

Review

Soluble axially substituted phthalocyanines: Synthesis and nonlinear optical response

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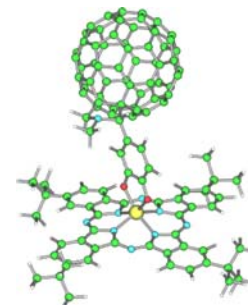
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This review lays special stress on describing the synthesis of soluble axially substituted or bridged indium, gallium and titanium phthalocyanine complexes and their electronic absorption characteristics, photophysical and nonlinear optical properties. The enhanced solubility of the axially substituted or bridged phthalocyanine monomers and dimers, compared to the chloro analogues, shows that the usual tendency of phthalocyanines to form aggregates can be effectively suppressed by axial substitution. Axial substitution in phthalocyanine complexes has provoked 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. The nanosecond nonlinear absorption and the optical limiting 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.

Graphical Abstract

A series of highly soluble axially substituted and bridged phthalocyanine and naphthalocyanine complexes have been synthesized. Axial substitution in phthalocyanine complexes has provoked 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.



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1. Introduction

New nonlinear optical (NLO) materials [1, 2], especially organic and polymeric ones, are essential to the development of optoelectronic technologies e.g. optical communications, high speed electro-optical information processing, high density data storage, spatial light modulation and switch, and have continued to be at the forefront of research activities since the mid-1980s. There are a large number of articles already concerning the design and preparation of these new materials over the past three decades, however, only a few appropriate nonlinear materials required for the practical NLO devices, including optical limiting devices, are available till now. There has thus been a continuing pronounced interest in the search for novel NLO materials coupled with desirable physical properties and a low cost. Design and preparation of new nonlinear optical active materials required for the practical NLO devices are still a challenge for many scientists.

Phthalocyanines (Pcs) are widely investigated organic compounds for many high-technology applications, such as nonlinear optics, photoconductivity, electrochromic and electroluminescent displays, photovoltaic cells, low-dimensional conductors, chemical sensors, optical data storage, recordable compact discs (CDs) and digital versatile discs (DVDs), Langmuir-Blodgett films, liquid crystals, photodynamic cancer therapy, rectifying devices, and others [3]. Among these applications, third-order optical nonlinearities are of main interest due to their highly delocalized π -electron systems giving rise to strong nonlinearities, ultrafast response times, and tremendous structural flexibility [4]. The introduction of a diversity of peripheral or axial substituents, metal insertion, variation of the main structure of the macrocycle and extension of conjugation have strong influence on the solubility, electronic absorption characteristics and the NLO responses of Pcs [3–5]. The measurement techniques used in the NLO studies of these materials are mainly electric field induced second harmonic generation (EFISH) [6], Z-scan methods [7], third-harmonic generation (THG) [8] and degenerate four-wave mixing (DFWM) [9].

It is well-known that many of the dyes including phthalocyanines used as nonlinear materials 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 [10]. 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 [11]. The tendency to aggregation is mainly dependent on the structural characteristics of the phthalocyanine compounds, e.g. in axial-substituted phthalocyanine compounds the intermolecular interactions are weaker than those without

such substituents. A lot of 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 (OL) 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 [12–14]. Moreover, axial substituents in Pcs influence favorably nonlinear optical absorption for the presence of a dipole moment perpendicular to the macrocycle in the axially substituted phthalocyanines [12, 14, 15]. The exploitation of the chemical reactivity of the bond M-Cl [M = Ga³⁺, In³⁺] and M=O [M = Ti⁴⁺ etc.] bonds, can allow the preparation of a series of highly soluble axially substituted and bridged Pc-complexes. Although there are several excellent review papers already concerned the NLO (including optical limiting) properties of phthalocyanines in the recent several years [4, 12, 16], but much less work has been done for emphasis on the synthesis of these compounds in these review articles, to which many readers have strong interests. For this reason, this review would be focused on the synthesis, electronic absorption characteristics, photophysical and nonlinear optical properties of axially substituted or bridged phthalocyanine complexes.

2. Synthesis and electronic absorption characteristics of phthalocyanines

The syntheses of phthalocyanines usually involve the cyclotetramerization of benzoic acid or its derivatives e.g. phthalic anhydride, phthalimide, phthalamide, o-cyanobenzamide or phthalonitrile [17]. In some cases where the formation of the macrocycle is inhibited, the higher reactivity of the isoindolinediimines can be used. Nonnucleophilic hindered base like 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) are very efficient reagents for the cyclotetramerization of phthalonitrile in solution, yielding substituted metal-free phthalocyanines (PcH₂), and metal phthalocyanine (in the presence of metallic salts such as InCl₃, CuAc₂, TiCl₄ and others). Symmetrically disubstituted precursors, for example, lead to either 1, 4, 8, 11, 15, 18, 22, 25- or 2, 3, 9, 10, 16, 17, 23, 24-octasubstituted Pcs. The accepted notation of these substitution positions is 1, 4- or 2, 3-, respectively. Asymmetric precursors, such as 3-, 4-, 3,4- or 3,5-substituted phthalonitriles, form a mixture of structural isomers during the cyclotetramerization as shown in Fig. 1. Hanack *et al.* [18] have been the first to separate the four isomers of tetrasubstituted Pcs and to undertake careful, detailed and extensive NMR-studies probing the influence of isomers on the NMR spectra of the Pcs. The NMR-spectrum of an isomeric mixture is only somewhat different from the pure

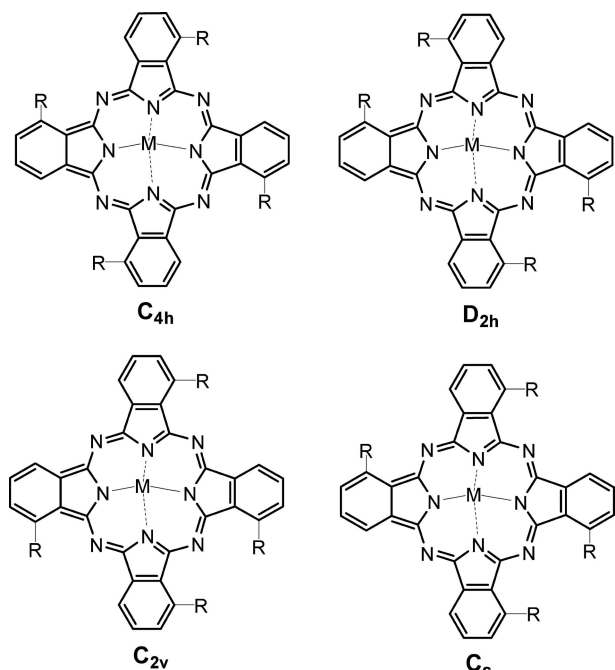


Figure 1 The four structural isomers of 1,(4)-tetrasubstituted phthalocyanine.

isomers, but it is still possible to draw definite conclusions about the structure. 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. Similarly, benzoannulated phthalocyanines like 1,2-naphthalocyanine (1,2-Nc), 2,3-naphthalocyanine (2,3-Nc), anthracenocyanine (2,3-Ac) and phenanthrenocyanine (9,10-Phc) can be prepared from the respective benzoannulated phthalonitrile under conditions similar to the synthesis of phthalocyanines.

The electronic absorption spectra of phthalocyanines 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 cm²/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 $E_u(a_{1u}^1 e_g^1)$ 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 [19]. Intermolecular interactions like aggregation give rise to effects like band broadening, blue shift of the Q - and B -

bands or to an observed splitting of the Q -band [20]. 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.

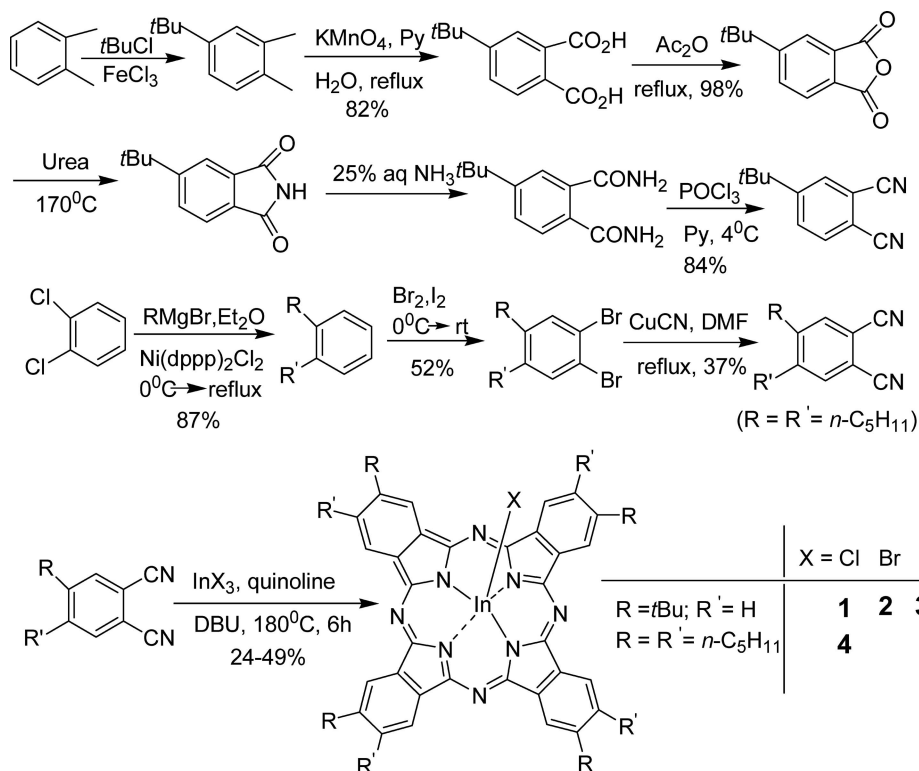
2.1. Indium phthalocyanines

2.1.1. Halogenoindium phthalocyanines

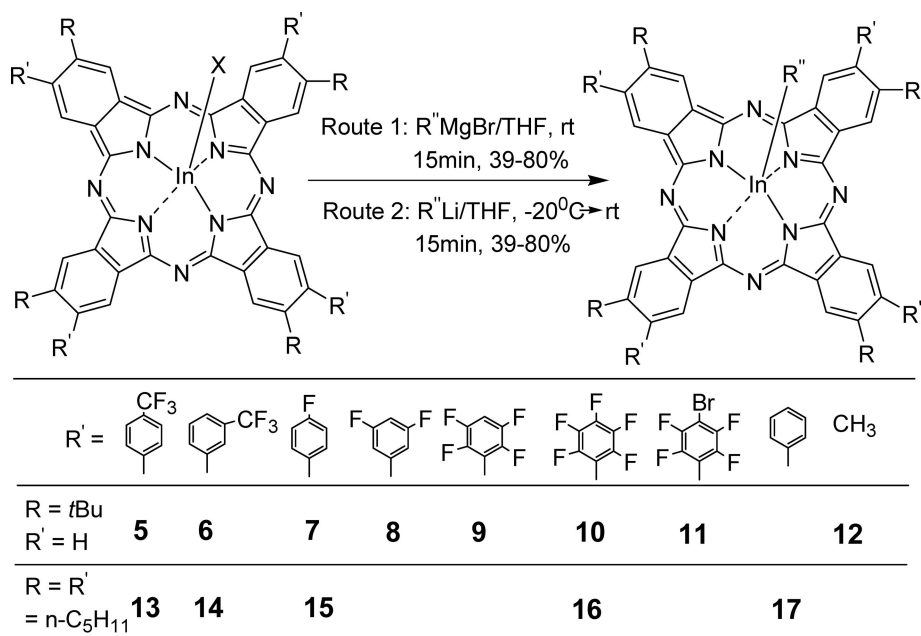
The synthetic route of halogenoindium phthalocyanines 1–4 is given in Scheme 1. The precursor of tetra-*tert*-butylphthalocyanines, 4-*tert*-butylphthalonitrile, is readily prepared starting from *o*-xylene in a six-step synthesis. Refinements to original synthetic route published by Luk'yanets [21] were developed in the group of Hanack [22]. The highly soluble complexes 1–4 were further purified by column chromatography and recrystallization before structural characterization. If InF₃ was used as the indium(III) halide, the corresponding fluoroindium phthalocyanine could not be prepared [23]. As we discussed above, an important characteristic of tetrasubstituted phthalocyanines is their high solubility. It's reasoned that the axial ligand inhibits intermolecular interactions in addition to the effect of asymmetric substitution. Aggregation in Pcs usually results in spectral shifts and changes in the band shapes. In the case of *t*Bu₄PInCl, the observed band shapes in absorption spectra change only a little over a concentration range from about 10⁻³ mM to greater than 20 mM. The largest difference in band shape was a wing near 800 nm that appeared in the concentrated samples. In Pcs without an axial ligand, like for example tetrakis(cumylphenoxy) substituted Pcs, there are much more pronounced spectral changes at these concentrations, like a substantial absorption band shift of about 54 nm for the 2, (3)-substituted isomer, and a peak extinction change of about an order of magnitude between 10⁻⁶ and 10⁻² M [23]. Compared to unsubstituted PcInCl, a slight red shift of the Q -band ($\Delta \sim 7$ –13 nm) and the B -band ($\Delta \sim 2$ –4 nm) is observed in these alkyl-substituted complexes 1–4 due to the electron-donating effect of the alkyl groups causing a decrease of the HOMO-LUMO gap [24]. It seems, however, that the electronic structure of the macrocycle is not very sensitive to structural changes arising by halogen Cl, Br, I at the axial position. In addition, the reaction of *t*Bu₄PInCl towards anions like OH⁻, I⁻ and S²⁻ was also investigated [23]. The refluxing of *t*Bu₄PInCl with potassium iodide or sodium sulfide in methanol yielded the complexes 3 and [*t*Bu₄PcIn]₂S, respectively, whereas no reaction was observed by refluxing *t*Bu₄PInCl with ammonium hydroxide in pyridine. The stability of the chloroindium phthalocyanine towards hydrolysis [25] is in contrast to the formation of the dimer [*t*Bu₄PcIn]₂S containing a μ -sulfo bridge. The latter complex was not very stable, but still could be isolated as a crude product [23].

2.1.2. Aryl- and alkylindium phthalocyanines

In contrast to indium porphyrins, indium phthalocyanine with axial ligands other than chlorine has rarely been



Scheme 1 Synthesis of the halogenindium phthalocyanines and their precursors.



Scheme 2 Synthesis of aryl- and alkylindium phthalocyanines.

synthesized. Among the axial ligands used in indium porphyrin chemistry, there are aryl and alkyl, sulphinato, sulphonato as well as alkylthio ligands. Recently, the synthesis of the axially substituted indium phthalocyanines has been described by Hanack *et al.* [26]. Compared with the chloro ligand, aryl substituents will introduce steric crowding and should reduce the tendency to form aggregates. 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 *t*Bu₄PcInCl and *t*Bu₄PcIn(*p*-TMP) [*p*-TMP = *p*-trifluoromethylphenyl] were quite large being in the order of 10 Debye [27]. Scheme 2 gives the synthetic route of the aryl- and alkylindium phthalocyanines **5–17**. With Grignard compounds, R''MgBr, the conversion to the aryl

substituted complexes proceeded rapidly at room temperature. The monolithio reactants $R''Li$ were too reactive at this temperature, so that byproducts like dilithio phthalocyanine formed almost exclusively [23, 26]. The stability of the products of the reaction of chloroindium phthalocyanines with metalorganic reagents was strongly dependent on the nature of the aryl or alkyl group. The only alkyl group that gives a stable alkylium complex was the simplest one: methyl. Furthermore, the indium-carbon bond in methylindium phthalocyanine **12** was cleaved oxidatively by reacting it with solutions of Br_2 or I_2 . The reaction products are the halogenoindium phthalocyanine **2**, **3** and bromo- or iodomethane, respectively.

The influence of different axial substituents on the electronic structure of the macrocycles is very small. The UV/Vis data of aryl, alkyl and chloro substituted indium phthalocyanine complexes are summarized in Table I. The ground state absorption cross sections for **1**, **5**, **10** in the region of interest for optical limiting, 450–620 nm, are shown on an expanded scale in Fig. 2. Each of these materials has a high transmission near 500 nm. tBu_4PInCl has an absorption cross section of less than $2 \times 10^{-18} \text{ cm}^2$, corresponding to a molar extinction coefficient of less than 500 L/(mol.cm), over the range 460–533 nm, even in concentrated solutions [11, 23, 26]. The measured absorption coefficients of the aryl-substituted materials vary by less than $\pm 30\%$ from that found in tBu_4PInCl over the range 430–610 nm. In the range 500–610 nm where the NLO studies were performed, **10** had a systematically larger absorption coefficient and **5** had slightly smaller ground state absorption than the tBu_4PInCl solution [11].

2.2. Indium naphthalocyanines

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. 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. From the point view of practical applications, research was mainly focused on phthalocyanines rather than naphthalocyanine compounds, due to their much higher tendency to aggregate and thus lower solubility, and due to the more pronounced sensitivity of Ncs towards oxidation [28]. The difficulties in synthesizing the precursors needed for the preparation of naphthalocyanines and the lower stability of naphthalocyanines might be among the reasons for the relatively small body of work on these complexes. Strategies to solubilize Ncs thus involve the formation of tetra- or octasubstituted Ncs carrying alkyl- or alkoxy substituents. The Ncs shown in Fig. 3 illustrate the substitution patterns hitherto realized (with alkyl, alkoxy and alkylthio substituents): 3, 12, 21,

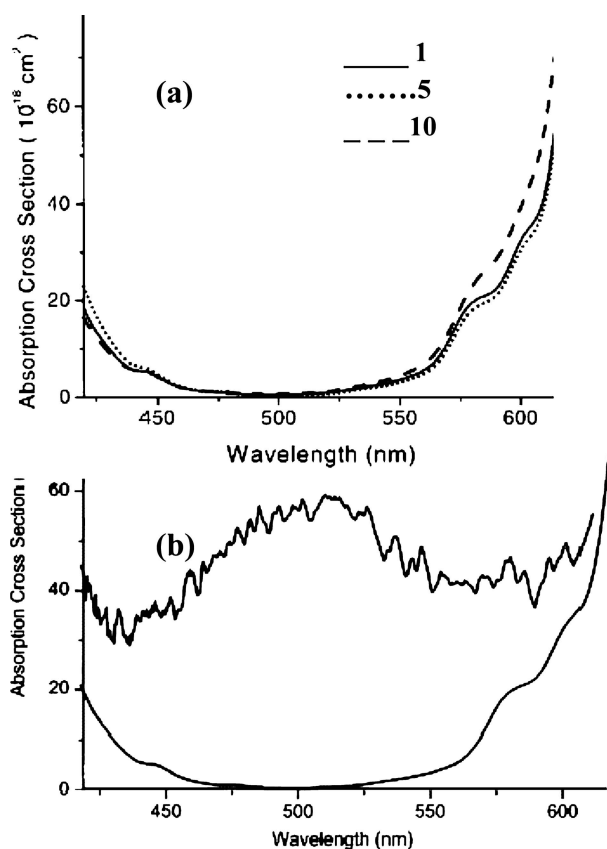


Figure 2 (a) Ground state absorption cross sections for **1**(—), **5**(.....) and **10**(---) in the region where each has a large nonlinear absorption; (b) The ground and excited state absorption spectra of **1**

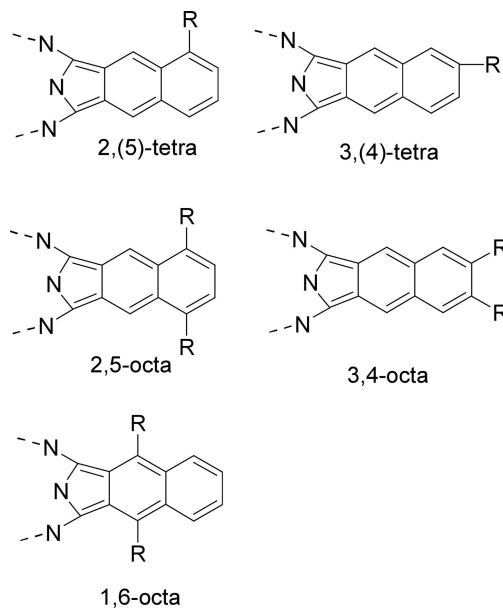


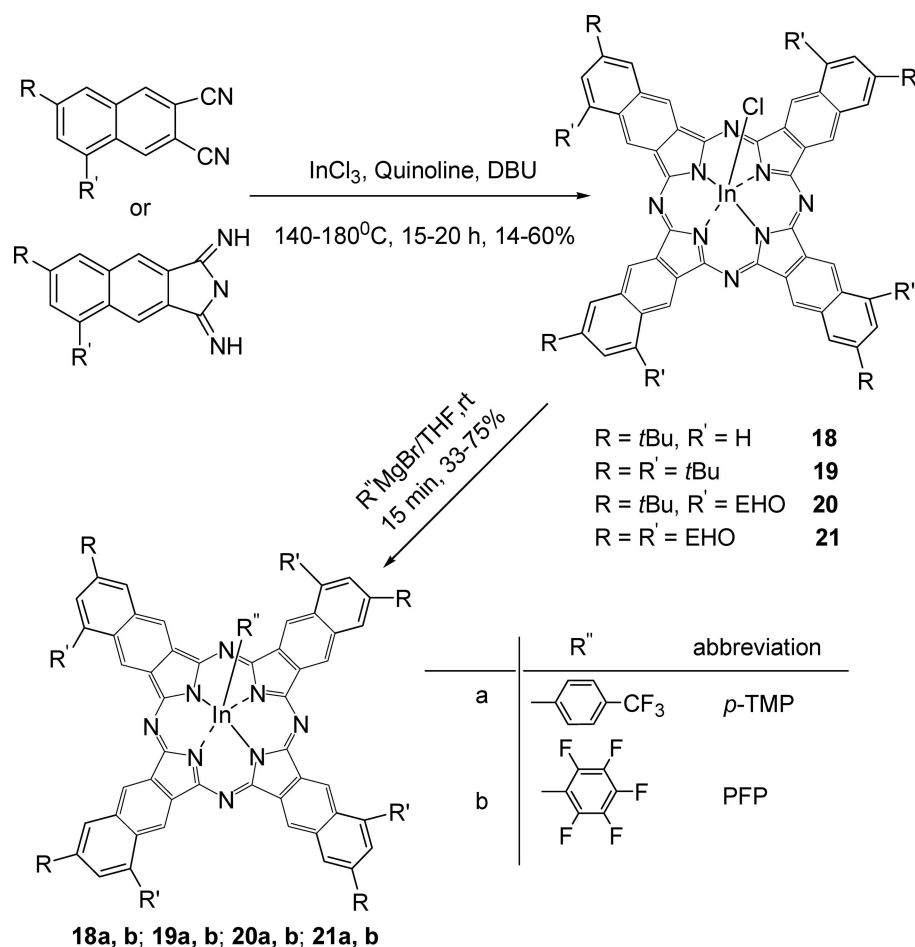
Figure 3 Substitution patterns in 2,3-naphthalocyanines hitherto realized.

30-tetra-, 2, 11, 20, 29-tetra-, 3, 4, 12, 13, 21, 22, 30, 31-octa-, 1, 6, 10, 15, 19, 24, 28, 33-octa-, 1, 3, 10, 12, 19, 21, 28, 30-octa-, and 2, 5, 11, 14, 20, 23, 29, 32-octasubstitution [29]. The solubility of the 1, 6, 10, 15, 19, 24, 28, 33-octasubstituted complexes is the highest of all these compounds. The same argumentation that has been

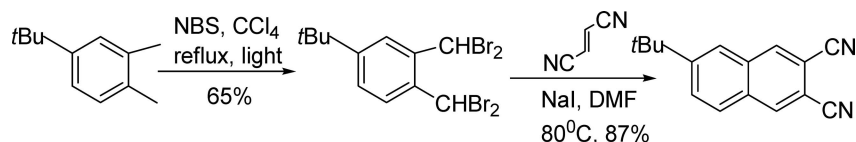
TABLE I UV/Vis data of halogeno, aryl and alkyl axially substituted indium phthalocyanines in chloroform[23]

Phthalocyanines R _x PcIn(R')	λ/nm				
	B(1.0)*	B(0.0)	Q(2.0)	Q(1.0)*	Q(0.0)
PcInCl	337.9	358.2	622.5	656.8	690.2
<i>t</i> Bu ₄ PcInCl(1)	339.7	359.5	628.2	667.1	697.3
<i>t</i> Bu ₄ PcInBr(2)	342.0	362.2	628.4	666.8	697.7
<i>t</i> Bu ₄ PcInI(3)	342.2	366.3	629.3	667.9	698.7
<i>t</i> Bu ₄ PcIn(<i>p</i> -CF ₃ C ₆ H ₄)(5)	340.9	369.3	628.6	667.3	698.0
<i>t</i> Bu ₄ PcIn(<i>m</i> -CF ₃ C ₆ H ₄)(6)	341.4	368.6	628.5	666.5	697.8
<i>t</i> Bu ₄ PcIn(<i>p</i> -FC ₆ H ₄)(7)	341.0	368.5	628.2	666.6	697.4
<i>t</i> Bu ₄ PcIn(3,5-F ₂ C ₆ H ₃)(8)	341.6	366.2	628.6	666.5	697.9
<i>t</i> Bu ₄ PcIn(2,3,5,6-F ₄ C ₆ H) (9)	341.9	368.9	628.8	667.0	698.0
<i>t</i> Bu ₄ PcIn(C ₆ F ₅)(10)	341.9	365.6	628.7	665.7	697.8
<i>t</i> Bu ₄ PcIn(<i>p</i> -BrC ₆ F ₄)(11)	341.1	366.4	628.9	667.4	698.2
<i>t</i> Bu ₄ PcIn(CH ₃)(12)	343.5	368.0	627.7	666.2	696.7
2,3-(C ₅ H ₁₁) ₈ PcInCl(4)	342.2	361.3	635.4	675.4	706.2
2,3-(C ₅ H ₁₁) ₈ PcIn(<i>p</i> -CF ₃ C ₆ H ₄)(13)	353.7	375.3	636.4	675.6	707.2
2,3-(C ₅ H ₁₁) ₈ PcIn(<i>m</i> -CF ₃ C ₆ H ₄)(14)	354.0	374.9	636.2	675.9	707.3
2,3-(C ₅ H ₁₁) ₈ PcIn(<i>p</i> -FC ₆ H ₄)(15)	354.6	375.0	635.8	674.9	706.7
2,3-(C ₅ H ₁₁) ₈ PcIn(C ₆ F ₅)(16)	349.3	370.1	636.3	675.7	707.5
2,3-(C ₅ H ₁₁) ₈ PcIn(C ₆ H ₅)(17)	353.6	375.9	635.8	676.2	706.6

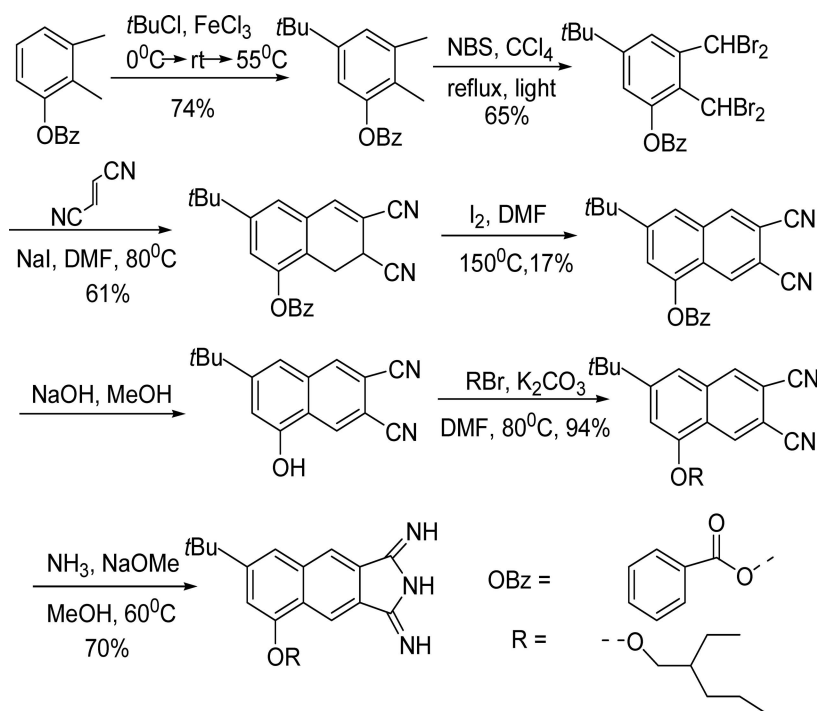
*All of these bands appear as shoulders.



Scheme 3 Synthesis of different octasubstituted and tetrasubstituted chloro- and aryl(naphthalocyaninato) indium complexes.



Scheme 4 Synthesis of 6-*tert*-butyl-2,3-naphthalonitrile.



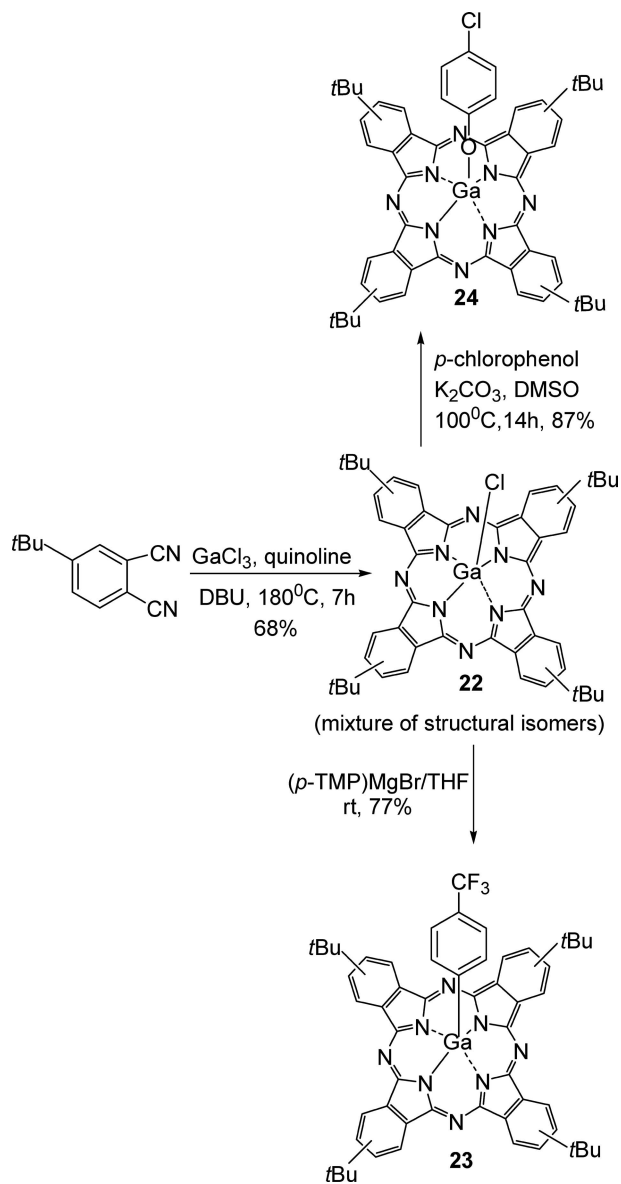
Scheme 5 Synthesis of [5'-*tert*-butyl-3'-(2-ethylhexyloxy)]benzo[f]isindolinediimine.

used to explain the high solubility of 1,4-octasubstituted phthalocyanines is valid. Substituents attached to adjacent isoindole units give rise to increasing steric hindrance. Thus aggregation of the complexes is inhibited. Unfortunately, these most soluble complexes are in the same time the least stable ones, which is attributed to the strong electronic effect of substituents in these positions (1,6-) on the macrocyclic π -electron system.

Hanack *et al.* synthesized substituted, highly soluble (naphthalocyaninato)-indium complexes with different axial ligands **18–21**; **18a, b**; **19a, b**; **20a, b**; **21a, b** (Scheme 3), developing a new unsymmetrical peripheral octasubstitution pattern, with alkyl and alkoxy substituents in the 2- and 4- positions of the Ncs [23, 28]. The precursor for 3,(4)-tetra-*tert*-butyl-2,3-naphthalocyanines, 6-*tert*-butyl-2,3-naphthalonitrile, can be available starting from *o*-xylene as illustrated in Scheme 4. The precursor for chloroindium 2,(5)-tetra-(2-ethylhexyloxy)-3,(4)-tetra-*tert*-butyl-2,3-naphthalocyanine [*t*Bu₄EHO₄(2,3-Nc)InCl, **20**] is 5'-*tert*-butyl-3'-(2-ethylhexyloxy)]-benzo[f]isindolinediimine, which is not as easily available as 6-*tert*-butyl-2,3-naphthalonitrile [23]. Scheme 5 gives the synthetic route for this precursor. The resulting chloro(naphthalocyaninato) indium complexes **19–21**

are much more soluble than **18** in organic solvents such as chloroform or toluene, due to the steric crowding produced by eight bulky substituents [28].

The UV/Vis results indicated that the tetra-*tert*-butyl-substituted Ncs **18**, **18a**, **18b** showed a stronger tendency to aggregate than the mixed octasubstituted Ncs did [23, 28]. This is certainly consistent with expectations from steric considerations. For the octasubstituted materials, the *tert*-butyl peripheral substituents were more effective at blocking aggregation than the 2-ethylhexyloxy (EHO) substituents were. The mixed substituent-*t*Bu₄EHO₄-materials with large axial substituents showed little evidence for aggregation even in highly concentrated solutions and films, as is illustrated by the band shapes and the bathochromic shifts of the *Q*-band maxima of different concentrated solutions of **20**, **20a**, **20b**. As an example, Fig. 4 gives the UV/Vis absorption spectra of a solution and thin films of **20**. The strong absorption appearing to the blue side of the *Q*-band in the spectra of *t*Bu₄(2,3-Nc)InCl and *t*Bu₄(2,3-Nc)InI, is not present in the spectra of the thin films of **20**. The band is broadened and a higher absorption is observed to the red side of the *Q*-band. The shape of the *Q*-band is not very much affected, similar to the observations made for all of the axially substituted indium phthalocyanines [28]. As predicted the in-



Scheme 6 Synthesis of gallium phthalocyanine monomers.

termolecular interactions, which are very strong between naphthalocyanines, are largely inhibited by this new type of substitution. The solubility of this compound in chloroform reached up to 160 mM.

2.3. Gallium phthalocyanines

Peripherally unsubstituted gallium phthalocyanines with an axial chloro, fluoro, hydroxy, ligand (PcGaX , $\text{X} = \text{Cl}$, F , OH) were studied in detail [30]. The disadvantage of peripherally unsubstituted phthalocyanines is their poor solubility in organic solvents. To overcome this problem, a variety of substituents have been attached to the macrocycle, in varying numbers and different substitution patterns. Tetra(*tert*-butyl)-substituted Pc's and their metal complexes are the most frequently used when solubility is required.

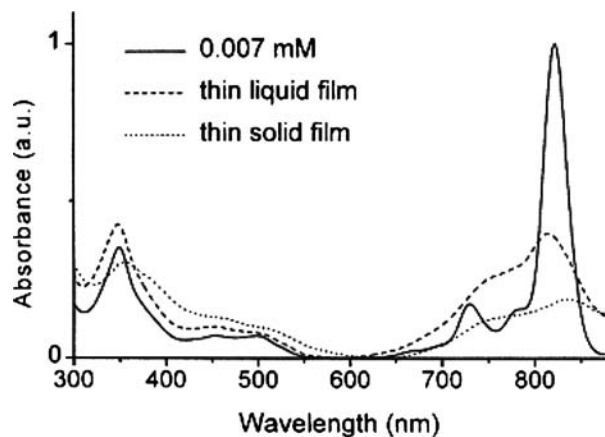


Figure 4 UV/Vis absorption spectra of a solution and thin films of $t\text{Bu}_4\text{EHO}_4(2,3\text{-Nc})\text{InCl}$.

Scheme 6 gives the synthetic route for the preparation of $t\text{Bu}_4\text{PcGaCl}$ (**22**), $t\text{Bu}_4\text{PcGa}(p\text{-TMP})$ (**23**) and $[t\text{Bu}_4\text{PcGa}(p\text{-CPO})]$ ($p\text{-CPO} = p\text{-Chlorophenoxy}$) (**24**). Compound **23** was synthesized by the reaction of freshly prepared 10-fold excess *p*-TMP Grignard reagent with $t\text{Bu}_4\text{PcGaCl}$ [31]. **24** was prepared by the reaction of $t\text{Bu}_4\text{PcGaCl}$ with *p*-chlorophenol in anhydrous DMSO at 110°C in the presence of K_2CO_3 [32]. Unlike the axially aryl-substituted gallium phthalocyanine **23**, whose *Q* and *B*-bands in the UV/Vis absorption spectra are shifted to the red by a few nanometers relative to $t\text{Bu}_4\text{PcGaCl}$, axially aryloxy substitution at central gallium atom gives rise to a weak (2–3 nm) blue shift of the *Q*-band. Comparison of the UV/Vis absorption spectra of thin film and dilute solution of **22** and **23** in CHCl_3 shows that the absorption spectra of thin films of **22** and **23** are apparently broadened. By comparing the thin film and dilute solution UV/Vis spectra of **22**, the position of the *Q*-band maximum is slightly shifted about 2.5 nm towards longer wavelength. In the case of **23**, the same comparison shows that the position of the *Q*-band maximum is almost unchanged, which is consistent with relatively weak aggregation of **23** in solution [31].

2.4. Titanium(IV) phthalocyanines

Phthalocyaninatotitanium (IV) oxide (PcTiO) is known to be a potential charge generation material [33]. This property and the possibility of preparing flexible films led to its use in photostatic machines or GaAsAl laser printers. Besides this, the structural and photochemical properties of peripherally substituted 1,(4)- or 2, (3)- R_xPcTiO , 2,(3)- NcTiO and 1,2- NcTiO have been intensively investigated for a better understanding of the carrier generation process [34]. The nonlinear optical properties of some phthalocyaninatotitanium(IV) oxides, e.g. PcTiO , Me_4PcTiO , $(\text{MeO})_4\text{PcTiO}$, $(\text{MeO})_8\text{PcTiO}$, and others, have been reported in order to study how the different peripheral substituents and substitution patterns of the rings can influence the reverse saturable absorption(RSA)

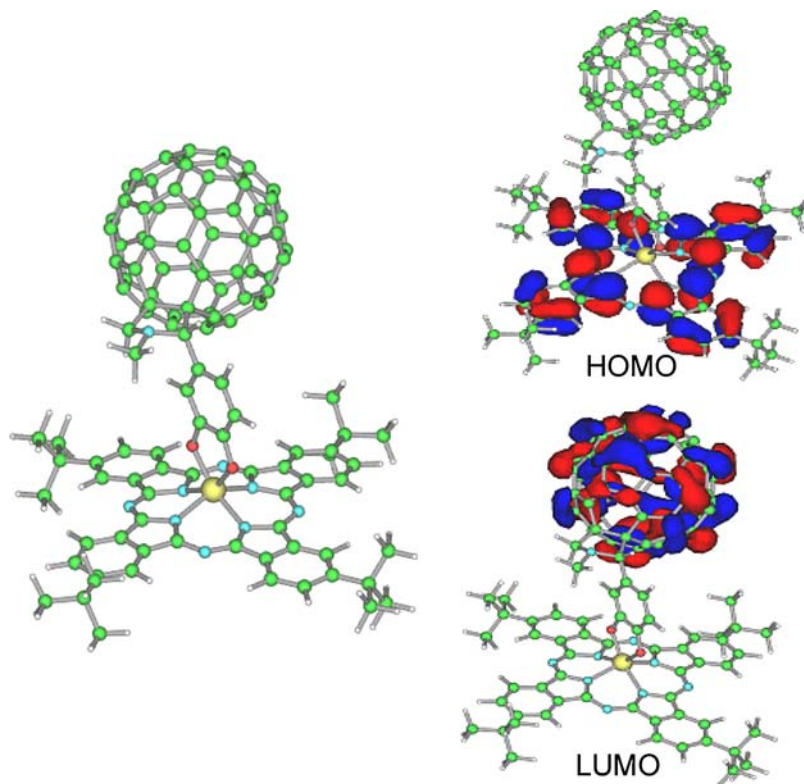
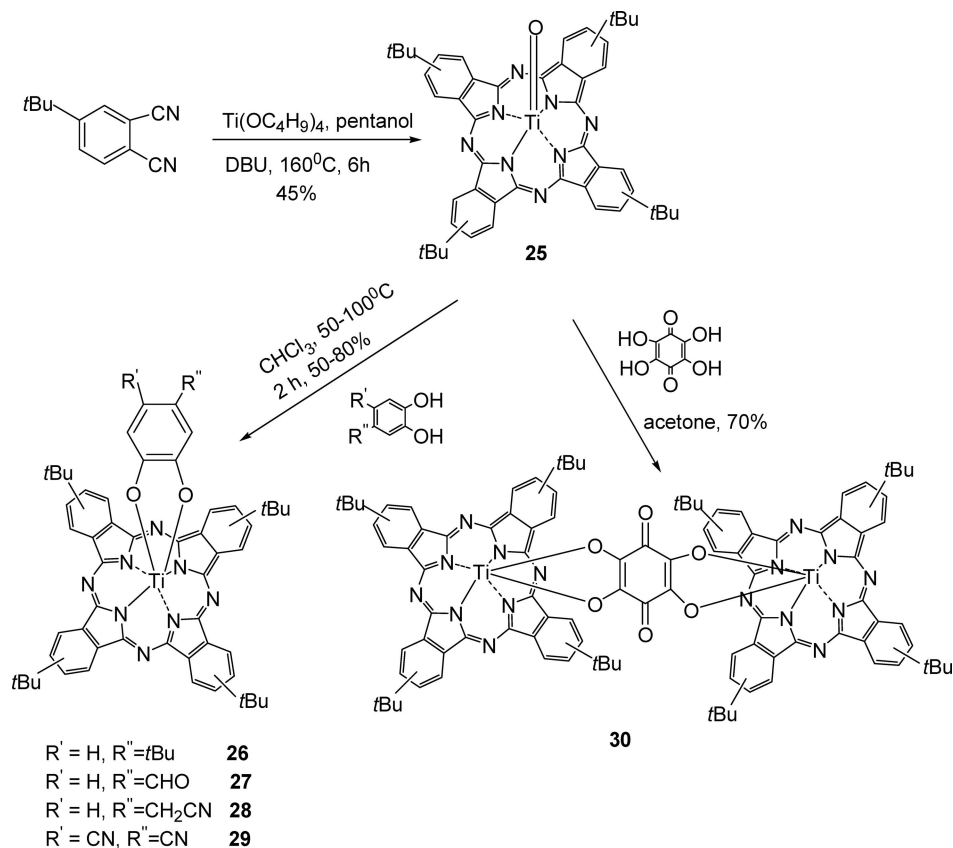


Figure 5 Optimized molecular structure and HOMO/LUMOs of titanium Pc-C₆₀ dyad calculated by HF/3-21G level using Gaussian-98 pack.

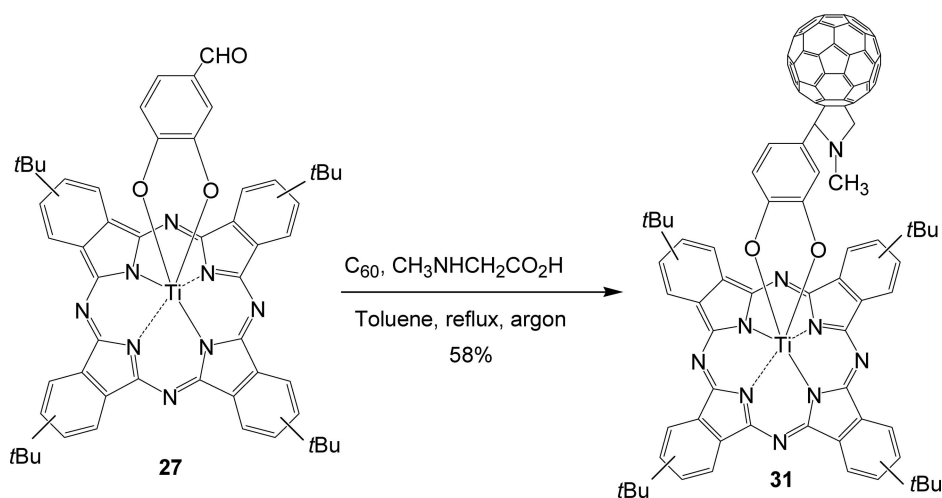
of the respective oxo-titanium Pc's solutions [35]. The results showed that the functionalization of the edges of the conjugated rings could result in a fine tuning of the NLO properties of Pcs when TiO constituted the central metal-ligand combination. A series of new axially substituted titanium (IV) phthalocyanine compounds (**25–30**, see Scheme 7) were synthesized by Barthel *et al.* through the reaction of Ti=O bond in *t*Bu₄PcTiO with catechol and other donor ligands under very mild conditions [36, 37]. The driving force of the reaction between *t*Bu₄PcTiO and the chelating agents, for example, 4-*tert*-butylcatechol, 3,4-dihydrobenzaldehyde, 2-(3, 4-dihydroxyphenyl)acetonitrile and 4,5-dihydroxy-phthalonitrile, is based on the electrophilic character of titanium(IV) and the nucleophilicity of oxygen atoms in catechol-based derivatives [38]. The reaction of tetrahydroxy-*p*-benzoquinone leads to the dimeric complex (*t*Bu₄PcTi)₂O₄(C₆O₂) (**30**). The large functionalized catechol ligands introduce steric hindrance above the macrocycle plane of the resulting complexes, and should inhibit molecular aggregation. The presence of electron-withdrawing substituents like CN, CHO, CH₂CN in the catechol-based ligands induces additional electronic effects consisting of a large charge separation and the localization of a partial positive charge on the axial aromatic ring. The 4-*tert*-butyl catechol substituted complex **26** is characterized by a blue shift of both the *Q*- and *B*-bands caused by the electron-donating ability of the axial component with respect to *t*Bu₄PcTiO [36, 37]. Compounds **27–29** show a red shift of the *Q*- and *B*-bands, which is caused by the electron-withdrawing CHO, CH₂CN, and CN substituents. The dimeric com-

plex **30** has practically the same UV/Vis absorption bands as the monomer *t*Bu₄PcTiO, and has a greenish color both in the solid state and in solution. And more, a titanium (IV) phthalocyanine with axial chirality was also prepared by the reaction of *t*Bu₄PcTiO with (*S*)-(–)- or (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl in methylene chloride at room temperature [39].

Phthalocyanines and fullerenes are well-known building blocks in the area of organic molecular optoelectronic and photonic materials science due to their unusual structures and outstanding electric, conducting and photophysical properties [40]. The combination of the good electron donor and light harvesting characteristics of phthalocyanines with the excellent electron-accepting properties, larger exciton diffusion length and low reorganization energy of C₆₀ is thus very challenging and will probably become of great importance in the near future [41]. The first Pc-C₆₀ dyad, in which C₆₀ was attached peripherally onto the phthalocyanine macrocycle, was synthesized by a Diels-Alder cycloaddition reaction between NiPc diene and C₆₀ in 1995 [42]. After this, only three new covalently linked Pc-C₆₀ derivatives, however, were prepared until now due to the difficulty in the preparation and isolation of asymmetric phthalocyanine precursor used for reaction with C₆₀ [43]. More recently, we successfully synthesized the axially substituted titanium Pc-C₆₀ dyad (**31**) with a convenient method (Scheme 8), which improves on the traditional asymmetrical phthalocyanine routine to covalently linked phthalocyanines with other functional molecules [44a]. Fig. 5 gives the HOMO/LUMOs and the optimized structure of Pc-C₆₀ dyad. Compared to the



Scheme 7 Synthesis of the catechol(phthalocyaninato)titanium(IV) complexes.



Scheme 8 Synthesis of the axially substituted titanium Pc-C₆₀ dyad.

UV/Vis absorption spectrum of *t*Bu₄PcTiO (**25**), the *Q*-bands of **27** and **31** are slightly shifted to the red due to the electron-withdrawing aldehyde and C₆₀ substituents. The weak absorption band at $\lambda = 430$ nm typically assigned to the [6,6]closed mono-substituted fullerene derivative was observed in the UV/Vis absorption spectrum of **31**. Upon excitation with a laser light of 420 nm, all compounds display a Stokes shift of the emission peak with respect to the location of the *Q*-band absorption in deaerated benzonitrile.

The fluorescence quenching was observed in benzonitrile, suggesting that intramolecular charge-separation might take place between phthalocyanine donor and fullerene acceptor, which was supported by the negative free-energy change calculated by the electrochemical data. The charge separation process was initially confirmed by applying 532 nm nanosecond laser photolysis. The quick rise-decay of the absorption band at 790 and 1020 nm was observed (Fig. 6). These two bands might be assigned to the formation of $\text{PcTi}^{\bullet+}$ and $\text{C}_{60}^{\bullet-}$, re-

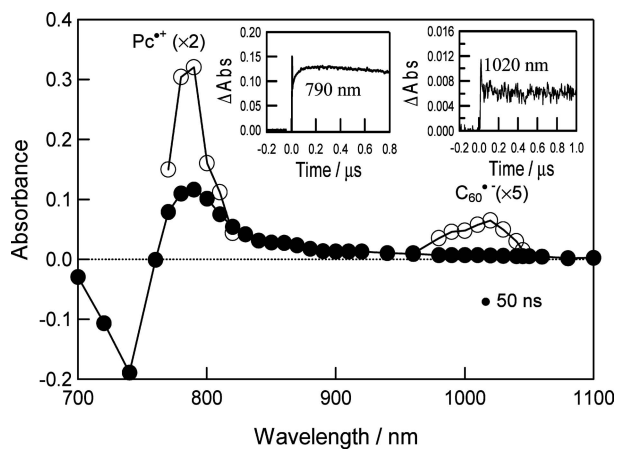


Figure 6 Transient absorption spectra of **31** (0.1 mM) in Ar-saturated benzonitrile ($\lambda_{\text{ex}} = 532$ nm). Inset: absorption-time profiles at 1020 and 790 nm.

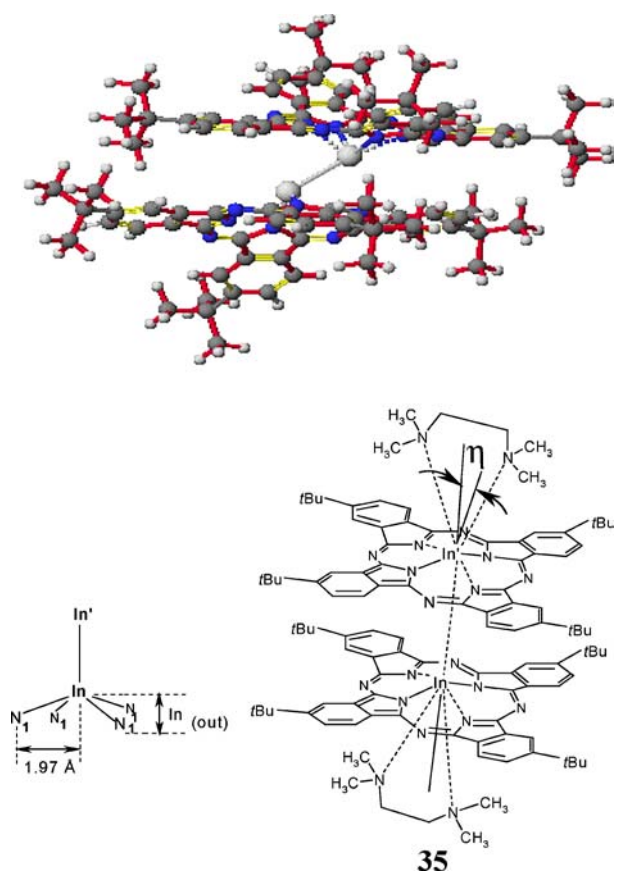


Figure 7 Optimized molecular structure of $t\text{Bu}_4\text{PcIn-InPc}/t\text{Bu}_4$ dimer without tmed ligands calculated by HF/3-21G level (upper panel) and EXAFS structure of $[t\text{Bu}_4\text{PcIn}]_2.2\text{tmed}$ (lower panel).

spectively. After more than five months when Chen *et al.* reported the synthesis, characterization and photophysical properties of **31** [44a], a greatly similar article concerning the same compound was surprisingly appeared in Tetrahedron homepage [44b] recently. Unfortunately, from the NMR and MS data they presented in Tetrahedron it can be seen that their compound is at least not pure because,

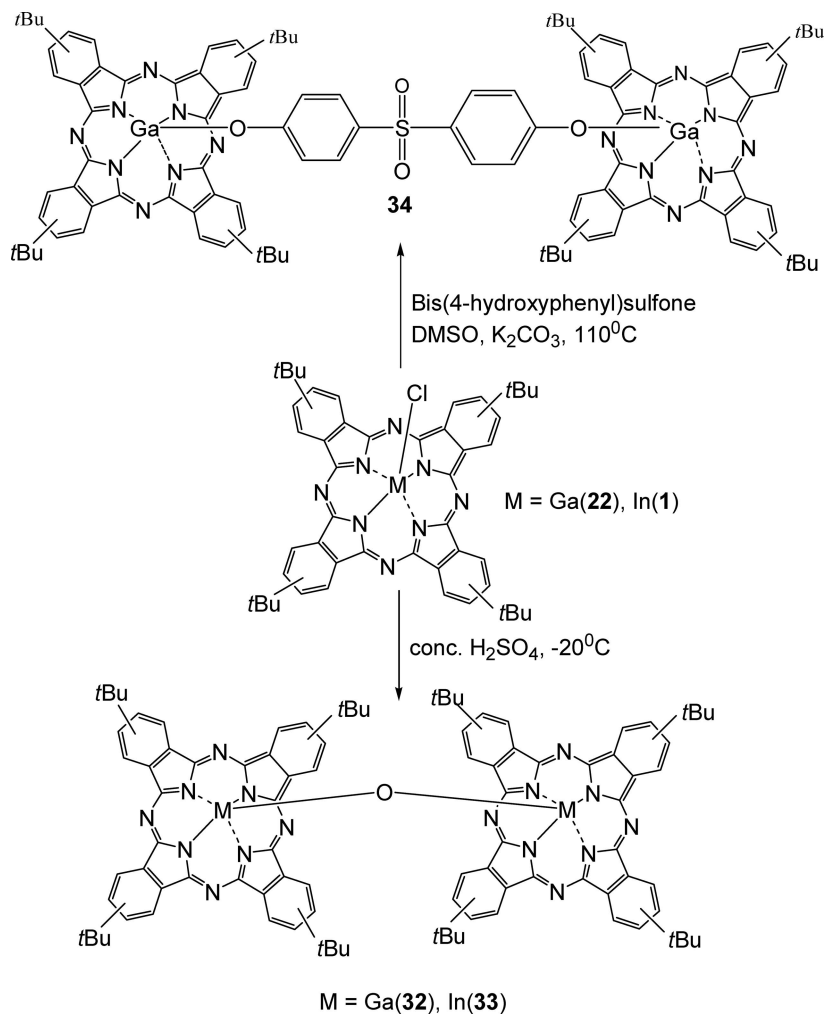
as they claimed, in their target compound a minor amount of the $t\text{Bu}_4\text{PcTiO}$ remains as a so-called by-product.

2.5. Gallium and indium phthalocyanine dimers

The μ -oxo-bridged unsubstituted gallium phthalocyanine dimer, $(\text{PcGa})_2\text{O}$, is known since 1997, it was synthesized by heating PcGaOH or PcGaOCH_3 , and was shown to exhibit good photoreceptor properties [45]. As shown in Scheme 9, The $[t\text{Bu}_4\text{PcM}]_2\text{O}$ dimers [$\text{M} = \text{Ga}^{3+}$ (**32**), In^{3+} (**33**)] were prepared by the reaction of $t\text{Bu}_4\text{PcMCl}$ ($\text{M} = \text{Ga}^{3+}$, In^{3+}) with excess of concentrated H_2SO_4 at -20°C [46]. 4,4'-sulfonyldiphenoxy (SDPO)-axially bridged gallium phthalocyanine dimer $\{[t\text{Bu}_4\text{PcGa}]_2.\text{SDPO}\}$ (**34**) was synthesized by the reaction of $t\text{Bu}_4\text{PcGaCl}$ with bis(4-hydroxyphenyl)sulfone in anhydrous DMSO at 110°C in the presence of K_2CO_3 [32]. The dimers **32–34** were found to be more soluble in many common organic solvents, even in methanol, and acetone, than their starting compounds $t\text{Bu}_4\text{PcGaCl}$ and $t\text{Bu}_4\text{PcInCl}$. The stability of **32** is, however, much higher than that of **33**. EXAFS analysis for **32** indicated that the distance between Ga and bridging oxygen atom was found to be 1.87 Å [47]. The inter-Pc distance in **32** is about 3.72 Å, which is in the quite good agreement with the reported value of 3.8 Å obtained from the theoretical calculation for the minimized structure of **32** [48]. When a rigid phthalocyanine molecule, which is not deformed by the metal atom, is assumed, the shortest metal atom and nitrogen distance amount to 1.97 Å. The gallium center is located 0.45 Å out of the plane described by the four nitrogen atoms directly bonded to it. Similar analysis for **33** shows that the indium center was found to be located 0.89 Å out of plane described by the four nitrogen atoms directly bonded to it. The distance between In and bridging oxygen atom is about 2.16 Å [48].

The UV/Vis absorption spectra of **32** and **33** in CHCl_3 have the pattern typical of metal Pcs. When compared with the UV/Vis absorption spectra of $t\text{Bu}_4\text{PcMCl}$ ($\text{M} = \text{Ga}^{3+}$, In^{3+}), formation of the μ -oxo metallophthalocyanine dimers **32** and **33** only leads to a weak (1–2 nm) blue shift of the *Q*-band and to a red shift (1.5 nm) of the *B*-band. The red shift of the *B*-band is related to the interaction of the oxygen atom with the central metal, gallium or indium. The shapes of the UV/Vis absorption spectra are solvent-dependent [46, 49]. The dimer **34** exhibits the similar electronic absorption characteristic. These very small blue-shifts suggest that the interactions between the two phthalocyanine rings in dimers in the ground state are very weak [32, 46].

Organometallic compounds containing metal-metal single bonds between the metallic elements of Group 3A (Al, Ga, In, Tl) are unusual, but can be of interest in the field of material sciences. Chen *et al.* have prepared the first dimeric indium phthalocyanine complex with an In–In bond (**35**) by a Wurtz-coupling



Scheme 9 Synthesis of axially bridged gallium and indium phthalocyanine dimers.

reaction of $t\text{Bu}_4\text{PcInCl}$ in the presence of N,N,N',N' -tetramethylethylenediamine (tmed) [50]. The role of the neutral tmed ligand is mainly to promote maximum coordinative saturation at the indium center. Theoretical calculation shows that stable dimer structure exhibits energy minimum (Fig. 7, upper panel) [51]. Its molecular structure (Fig. 7, lower panel) has further been confirmed by extended X-ray absorption fine structure (EXAFS) spectroscopy [50], which is considered to be a powerful technique for the determination of the local structure of a specific atom, regardless of the state of the sample. EXAFS provides information on the coordination number, the nature of the scattering atoms surrounding the absorbing (excited) atom, the interatomic distance between the absorbing atom and the back-scattering atoms and the Debye-Waller factor, which accounts for the disorders due to static displacements and thermal vibrations [52]. By EXAFS measurements the In-In distance, was found to be 3.24 Å. The molecular planes are tilted, with respect to the axis connecting the centre of the molecules, by an angle of 14.57° . The strong peak at 110 cm^{-1} in the Raman spectrum of **35** is ascribed to the In-In vibration, but pointing to a weak In-In bond.

3. Photophysical properties of gallium and indium phthalocyanines

The photophysical data of some indium and gallium phthalocyanines [14, 46, 50, 53] are summarized in Table II. 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. An example for the typical steady-state absorption and fluorescence spectra of $[t\text{Bu}_4\text{PcGa}]_2 \cdot \text{SDPO}$ in anhydrous toluene was shown in Fig. 8a. For all compounds, steady-state fluorescence spectra in deaerated toluene ($\lambda_{\text{ex}} = 410\text{ nm}$) show the mirror image of the corresponding UV/Vis absorption bands with small Stokes-shifts, implying 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 SPDO-bridged dimers exhibit longer τ_f values. The decrease in the τ_f value was observed for the dimer with TFP-spacer [53].

TABLE II Photophysical properties of some indium and gallium phthalocyanines in deaerated anhydrous toluene. (τ_f : fluorescence lifetime at emission peak wavelength, $\lambda_{ex} = 410$ nm; τ_T : triplet excited state lifetime, $\lambda_{ex} = 355$ nm; K_{TT} : T-T annihilation rate constant; K_{O_2} : second-order rate constant)

Samples	λ_{max}^{abs} (nm)	λ_{max}^{fluo} (nm)	$\Delta\nu^{stokes}$ (cm)	τ_f (ps)	λ_{max}^T (nm)	τ_T (μ s)	k_{TT} ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)	k_{O_2} ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)
<i>t</i> Bu ₄ PcInCl	695	705	204	470	520	46	6.510^9	2.2×10^9
<i>t</i> Bu ₄ PcIn(<i>p</i> -TMP)	696	701	103	280	520	22	4.5×10^9	2.2×10^9
[<i>t</i> Bu ₄ PcIn] ₂ O	694	705	225	638	520	42	4.5×10^9	2.1×10^9
[<i>t</i> Bu ₄ PcIn] ₂ (TFP)	694	705	225	350	520	35	6.2×10^9	2.2×10^9
[<i>t</i> Bu ₄ PcInCl] ₂ .did	692	703	226	470	520	38	2.3×10^9	2.2×10^9
[<i>t</i> Bu ₄ PcIn(<i>p</i> -TMP)] ₂ .did	694	706	245	400	520	33	3.0×10^9	2.3×10^9
<i>t</i> Bu ₄ PcGaCl	693	702	185	2570	520	257	4.3×10^9	2.2×10^9
<i>t</i> Bu ₄ PcGa(<i>p</i> -TMP)	696	701	103	2480	520	200	4.9×10^9	2.0×10^9
[<i>t</i> Bu ₄ PcGa] ₂ O	692	701	186	3570	520	357	3.2×10^9	2.0×10^9
[<i>t</i> Bu ₄ PcGa] ₂ .SDPO	692	712	406	3460	520	667	3.0×10^9	2.1×10^9

$\epsilon_T = 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$; TFP: 2,3,5,6-tetrafluorophenylene; did: 1,4-diisocyanobenzene.

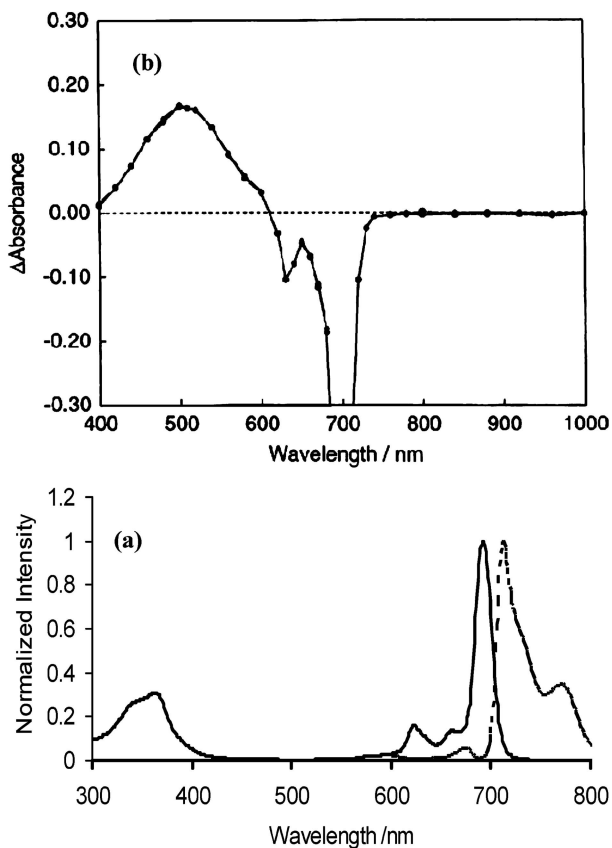


Figure 8 (a) Normalized steady-state absorption and fluorescence spectra and (b) nanosecond transient absorption spectrum of [*t*Bu₄PcGa]₂.SDPO.

The nanosecond transient absorption spectra were observed by the excitation of the Pc derivatives with 355 nm laser light in deaerated toluene. For all compounds, their transient absorption spectra are almost similar. A typical transient absorption spectrum of [*t*Bu₄PcGa]₂.SDPO was shown in Fig. 8b. On addition of O₂, 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 O₂, yielding probably ¹O₂. The intersystem cross quan-

tum yield of *t*Bu₄PcGaCl is only about 50% of the value of that for the *t*Bu₄PcInCl. Zhu *et al.* reported the ultrafast dynamics of the excitons in a series of axially and bridged indium and gallium phthalocyanine thin films very recently [54], and found that the compounds containing indium have larger intersystem crossing (ISC) rates than those containing gallium or titanium. The ratio of ISC rate of indium phthalocyanines to titanium or gallium ones is about 2–3. Perry *et al.* also indicated the phthalocyanines using a heavy-atom as central metal usually exhibit excellent optical limiting properties [13] because the heavy atom would accelerate the ISC process.

The decay of the 520 nm band in the presence of O₂ obeys first-order kinetics, giving the $k_{\text{first-order}}$, which increases with the concentration of added O₂; from the pseudo-first-order relation, the second-order rate constants for the reaction with O₂ (k_{O_2}) were evaluated as listed in Table II. Dimers and monomers have the almost same k_{O_2} values. The excited triplet state lifetimes (τ_T) of indium phthalocyanines are shorter than those of gallium phthalocyanines by a factor of about 1/10. Among all Pc compounds, [*t*Bu₄PcGa]₂.SDPO exhibits the longest triplet excited state lifetime, up to 667 μ s. In the indium phthalocyanine monomers, the *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. 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.

4. Nonlinear optical properties of indium, gallium and titanium phthalocyanines in solutions

A very convenient and fast experimental method to assess materials for NLO (including optical limiting) is the open aperture Z-scan[7] 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 fit-

ting theory [7, 55]. As an example, the nanosecond open aperture and 40% aperture Z-scans for a 22 mM solution of *t*Bu₄PcInCl in chloroform at 532 nm are shown in Fig. 9 [23]. The fluence at the focus of the incident beam was gradually raised from 0.2 to 28 mJ/cm². The relative transmission decreases with rising incident fluences. The results demonstrated that *t*Bu₄PcInCl 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 mJ/cm² 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 mJ/cm²). 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 focus at $z \sim 75 \mu\text{m}$. The nonlinear absorption coefficients (NACs), α_{NL} , were derived from measurements of the nanosecond nonlinear transmission between 500 and 620 nm [23]. The initial change in the relative transmission occurs at smaller incident fluences as the wavelength increase from 500 to 570 nm. This corresponds to an increase of the nonlinear absorption coefficients with increasing wavelength over the range 500 to 590 nm. The complexes **5** and **10** have NACs that are generally larger than those of *t*Bu₄PcInCl over most of this wavelength range. These larger α_{NL} resulted in lower thresholds, which are defined as the input energy required to achieve $T_{(\text{F})} = 0.5 T_{(\text{F} = 0)}$, for optical limiting in the aryl substituted materials [11, 23].

Similar to *t*Bu₄PcInCl [11, 13], all the phthalocyanine complexes reviewed here 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 ns pulses generate analogous excited states whose absorptivity is larger than in the ground state in the spectral window. The nonlinear response of *t*Bu₄PcMCl [M = In, Ga] is obviously improved by axial substitution and dimerization. In the aryl-axially substituted indium phthalocyanine complexes e.g.

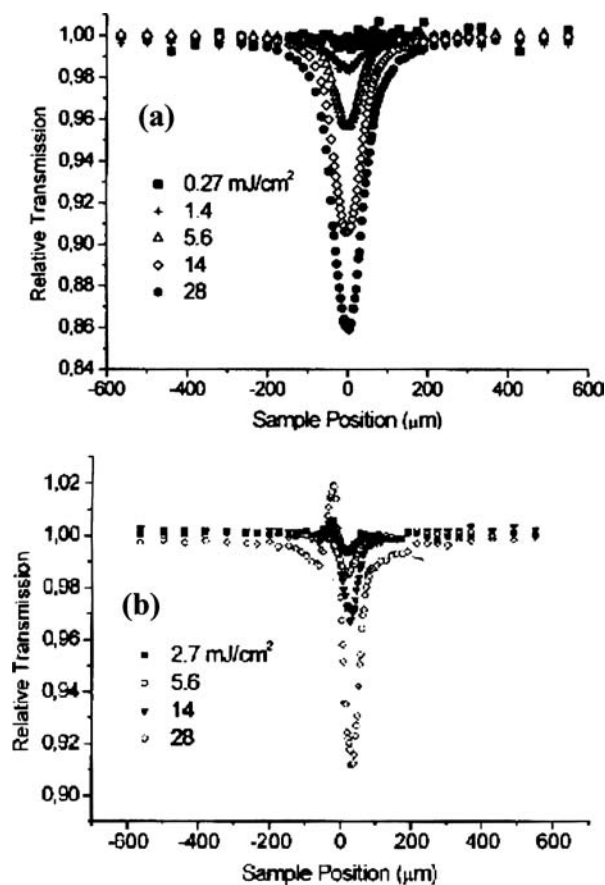


Figure 9 Z-scans as a function of the incident fluence of *t*Bu₄PcInCl (22 mM/CHCl₃) at 532 nm: (a) open aperture and (b) 40% aperture [23].

*t*Bu₄PcIn(*p*-TMP) the nonlinear absorption begins at a lower fluence than for *t*Bu₄PcInCl. 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*Bu₄PcIn]₂(TFP) in CHCl₃ 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 [56].

The comparison of γ_{EFISH} and β_{HRS} (HRS: hyper Raleigh scattering) values [48] shows the influence of reduction of symmetry of the phthalocyanine ring and the intramolecular stacking on the second order nonlinear optical properties. In comparison with compounds **25** and **26**, the dimeric Pc **30** that lacks a permanent dipole moment gives rise to an enhanced electronic contribution to γ_{EFISH} . Theoretical calculation shows that the inter-Pc distance in **30** reaches up to 10 Å, which is far too large to envisage any interaction between the two halves of the molecules that could have an effect on the NLO properties. The dipole moment value of the dimer **32** is very small

(only 0.3 Debye) when compared to those of compounds $t\text{Bu}_4\text{PcGaCl}$ and $t\text{Bu}_4\text{PcGa}(p\text{-TMP})$ (6.6D for the former and 4.9 D for the latter); however, this dimer exhibits a higher $\beta_{\text{HRS}}(1.06 \mu\text{m})$ value (86×10^{-30} esu) with respect to $t\text{Bu}_4\text{PcGaCl}$ and $t\text{Bu}_4\text{PcGa}(p\text{-TMP})$ as a result of the higher number of π -electrons distributed in two planes, which are in this case closely spaced [48].

5. All-optical reflectance control based on photoinduced complex refractive index changes in guided mode thin films

All-optical parallel switching devices and spatial light modulator (SLM) have attracted much interest especially in the fields of optical data communication and optical parallel data processing. No practical device is, however, available except some prototypes or SLMs based on liquid crystals (LC) so far. The response time of LC-SLM is controlled by the electric field induced motion of LC, about a few hundreds of microsecond (μs) for ferroelectric LC and a few tens of milliseconds (ms) for nematic LC. The spatial resolution of LC-SLM is only about 10–20 μm . The multiple-quantum-well (MQW) SLMs have been developed to show spatial resolutions of 5–7 μm and a response time of 1 μs or faster [57]. Although several types of devices for optical parallel data processing have been proposed based on other principles such as surface plasmon resonance (SPR), guided wave mode and Fabry-Perot (FP) resonance [58], all of these devices could not exceed the characteristics of LC-SLM especially in the response time.

Nagamura and his coworkers have developed new materials showing ultrafast color changes in picosecond(ps)-femtosecond(fs) time regions due to photoinduced electron transfer and reverse reactions [59], or formation and decay of excitons in semiconductor nanoparticles [60]. In order to fully utilize these materials in ultrafast parallel processing, the authors proposed a new all-optical spatial light modulation using guided optical waves (guided mode) and its resonance shifts by complex refractive index changes upon photoexcitation of an organic dyedoped polymer thin film [61]. Less than 20 ns rise and 30 ns fall were observed for CuPcS-doped polyvinylalcohol (PVA) thin film. The fall time was about 4 μs for $t\text{Bu}_4\text{PcInCl}$ -doped polystyrene thin film and about 0.5 ms for ZnPcS-doped PVA thin film. All these fall times corresponded to the excited triplet state lifetimes. The transient absorption spectra were observed by fs and ns laser excitation for several axially substituted or bridged indium or gallium phthalocyanine-doped polytetracyclododecene thin films [51, 62]. They all gave transient reflectance with a few to a few tens of microseconds response in guided mode geometry upon excitation with ns laser due to the formation and decay of the excited triplet state. The reflectance was controlled repeatedly and reversibly for many times as synchronized with the formation and decay of the excited triplet state phthalocyanine. Bridged phthalocyanine dimers showed almost the same response as

those of monomers reflecting weak chromophore interactions in these phthalocyanines containing four peripheral bulky *tert*-butyl groups. The response time of the recovery in the guided mode geometry was controlled over a wide range from ns, μs to sub-ms by simply selecting the central metal ion of phthalocyanines. These results will contribute a great deal to make ultrafast all-optical spatial light modulation such as on-line optical correlation.

6. Summary and outlook

Phthalocyanines offer a tremendous degree of design flexibility that they may be employed to fabricate practical organic NLO devices. The exploitation of the chemical reactivity of the bond M-Cl [M = Ga³⁺, In³⁺] and M=O [M = Ti⁴⁺] bonds can allow the synthesis of a series of highly soluble axially substituted and bridged phthalocyanine and naphthalocyanine compounds. The enhanced solubility of the resultant monomers and dimers, compared to the chloro analogues, shows that the usual tendency of phthalocyanines or naphthalocyanines to form aggregates can be effectively suppressed by axial substitution. Axial substitution in Pc complexes has provoked 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.

It has long been recognized that intense laser beams can easily damage delicate optical instruments, especially the human eye and consequently the field of optical limiting, one of the most fundamental and important applications of nonlinear optics, has invested much effort into the research of new materials and processes in an attempt to afford some measure of protection from such beams. The first practical NLO application of phthalocyanine and the related compounds in the near future will probably be for optical limiters because among the all technological applications optical limiting is closest to realization. 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 future effort would be being devoted to preparing the novel reliable Pc-based organic or polymeric functional materials; determining the relationship between the fundamental structural parameters, and photophysical and nonlinear optical properties of materials; and to optimally combining materials and devices to make functional elements which perform advanced nonlinear optical functions which ultimately will find application in electronic and photonic systems.

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