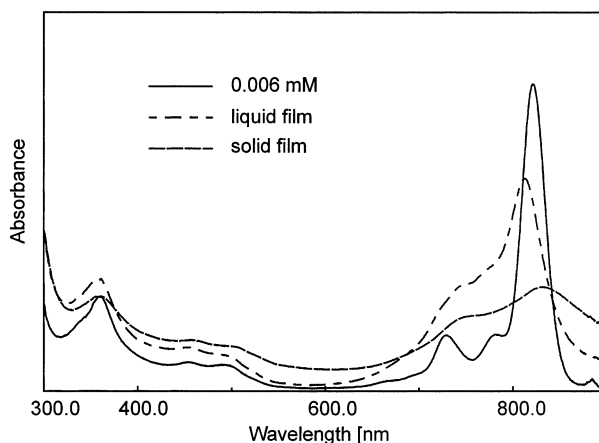


Fig. 8. UV–vis spectra of a liquid and a solid film of ($t$-Bu)$_4$(EHO)$_4$NcIn($p$-TMP) **9b** compared to that of a dilute solution.

It appears that in the naphthalocyanines, as in the phthalocyanine compounds, there is a better suppression of the intermolecular interactions in the axially aryl substituted macrocycles **9b** than the axially substituted chloro compound **9a**. The perfluoro substituted $(t\text{-Bu})_4(EHO)_4NcIn(PFP)$ **9c** was even more soluble than **9b**.

The tetra *tert*-butyl substituted materials showed a stronger tendency to aggregate than the mixed octa substituted materials. Fig. 9 shows the UV–vis spectrum of $(t\text{-Bu})_4NcInCl$ (**11a**) in $CHCl_3$ at different concentrations. The dilute solution ($\sim 0.007$ mmol $l^{-1}$) shows the Q-band at 807 nm. It was yellow green to the eye. Even at a comparatively low concentration (0.039 mmol $l^{-1}$), the spectrum near the Q-band becomes split, consistent with the formation of an aggregate. This is even more apparent in the 2.4 mmol $l^{-1}$ solution. The B-band at 350 nm is also split and there is a broad absorption plateau that restricts the width of the transparent region in the visible.

The spectra of the octa ethylhexyloxy $(EHO)_8$ substituted complexes were also recorded at several concentrations. At low concentrations, the spectra were similar to those of the mixed $(t\text{-Bu})_4(EHO)_4$ complexes. The Q-band in **10a** is shifted 2.5 nm to the red of that in **9a**. To the eye, the color of the diluted solutions was almost the same yellow–orange. In the spectra of a 15 mmol $l^{-1}$ solution, it was clear that the octa ethylhexyloxy $(EHO)_8$ substituted complex, **10a**, had a larger tendency for aggregation than the mixed substituent material, **9a**. We did find that the solubility of the axially aryl substituted indium naphthalocyanines **9b** and **10b** was higher in solvents of medium polarity than the chloro substituted complexes **9a** and **10a**.
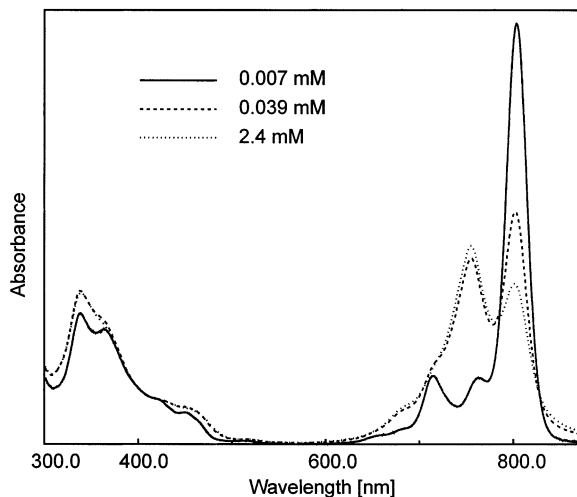


Fig. 9. UV–vis spectra of $(t\text{-Bu})_4NcInCl$ (**11a**) at different concentrations.

Finally, the octa-*tert*-butyl substituted indium naphthalocyanines **8a**–**c** were also synthesized according to Scheme 2. The UV–vis spectrum in $CHCl_3$ of $(t\text{-Bu})_8NcInCl$ **8a** had a Q-band maximum at 812.5 nm, which is 5.5 nm higher than the tetra-*tert*-butyl substituted compound $(t\text{-Bu})_4NcInCl$ **11a**. Apparently, both the

steric or the electron donating effect of four additional *tert*-butyl groups is insufficient to cause a large shift. The shape of the B-band absorption of **11a** was similar to that of the tetra substituted compound **8a**, but the maximum is shifted 5–6 nm to longer wavelength. The color of dilute solutions is also yellow–green.

The UV–vis spectra of $(t\text{-Bu})_8\text{NcIn}(p\text{-TMP})$ (**8b**) and $(t\text{-Bu})_8\text{NcIn}(\text{PFP})$ (**8c**) are all similar. Fig. 10 shows the UV–vis spectra of $(t\text{-Bu})_8\text{NcIn}(p\text{-TMP})$ (**8b**) in CHCl$_3$ at different concentrations and of a thin film.

The Q-band of **8b** is only 3 nm shifted to the blue in comparison with **11a** (see Fig. 9), but this and the stronger absorption in the blue makes a smaller window of high transparency in the visible. Only small shifts were observed between substitution of the chloro and the perfluoro aryl substituent. Dilute solutions of **8b** and **8c** were also of green–yellow color. The materials with eight *tert*-butyl substituents show a low tendency to aggregate.
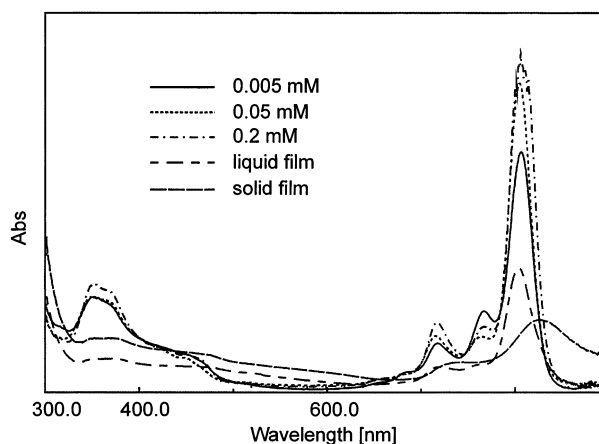


Fig. 10. UV–vis spectra of $(t\text{-Bu})_8\text{NcIn}(p\text{-TMP})$ (**8b**) at different concentrations and as a liquid and solid film.

Fig. 11 shows the spectra of several concentrations as well as the spectrum of a thin film of $(t\text{-Bu})_4\text{NcIn}(p\text{-TMP})$ (**11b**). The spectra of $(t\text{-Bu})_4\text{NcIn}(\text{PFP})$ (**11c**) are quite similar to those of the *p*-TMP substituted **11b**. The Q-band of **11b** is only 0.5 nm blue shifted from that in $(t\text{-Bu})_4\text{NcInCl}$ (**11a**). We observe that in the tetra-(*tert*-butyl) materials, as in the other naphthalocyanines, the axial ligands synthesized here do not alter the spectra of the complexes very much.

If one compares the spectra of concentrated solutions of the tetra substituted $(t\text{-Bu})_4\text{NcIn}(p\text{-TMP})$, **11b,** with the spectra of the chloro compound, **11a,** shown in Fig. 9, it can be seen that in this case, there is less aggregation with an aryl substituent rather than a chloro substituent in the axial position.

In summary, the spectra of dilute solution of all the naphthalocyanine materials synthesized were very similar. The observed shifts in the absorption bands were only a few nanometers at most for any of the peripheral and axial substituents used. The basic electronic structure of the molecules seems insensitive to the axial
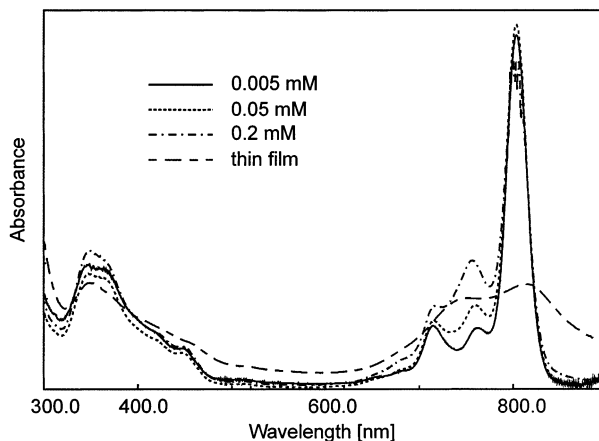
Fig. 11. UV–vis spectra of $(t\text{-Bu})_4\text{NcIn}(p\text{-TMP})$ (**11b**) at different concentrations and as a thin film.

substituents in both the indium phthalocyanines and naphthalocyanines. However, the concentration dependence of the spectra show that in the naphthalocyanines, the axial and peripheral substituents do have a substantial effect on propensities to aggregate. Qualitatively, the naphthalocyanines aggregated more strongly than the phthalocyanines, as expected. A smaller tendency to aggregate was found in the materials with eight (rather than four) peripheral substituents and with the larger aryl axial substituents. This is certainly consistent with expectations from steric considerations. For the octa substituted materials the *tert*-butyl peripheral substituents were more effective at blocking aggregation than the ethyl-hexyloxy (EHO) substituents. The mixed substituent, $(t\text{-Bu})_4(\text{EHO})_4$, materials with a large axial substituent showed very little evidence for aggregation even in a very concentrated and a pure film. It is reasonable that the greater entropy in the mixed substituents both enhances the solubility and inhibits aggregation.

### 4.2. Nonlinear optical properties

The nonlinear optical properties, photophysical processes and their dynamics in the different naphthalocyanine materials were studied using the same techniques as were used for the phthalocyanines. Degenerate four-wave mixing (DFWM) on $(t\text{-Bu})_4\text{NcInCl}$ (**11a**) measurements on a $4 \times 10^{-4}$ M solution at 720 nm are shown in Fig. 12. There is a large signal, due to the excited state population, that exhibits both a fast ($< 10$ ps) and a slow ($> 10$ ns) relaxation time. The intersystem crossing and orientational relaxation times of the analogous indium phthalocyanines are 200 to 300 ps [6]. It does not seem likely that they are the origin of the $> 10$ ps relaxation time. On the other hand, aggregation is known to drastically shorten the relaxation times of phthalocyanines [46]. Since the spectrum, in Fig. 9, showed that this sample consisted both of the monomer and aggregate, it seems reasonable to assign the two observed decay times to a fast decay of the excited
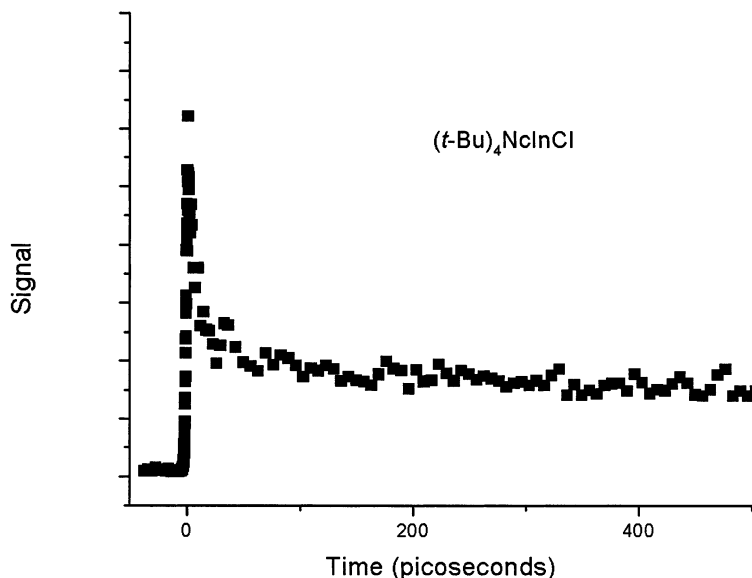
Fig. 12. Degenerate four-wave mixing (DFWM) on ($t$-Bu)$_4$NcInCl (**11a**) at 720 nm.

state in the aggregate and a long lived excited state in the monomer respectively. The sample slowly degraded with irradiation during this experiment.

We performed open aperature Z-scans on a 2.4 mM solution of ($t$-Bu)$_4$NcInCl at 640 nm, in the transmission window of this material. This is shown in Fig. 13. It shows the transmission of the material as a function of distance from the focus of an f/5 optical system.

The light intensity increases and the transmission falls as the sample approaches the focus. This is the signature of a positive nonlinear absorption coefficient and a material that sometimes called a 'reverse saturable absorber'. The apparent nonlinear absorption constant for nanosecond pulses derived from this Z-scan was about a factor of 5 or so or more smaller than is typical for a good nonlinear absorber. A relatively small nonlinear absorption coefficient is consistent with the fact that a fraction of the material in solution is in the form of aggregates with short excited-state relaxation times. This, of course, means that the material is not as effective as an optical limiting material at these concentrations. We also performed Z-scans on a 2.4 mM solution of the corresponding iodo-indium naphthalocyanine, ($t$-Bu)$_4$NcInI. It was also a reverse saturable absorber with an apparent nonlinear absorption constant comparable to the chloro material. The spectrum of this material showed considerable aggregation. The iodo material showed photochemical decomposition upon extensive irradiation.

In order to reduce the deleterious effects of aggregation on the nonlinear absorption of the indium naphthalocyanines, we proceeded to study the materials with eight peripheral substituents. The octa ethylhexyloxy (EHO)$_8$ substituted complexes showed a stronger tendency to aggregate than the mixed, ($t$-Bu)$_4$(EHO)$_4$,
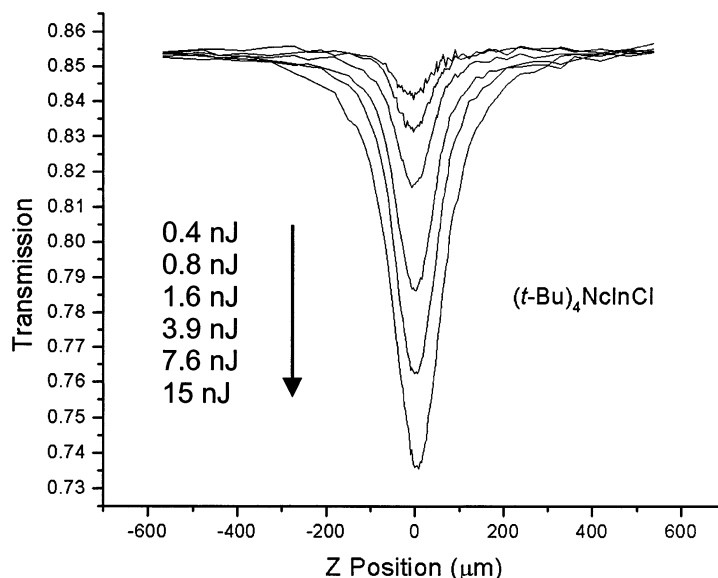
Fig. 13. Z-Scan of a 2.4 mM solution of (*t*-Bu)$_4$NcInCl (**11a**) at 640 nm; the incident energy is increasing from 0.4 nJ to 15 nJ.

substituent materials. Figs. 8 and 9 show that the latter materials showed very little aggregation, even in quite concentrated solution. Among these, the material with an axial *para*-trifluoromethyl phenyl group (*p*-TMP) was more resistant to aggregation over time. Z-scans were performed on (*t*-Bu)$_4$(EHO)$_4$NcIn(*p*-TMP) (**9b**) at different wavelengths within the transmission window of this naphthalocyanine. We verified that this material is a nonlinear absorber between 550 and 640 nm.

Nonlinear transmission and optical limiting experiments were also performed at 550 and at 580 nm on a sample that was in a 21 μm cell at 40 mM. From these studies and assuming the intersystem crossing rate is fast and the quantum yield for formation of the triplet is ca. 1, we found excited state cross sections of $1.2 \pm 0.3 \times 10^{-16}$ cm$^2$ at 550 nm and $1.2 \pm 0.3 \times 10^{-16}$ cm$^2$ at 580 nm. These measured excited state cross sections are larger than those typically observed in the phthalocyanines.

Optical limiting by a 21 μm thick sample of 40 mM sample of (*t*-Bu)$_4$(EHO)$_4$NcIn(*p*-TMP) (**9b**) is shown in Fig. 14.

The initial transmission of this naphthalocyanine sample was 76%, (the sample window transmission was 92.5%, so that the total transmission of the nonlinear cell was 70%). The observed threshold, where the sample transmission has dropped to 50% of the low intensity transmission, was $10 \pm 2$ nJ. The change in slope at $\sim 10$ μJ ($10^4$ nJ in the figure) input energy corresponded to the formation of a photochemical product with a lifetime longer than a few seconds. Such changes are usually evidence for damage to the limiter material. However, unlike other examples of photochemical damage to limiter materials, this damage recovers. At least partial reformation of the original material with a time constant of a few minutes to an hour or so was observed.
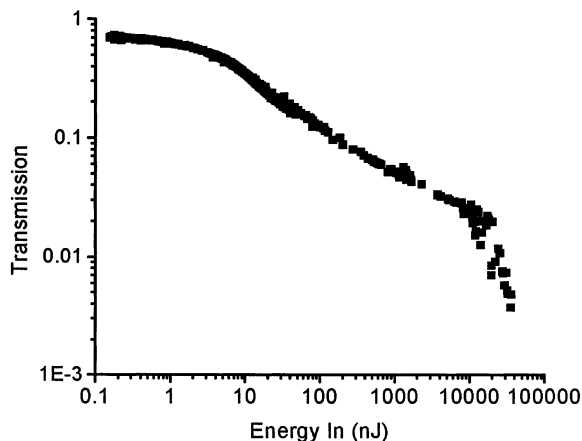
Fig. 14. Optical limiting by a 40 mM sample of $(t\text{-Bu})_4(\text{EHO})_4\text{NcIn}(p\text{-TMP})$ (**9b**) at 580 nm; the sample was 21 μm thick and had $T_0 = 76\%$.

The picosecond characterization of the naphthalocyanine photophysics, consisted of transient absorption spectra and DFWM measurements on the octa substituted materials. These picosecond experiments were at intensities sufficient to induce photochemical changes similar to those observed at high intensities in the nanosecond experiments. Consequently, it was not possible to determine the relaxation and intersystem crossing rates quantitatively. However, we were able to record the spectrum of one of the photochemical intermediates and observe the decay. The recovery was observed a CW white light source at specific times after the sample was irradiated. The photoproduct exhibits a broad band absorption between 530 and 650 nm. Part of the absorption decays with a lifetime of $\sim 15$ min. The rest decays away in about 12 h.

## 5. Summary and conclusions

The synthesis of a variety of new aryl substituted indium phthalocyanines and naphthalocyanines was described. Preliminary optical studies were performed on most of these materials. Among the phthalocyanines, the materials with tetra-*tert*-butyl peripheral substitution and (*para*-trifluoromethyl)phenyl-, and perfluorophenyl- axial substituents (**11b–c**) were found to be sufficiently soluble to be potentially useful for optical limiting. The phthalocyanines with the bulky substituents showed little evidence for aggregation even at high concentrations.

For each of the indium phthalocyanines studied, excitation in the visible initially gives an excited singlet state that evolves into a triplet state with a quantum yield near 1 and an intersystem crossing time of about 300 ps. The triplet state lifetime is much longer than 10 ns. This means that the nanosecond nonlinear absorption is dominated by the absorption from an orientationally averaged triplet state. An

axially iodo substituted phthalocyanine did show a faster intersystem crossing rate, by about a factor of two. This, gives a small improvement in the nanosecond nonlinear absorption and optical limiting. In both the triplet and singlet state, the excited state cross section is larger than that in the ground state over the range between 420 and about 620 nm.

The refractive index of the triplet state of the indium phthalocyanines was found to be larger than that of the ground state at 532 and 590 nm, so an increase in index is seen upon excitation. The thermal index changes that occur after excitation cause a decrease in the index. The sum of these two effects give the observed refractive index changes in these materials a complex time and spatial dependence.

The indium naphthalocyanines aggregate more extensively than do the phthalocyanines, as might be expected from the larger van der Waals forces. We showed that it was possible to inhibit the aggregation with eight peripheral *tert*-butyl (*t*-Bu, **8a**–**c**) or a mixture of (*t*-Bu) and ethylhexyloxy (EHO) substituents (**9a**–**c**). Even with the of $(t\text{-Bu})_4(\text{EHO})_4$ material, a bulky *p*-TMP axial substituent was required to inhibit the slow aggregation of prepared solutions.

Two distinctly different excited state lifetimes were observed after excitation of some of these naphthalocyanines. Apparently, the excited state of a monomer has a lifetime longer than 10 ns, consistent with that found in the indium phthalocyanines. The short lifetime was observed when aggregates were present in the solution. Presumably, the excited state of the aggregates has a lifetime of less than 10 ps. We expect that the initial excitation of the monomer is into a singlet state, with an evolution into a triplet state as in the phthalocyanines. However, we could not determine the intersystem crossing rate.

The nonlinear absorption coefficients, $\alpha_{NL}$, were measured between 500 and 620 nm for the phthalocyanines and out to 640 nm for the naphthalocyanines. In the phthalocynanines, the aryl substituted materials generally had larger values of $\alpha_{NL}$ that increased with increasing wavelength over the range 500 to 590 nm. This larger $\alpha_{NL}$ resulted in lower thresholds for optical limiting in the aryl substituted phthalocyanine materials. The higher thresholds observed in the range 500 to about 530 nm were traced to a small ground state absorption cross section, $\sigma_0$. It was less than $2 \times 10^{-18}$ cm$^2$ in this range.

Among the indium phthalocyanine materials studied here, the nonlinear absorption and refraction properties were surprisingly robust to axial substitution. A substantial variation in the axial substituent had only a small effect on the excited state absorption cross section and the associated nonlinear absorption coefficient. In the naphthalocyanines, variations in both the axial and peripheral substituents caused only minimal changes in the spectra of the monomers. Changes in the substituents did change the extent of aggregation in the naphthalocyanines, presumably via steric effects. Since the aggregates of the indium naphthalocyanines appear to have very short upper state life times, changing the substituents did cause large differences in the observed nanosecond nonlinear absorption coefficients and optical limiting. Inhibiting aggregation in the naphthalocyanines clearly enhanced the nanosecond nonlinear absorption coefficients and the efficiency of optical limiters based on these materials.

The indium phthalocyanines are useful materials for optical limiters in the 480–580 nm range. They have a high photopic and scotopic transmission. The nonlinear absorption in the indium phthalocyanines is reasonably well described by the simple model shown in Fig. 1. Among the different phthalocyanines examined here the ($t$-Bu)$_4$PcIn($p$-TMP) material had a lower threshold than ($t$-Bu)$_4$PcInCl, and a better photochemical stability than ($t$-Bu)$_4$PcIn(PFP).

Expanding the ring structure to a naphthalocyanine was a successful strategy to move the transmission window and the range of effective optical limiting to the red (520–660 nm). However, in order to be effective limiters, the naphthalocyanine materials must be designed to resist aggregation. Among the naphthalocyanines, ($t$-Bu)$_4$(EHO)$_4$NcIn($p$-TMP) (**9b**) 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 has 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, could be useful in practical limiters.

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