# Synthesis of a Bisphthalocyanine and Its Nonlinear Optical Properties

**Mario J. F. Calvete,[a] Danilo Dini,[a] Steven R. Flom,[b] Michael Hanack,*[a] Richard G. S. Pong,[b] and James S. Shirk[b]**

**Keywords:** Phthalocyanine / Dimer / Binuclear complex / Reverse saturable absorption / Excited state absorption / Pulsed laser

The synthesis and the nonlinear optical properties of an axially substituted binuclear InCl/InCl phthalocyanine **1** with an unsymmetrical substitution pattern are described. The preparation of this new type of binuclear phthalocyanine has been carried out through a multi-step synthetic strategy, which was specially developed for binuclear phthalocyanines. The study has been carried out with the aim of analyzing which variations of the electronic properties accompany the unsymmetrical extension of the π-electron system of a binuclear Pc when compared to a mononuclear Pc (the complex *t*Bu$_4$PcInCl is here taken for comparison). The nonlinear optical properties of InCl/InCl phthalocyanine **1** in toluene were studied with the Z-scan technique in both open- and closed-aperture configurations at 532 nm with nanosecond laser pulses. The binuclear complex displayed a positive nonlinear absorption coefficient. It is found that the linear optical properties were little changed but the optical limiting effectiveness of the binuclear fused phthalocyanine **1** is lower relative to *t*Bu$_4$PcInCl. Explanations for such differences are given.

## Introduction

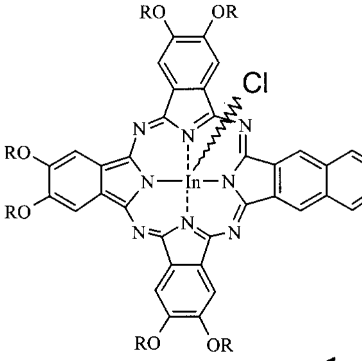
Phthalocyanines (Pcs) and their derivatives have practical importance as dyes and pigments with intense blue or green color,[1,2] as well as for catalytic applications.[3] They have recently also received considerable attention as active materials for organic electronics,[4] xerography,[5] sensors,[6] photovoltaic cells,[7] electrochromic devices,[8] nonlinear optics[9] and recordable DVDs[10] among other applications.[11–16] Their high thermal and chemical stability, well-defined optical absorption, semiconducting and photoconducting properties, their ability to coordinate a large number of central atoms and their ease of preparation add to their attractiveness.[17] These features arise from: (i) The presence of an extended network of π-electrons; (ii) the planarity of the Pc skeleton; (iii) the high symmetry and aromaticity of the Pc structure; and (iv) the presence of a coordinating central cavity formed by donor nitrogen atoms.[18] The conjugated network of π-electrons is also a structural prerequisite for the verification of nonlinear optical (NLO) phenomena[19] in Pcs since it confers high electrical polarizability and fast charge redistribution when the conjugated molecule interacts with rapidly varying and intense electromagnetic fields.[20]

The versatility of Pc synthetic organic chemistry[21,22] has led to a large variety of Pc structures differing in the number, nature and position of peripheral substituents,[23–27] with various coordinating central atoms,[17] axial ligands,[28,29] and with a variable number of linkages between Pc rings in oligomeric[30,31] or polymeric species.[32] Among the many possibilities for varying the Pc structure, the expansion of the π-electron system through the synthesis of naphthalocyanines (Ncs) is the most common. The preparation of fused binuclear planar phthalocyanines[33–37] is another interesting approach since it leads to condensed Pc-based systems with distinct electronic properties with respect to those of the separated Pc units.[33–36,38–43] To date, the reported binuclear-fused Pcs referred to structures in which the coordinating central metals have no axial ligands.[33–36,40,41,43–46] The presence of axial ligands in Pc molecules, however, has favorable effects on their NLO properties (see below).[47–50] Since mononuclear Pcs with In and Ga and an axial ligand as central moieties are known to be effective systems for optical limiting applications,[46,51–57] we decided to direct our research also to the synthesis of the binuclear indium phthalocyanine **1** using a preparative approach which was developed in our laboratory.[33] A similar binuclear bisphthalocyanine with two different central metals (Ni and Cu), has been described by us before.[33a] The proposed strategy allows the synthesis of a binuclear structure **1** with a double concentration of the central moieties and phthalocyanine rings per single molecular unit.

---

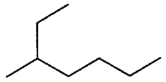
[a] Institut für Organische Chemie, Universität Tübingen,
Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-mail: hanack@uni-tuebingen.de
[b] Optical Sciences Division, Naval Research Laboratory,
Washington, DC 20375, USA

DOI: 10.1002/ejoc.200500175



**1**

R =



The reason for the choice of an unsymmetrical pattern of substitution in binuclear system **1** with one unsubstituted ring is due to the major easiness of its separation and purification in the process of synthesis (Scheme 2).

## Results and Discussion

### Synthesis of Axially Substituted Binuclear Phthalocyanine 1

A multistep procedure (Scheme 1 and Scheme 2) is necessary to synthesize the binuclear-fused phthalocyaninato indium chloride **1**. Following a method developed by our group we first synthesized and isolated compound **4** (**ABBB** product)[33] containing Mg as central metal (Scheme 1), by statistical condensation of the dinitriles **2** and **3** (see Exp. Sect.). Mg is initially inserted in complexes **4** and **7** instead of InCl because during the several subsequent steps the InCl moiety would not be kept coordinated by macrocycles **4**–**7**. Mg as central metal in complex **7** can be easily replaced in the final steps by the InCl moiety (see Scheme 2).[56]

The other statistical products **AAAB**, **AABB**, and **ABAB**m which are formed in different amounts during the synthesis of **4** (Scheme 1), were discarded after separation of **4** by column chromatography on silica gel. The reaction between **4** and (tetraphenyl)cyclopentadien-1-one in dry toluene produced **5** in high yield (ca. 90%). The subsequent reaction of **5** with fumaronitrile produced **6** in high yield (> 80%). Dehydration of **6** with DBU in anhydrous toluene at 110 °C (Scheme 1) gave **7**.

For the preparation of **8** (Scheme 2) we also used the statistical condensation method.[33] The substituted Pc dinitrile **7** and a ten-fold excess of phthalonitrile were allowed to react in the presence of magnesium(II) pentanolate in *n*-octanol at 175 °C, to give **8** after 24 hours (Scheme 2). The other main product of this reaction was unsubstituted PcMg, which was easily separated from **8** by chromatography on silica gel (see Exp. Sect.). Other statistical products were produced in negligible amounts since the ten-fold excess of phthalonitrile used in this reaction gave mainly **8**. Since $Mg^{II}$ as coordinating metal is relatively easy to remove from the cavity of the Pc macrocycle, e.g. with $CF_3COOH$,[56] the formation of the metal-free binuclear phthalocyanine **9** could be easily achieved. Compound **9** was directly transformed into the binuclear phthalocyanine **1** (Scheme 2) by treatment with $InCl_3$ in DMF.

### NMR Spectroscopy

The $^1H$ NMR spectra of **1** and **8** are quite similar since the macrocycles in the binuclear Pcs are identical. The introduction of a central metal with an axial ligand (InCl in this case) did not totally prevent molecular aggregation in solutions of **1**, since the binuclear Pcs possess one unsubstituted ring. However, aggregation is more evident in the metal-free Pc **9**, as observed in the aromatic region of its $^1H$ NMR spectrum.

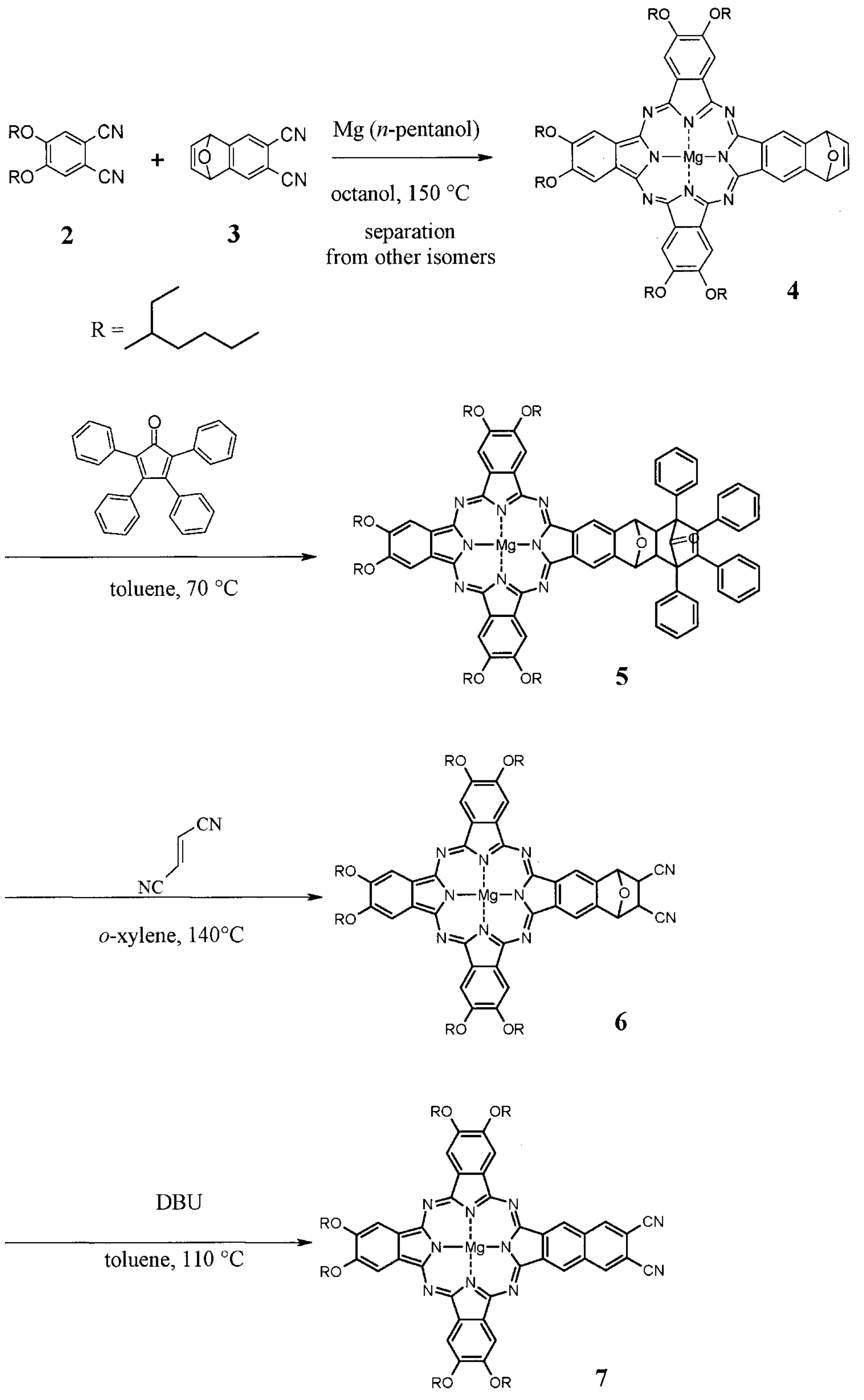
In the $^1H$ NMR spectra of **1** and **8** the aromatic region (range: 6–9 ppm) exhibits asymmetric peaks which are ascribed to aggregation (see Exp. Sect.). The $^1H$ NMR spectrum of **1** shows at $\delta$ = 6.91 ppm the protons H-25, H-30, H-33 and H-38 (Scheme 2). Signals at $\delta$ = 7.17 and 7.28 ppm are attributed to H-17 and H-15, respectively. The signals of H-10, H-9 and H-2 appear between 7.40 and 7.90 ppm, while the H-1 and H-8 protons are centered around 8.84 ppm.

For **9**, the characteristic NH peaks can be seen at –0.26 and –0.45 ppm. Since these protons are not equivalent, due to the asymmetry of the molecule, two peaks appear in the referred region. The $^{13}C$ NMR spectra are also quite similar for the compounds **1**, **8** and **9** (see Exp. Sect.). The corresponding carbon atoms in **1**, **8** and **9** show NMR peaks which appear in the same region. For instance, the $^{13}C$ NMR spectrum of **1** shows the aromatic carbon peaks for C-22, C-25 and C-30 in the region around 105 ppm. The C-1, C-8, C-9 and C-2, C-7, C-10 carbon atoms of the unsubstituted part of the binuclear Pc **1** are centered at $\delta$ = 124 ppm and 129 ppm, respectively. Carbon atoms C-15 and C-17 are allocated at $\delta$ = 127.5 and 128.2 ppm, respectively. The alkyloxy-substituted aromatic carbon atoms C-23, C-24, C-31 are seen around 153 ppm.

### IR and UV/Vis Spectroscopy

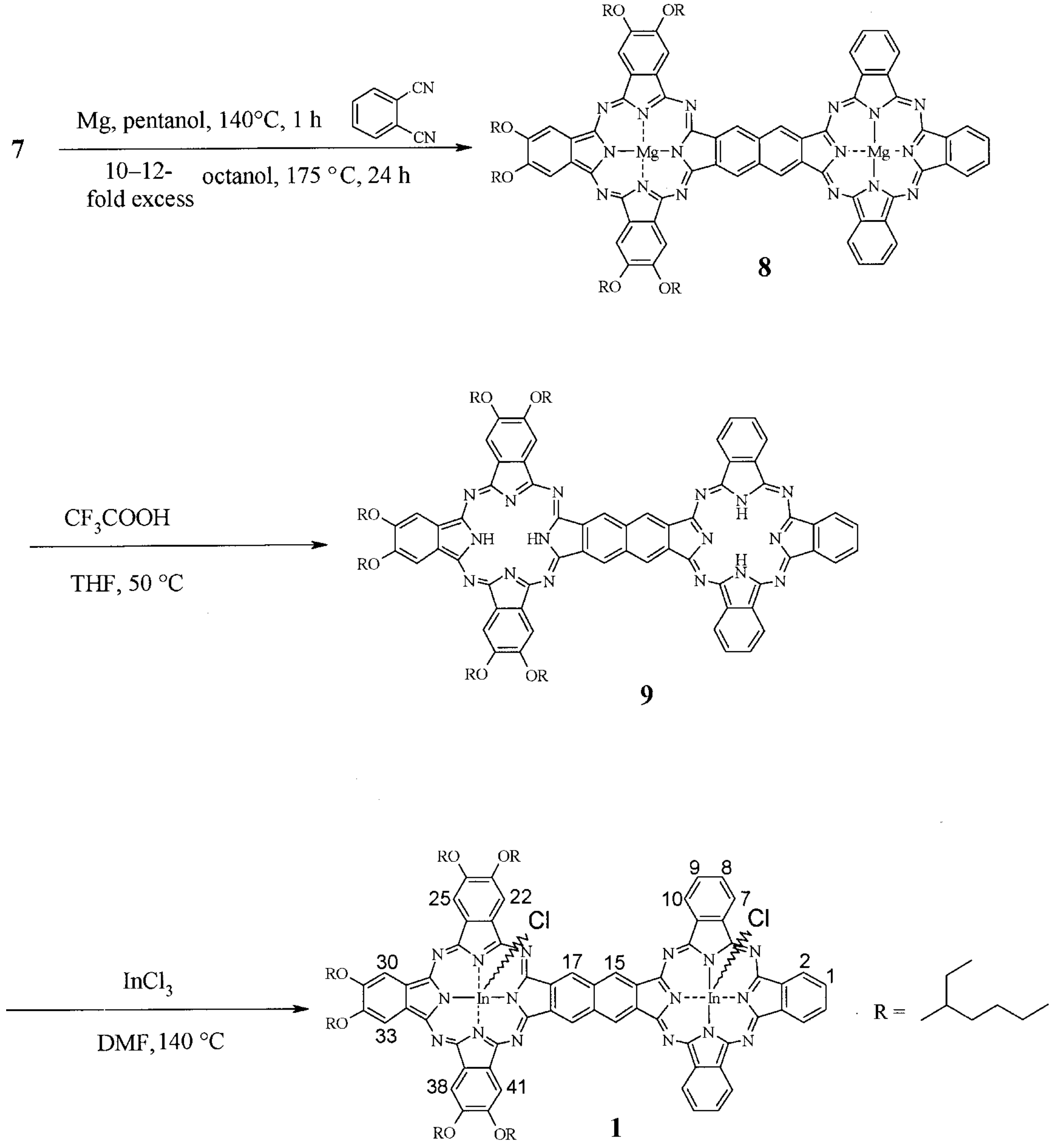
The IR spectra of compounds **1, 8** and **9** resemble those of mononuclear phthalocyanines. The IR spectrum of **9** (metal-free binuclear Pc) has the typical NH stretching band at 3298 $cm^{-1}$ which, of course, is not seen in compounds **1** and **8**.

From the analysis of all the reported spectra we could not determine whether **1** is constituted by one isomer (with chlorines either in *syn* or *anti*), or a mixture of both forms.[42] Ordinary separation techniques did not allow the resolution of the different topoisomers of **1**, which we have shown with similar compounds earlier.[58]



Scheme 1. Synthesis of the unsymmetrical PcMg **7**, starting from dinitriles **2** and **3**.

The UV/Vis spectra of dilute solutions of **1** and **8** are shown in Figure 1, the main peaks of absorption of the binuclear Pcs **1**, **8** and **9** (in $CH_2Cl_2$) are listed in Table 1. When comparing the optical spectra of the binuclear Pcs with the respective monomers [**1** with $(RO)_8PcInCl$ (R = 2-ethylhexyl) and **8** with $(RO)_8PcMg$ (R = 2-ethylhexyl)], little red shift is observed for the more intense peak of the group of Q-bands of the binuclear systems. This indicates that there is an apparent little increase of π-electron delocalization in passing from mononuclear to the binuclear systems



Scheme 2. Synthesis of the binuclear Pc **8**, precursor for the preparation of the axially substituted binuclear PcInCl **1** via metal-free binuclear $PcH_2$ **9**.

**1**, **8** and **9**.[33] The peripheral substituent 2-ethylhexyloxy in monomeric $(RO)_8PcInCl$ and $(RO)_8PcMg$, and dimeric **1**, **8** and **9** is not racemic.

The new features observed in the spectra of the binuclear complexes are shoulders that appear approximately 25 nm red-shifted with respect to the most intense Q-band maxima. The change in the spectra indicates that the two condensed Pc rings show an almost independent behavior in terms of π-electron delocalization. In fact, no mesomeric structures for compounds **1**, **8** or **9** including both rings can be drawn.

Another minor reason for the small variations in the UV/Vis spectra of mononuclear and binuclear systems might be the loss of planarity in the binuclear molecules, even though modeling with the MM1 program shows that the structure

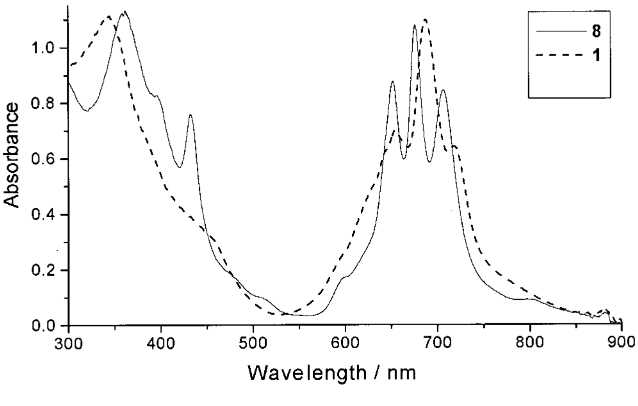


Figure 1. UV/Vis spectra of Pcs **8** (——) and **1** (----) for comparison (cuvette thickness: 10 mm; concentrations < $1 \times 10^{-4}$ M) in $CH_2Cl_2$.

Table 1. Wavelengths and molar extinction coefficients in correspondence of the Q and B bands of binuclear Pcs **1**, **8** and **9**, and mononuclear $(RO)_8PcMg$ and $(RO)_8PcInCl$. All spectra were recorded in $CH_2Cl_2$ as solvent. (R = 2-ethylhexyl).[a]

| Compound | $Q_{0-1}$/nm [log(ε/mol$^{-1}$ cm$^{-1}$ L)] | $Q_{0-0}$/nm [log(ε,mol$^{-1}$ cm$^{-1}$ L)] | $Q_{1-1}$/nm [log(ε,mol$^{-1}$ cm$^{-1}$ L)] | $B_{0-0}$/nm [log(ε, mol$^{-1}$ cm$^{-1}$ L)] | $B_{0-1}$/nm [log(ε, mol$^{-1}$ cm$^{-1}$ L)] |
|---|---|---|---|---|---|
| **8** | 706.0 (sh)<br>[4.78] | 676.0<br>[4.89] | 652.0 (sh)<br>[4.79] | 432.5<br>[4.73] | 362.0<br>[4.90] |
| **9** | 688.0<br>[4.28] | 673.0<br>[4.35] | 667.0 (sh)<br>[4.27] | – | 358.0<br>[4.45] |
| **1** | 724.0 (sh)<br>[4.46] | 689.0<br>[4.69] | 663.0<br>[4.49] | – | 353.0<br>[4.70] |
| $(RO)_8PcMg$ | – | 679.0<br>[5.31] | 613.0 (sh)<br>[4.69] | – | 360.0<br>[5.01] |
| $(RO)_8PcInCl$ | – | 698.5<br>[5.20] | 629.5 (sh)<br>[4.59] | 446.0<br>[4.34] | 362.5<br>[4.91] |

[a] Concentrations are $2.2 \times 10^{-5}$, $1.4 \times 10^{-5}$ and $9 \times 10^{-6}$ M for dimeric **1**, **8** and **9**, respectively. Solutions of monomeric $(RO)_8PcMg$ and $(RO)_8PcInCl$ were $7 \times 10^{-6}$ and $1.4 \times 10^{-5}$ M, respectively.

with minimum energy for the metal-free compound **9** remains planar. Modeling of **1** was inconclusive but it is conceivable that the indium atoms in **1** may force the two rings into a nonplanar conformation because of the deformation induced by the setting of the indium atom inside the ring cavity. Similar to the mononuclear complexes $(RO)_8PcMg$ and $(RO)_8PcInCl$ whose spectral features are listed in Table 1, the binuclear Pcs exhibit a red shift in going from the Mg/Mg binuclear Pc **8** to the In/In binuclear Pc **1** (Figure 1). The observed red shift is therefore due to the influence of the different central metals, but not to a more extended π-electron delocalization in the binuclear complexes. The lack of significant spectral shifts in passing from mononuclear to binuclear complexes has been theoretically rationalized by means of Density Functional Theory calculations with the binuclear equivalent of **1**, containing GaCl instead of InCl as central moieties.[57]

## Nonlinear Optical Properties of 1

One of the purposes for the synthesis of binuclear InCl/InCl phthalocyanine **1** was also to determine whether a side-by-side phthalocyanine complex had superior optical limiting properties and to compare these properties with those of the state-of-the-art molecule $t\mathrm{Bu}_4\mathrm{PcInCl}$.[46a,51] Pcs and Ncs exhibit nonlinear optical properties and are especially effective for optical limiting (see our review in this journal).[9b] The effect of optical limiting is the reversible decrease of transmittance of an optical system upon increase of the incident light intensity at a system-characteristic threshold value of incident intensity.[47,48] Compounds like Pcs and Ncs exhibit an optical limiting effect through the mechanism of sequential two-photon absorption.[47] In this mechanism, the absorption of the first photon brings the molecule into an excited state which has a sufficiently long lifetime to absorb a second photon at the same frequency of excitation. Optical limiting takes place if the absorption cross-section of the excited state is higher than that of the ground state at the frequency of excitation.[47,48] In phthalocyanines and analogues the absorption of the second photon occurs when the molecule is in an excited triplet state generated after intersystem crossing. In Pcs, if central moieties like GaX or InX [X = Cl, Br, *para*-(trifluoromethyl)phenyl, pentafluorophenyl][46,51–53] are used, optical limiting is particularly effective due to the heavy-metal effect of the central atom (which accelerates intersystem crossing), and the spacing effect of the axial ligand X, which prevents intermolecular aggregation, and thus stabilizing the triplet excited state even at high concentrations.[46]

Nonlinear optical transmission was evaluated for **1** in toluene solution. The nonlinear optical experiments were performed at 532 nm, near the middle of the transmission window that extends from about 450 nm to just beyond 600 nm (Figure 2). In order to maximize the nonlinear signals, the optical studies were performed on a concentrated solution, nominally 5 mM, near the solubility limit of **1** in toluene. The linear optical spectrum of the sample used for nonlinear characterization is shown in Figure 2.

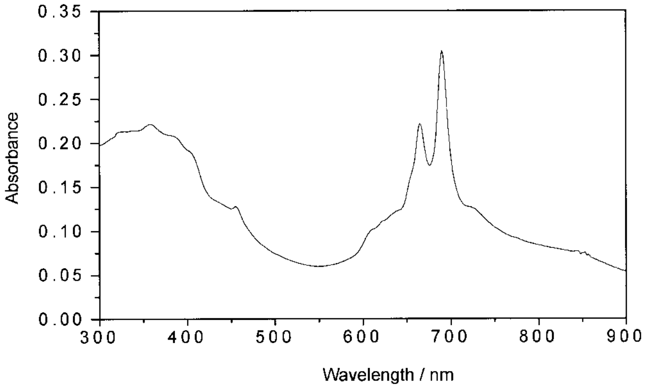


Figure 2. UV/Vis spectrum of **1** in toluene used for Z-Scan measurements (sample thickness: 31.5 μm; concentration: $5 \times 10^{-3}$ M).

There are some changes in the absorption bands in passing from a dilute ($< 10^{-4}$ M in Figure 1) solution to the saturated solution shown in Figure 2.[59] A shoulder at 724 nm becomes less defined and its magnitude is diminished with increasing concentration. In addition there is additional absorption extending to wavelengths longer than those associated with Q-band absorption in the spectrum (Figure 2). This is consistent with a new broad underlying absorption due to molecular aggregation in the more concentrated solution used for the nonlinear measurements. Evidently, the enlargement of the ring size and a lower number of substituents per condensed Pc ring in binuclear **1** lead to an increased tendency towards aggregation with respect to the mononuclear material $(RO)_8PcInCl$. In addition, there is also evidence for light scattering in the spectra of the nearly saturated solution of binuclear **1**.

It is expected that the presence of a racemic mixture for the chiral peripheral substituent RO in **1** does not alter considerably its solubility with respect to a dimeric PcInCl with enantiomerically pure peripheral substituents. This is because the lack of planarity of the condensed macrorings and the spacing effect of the axial substituents do not allow a very close packing of the peripheral substituents in aggregated **1**. As a consequence of that, the interactions between peripheral substituents belonging to different dimers are not strong enough to determine the relative orientations of **1** in an aggregated state. In conclusion, the behavior of dimeric Pc **1** in terms of aggregation is not dependent on the nature of the absolute configuration of the chiral center in the peripheral substituent 2-ethylhexyloxy.

The Z-scan technique[60] was used to study the nonlinear absorption and refraction of **1** for nanosecond pulses. The apparatus has been described previously.[46] The laser was a spatially filtered, doubled Nd:YAG laser at 532 nm with a pulse duration of 7 ns (Full-Width Half-Maximum) and a repetition rate of up to 10 Hz. It produced a near-Gaussian beam ($M^2 \approx 1.2$) using approximately f/5 optics. The energy, $E_{in}$, of the incident radiation was varied over the range $10\,nJ < E_{in} < 1500\,nJ$. This corresponds to peak fluences at the sample ranging from $0.17\,J\,cm^{-2}$ to $17\,J\,cm^{-2}$. The transmittance of the sample was measured as a function of the sample position along the optical axis with either open or 40% transmitting apertures at the detector. The zero position corresponds to the beam focus.[46]

The Z-scan profiles in the open-aperture configuration[60] are shown in Figure 3. At each of the excitation energies shown in the figure caption, the saturated solution of binuclear PcInCl **1** in toluene shows a decreasing transmission as the focal position is approached. Compound **1** clearly has a positive nonlinear absorption coefficient; it is a reverse saturable absorber and an optical limiter against nanosecond pulses at 532 nm. A small, intensity-dependent offset is seen between the scans in Figure 3. The origin of this is not clear.

The transmission at focus as a function of incident energy is shown in a logarithmic scale in Figure 4 and has a regular linear profile as evidenced in Figure 5. The threshold for optical limiting, defined as the incident energy at which the transmission is half the transmission at low intensity, is ca. 700 nJ. This threshold is significantly higher than that observed for $tBu_4PcInCl$.

In order to compare the nanosecond nonlinear transmission properties of the side by side binuclear InCl/InCl phthalocyanine dimer **1** with the monomeric $tBu_4PcInCl$ we consider the nonlinear absorption coefficient, $a_{NL}$, of the two materials. The magnitude of $a_{NL}$ depends on the *difference* between the excited and ground-state absorption cross-sections:[46,61,62]

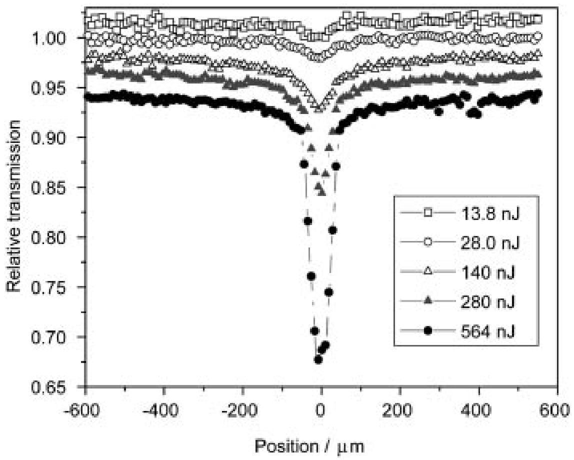


Figure 3. Z-scan profiles of the relative transmittance of binuclear PcInCl **1** saturated solution in toluene at 532 nm as a function of the sample distance from the focus (sample position = 0) in the open-aperture configuration. The value of the incident energy (in nJ) is specified for each profile.

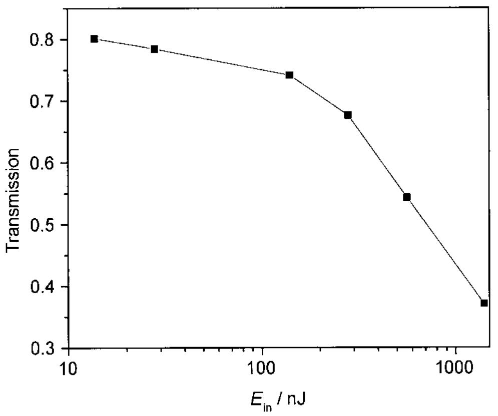


Figure 4. Variation of the sample transmittance with incident energy $E_{in}$ at 532 nm for the saturated solution of **1** in toluene at the focus of a Gaussian beam collimated with f/5 optics. Points are taken from the corrected minima of the Z-scan profiles run in the open-aperture configuration.

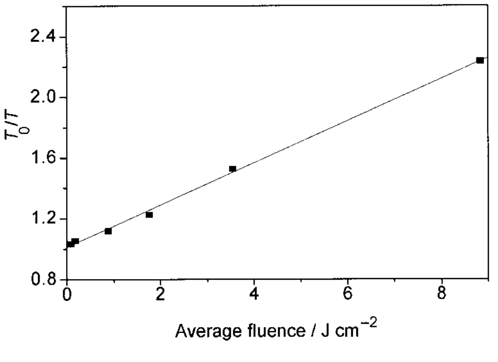


Figure 5. Variation of the reciprocal of normalized transmittance at 532 nm for the saturated solution of **1** in toluene as a function of the incident fluence $F_{in}$ at 532 nm.

$$\alpha_{NL} = \frac{N_T\sigma_0(\sigma_{exc} - \sigma_0)}{2h\nu} \quad (1)$$

where $\sigma_0$ is the ground-state absorption cross-section (in cm$^2$) for incident photons with energy $h\nu$, $\sigma_{exc}$ is the *effective* excited-state absorption cross-section (in cm$^2$) for incident photons with energy $h\nu$, and $N_T$ is the total density of the molecular absorber (in cm$^{-3}$).

Excited-state absorbers like Pcs and analogues have fluence ($F$ in J cm$^{-2}$) and not intensity ($I$ in W cm$^{-2}$) dependent absorptive properties. Assuming that the lifetime of the excited state is comparable to or longer than the laser pulse width, the variation of the reciprocal of the normalized transmission, $T_0/T$ being $T_0$ the linear transmittance, is given by the formula:[61–65]

$$\frac{T_0}{T} = \left\{1 + \frac{N_T\sigma_0(\sigma_{exc} - \sigma_0)}{2h\nu} L_{eff} F\right\} \quad (2)$$

Equation (2) is valid when the excited-state absorber is in the configuration of an optically thin film. In Equation (2) $N_T$, h$\nu$, and $L_{eff}$ are the total density of the molecular absorber (in cm$^{-3}$), the energy of a single photon (in J) at the analyzed wavelength, and the effective length of the optical path (in µm), respectively. The effective length of the optical path $L_{eff}$ is defined as $L_{eff} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ where $\alpha_0$ and $L$ represent the linear absorption coefficient at the given wavelength and the actual length of the optical path, respectively.

In Figure 5 the variation of $T_0/T$ with incident fluence $F$ is shown. It varies linearly with the incident fluence as expected from Equation (2).[46,61,62] The slope is $S = 0.14$ cm$^2$ J$^{-1}$.

$$\alpha_{NL} = \frac{S}{L_{eff}} \quad (3)$$

The value of $\alpha_{NL}$ can be calculated directly from the slope $S$ of the curve in Figure 5.[61]

At this concentration binuclear PcInCl **1** solution has $\alpha_{NL} = 47$ cm J$^{-1}$. Taking into account this value of $\alpha_{NL}$ and $\sigma_0 = 1.5\times10^{-17}$ cm$^2$ from the spectrum in Figure 2, Equation (1) gives $\sigma_{exc} = 2\times10^{-17}$ cm$^2$ for **1**. At the same wavelength mononuclear $t$Bu$_4$PcInCl shows a higher effective excited-state absorption cross-section, approximately $\sigma_{exc} = 6\times10^{-17}$ cm$^2$. The ground-state cross-section for $t$Bu$_4$PcInCl is $\sigma_0 = 2\times10^{-18}$ cm$^2$[46,51] and it results much smaller than that for binuclear compound **1** at the wavelength of analysis.

The comparison of the *effective* excited-state absorption cross-section values indicates that condensing the PcInCl as in compound **1** does not lead to an improvement of the optical limiting effect for nanosecond pulses compared to $t$Bu$_4$PcInCl. The assumption made in applying Equation (2) to this data was that the lifetime of the excited state is comparable to or longer than the pulse width. Given the small wavelength shift in the maximum of the linear absorption spectra of mono- and binuclear complexes, it is expected that the excited-state spectra of mononuclear $t$Bu$_4$-PcInCl and binuclear PcInCl **1** (not reported here), will not show substantial differences in terms of the wavelength at which the maximum is located. Therefore, the observed smaller effective cross-section of **1** in the excited state with respect to $t$Bu$_4$PcInCl is not ascribed to the different spectral features of their excited states. It probably results from the shortening of the excited-state lifetime in the fused system **1**, which does not allow the efficient populating of the level associated with such a short-lived excited state.[66] This would be a consequence of the exciton–exciton annihilation induced by the greater degree of aggregation in the binuclear material (intermolecular effect). Moreover, it is also possible that the efficiency of pumping binuclear **1** into an absorbing excited state is intrinsically lower because the fused system (of which both rings are only weakly interacting as shown by the linear absorption spectroscopy) allows the possibility of independent excitation in either of the two rings, and at high excitation fluences, exciton–exciton annihilation can occur as a consequence of having both rings excited simultaneously in the condensed system (intramolecular effect).

The observed figure of merit, $\sigma_{exc} - \sigma_0$,[46,62] is approximately an order of magnitude larger for $t$Bu$_4$PcInCl than for binuclear PcInCl **1** because of the higher ground-state absorption cross-section of **1** as well as the reduced excited-state cross-section. This, in turn, is apparently a result of the higher extent of aggregation. The main absorption bands of **1** are not red-shifted with respect to (RO)$_8$PcInCl (Table 1).[46,51,61] Evidence of increase of electronic conjugation and polarizability in a binuclear phthalocyanine like **1** has not been found through the evaluation of the linear and nonlinear optical properties.

We also performed Z-scans with a 40% aperture at each of the energies shown above in Figure 3 in order to assess the nonlinear refractive contributions. It was difficult to extract quantitative nonlinear refractive information because the closed-aperture transmission curves had an unsymmetrical profile. However, from the shape of these curves, it is clear that the index change is negative with an increase in fluence. At 532 nm, the binuclear PcInCl **1** exhibits a defocusing nonlinearity. This nonlinear refraction is probably mostly of a thermal origin, but an excited-state electronic contribution cannot be excluded a priori.

## Conclusion

The objective of the present work was the synthesis of binuclear axially substituted metal phthalocyanine **1** containing indium chloride as central moiety (**1**: InCl/InCl binuclear phthalocyanine) and, inter alia, the determination of its nonlinear optical transmission.

By a statistical synthesis from phthalonitriles **2** and **3**, the fused Pc **1** was obtained from a multistep synthesis according to Scheme 1 and Scheme 2.

The optical limiting properties of **1** in toluene were evaluated at 532 nm with nanosecond laser pulses using the Z-scan technique in both open- and closed-aperture configurations. In the open-aperture experiments the variation of sample transmittance was consistent with the fact that binuclear PcInCl **1** behaves as a reverse saturable absorber having an effective excited-state absorption cross-section equal to $2\times10^{-17}$ cm$^2$ at 532 nm. This value is similar to but smaller than that found for monomeric *t*Bu$_4$PcInCl in toluene solution.[46a] Therefore, the optical limiting effectiveness of **1** is lower with respect to *t*Bu$_4$PcInCl partially due to the higher linear absorption of **1** in the ground state. This is apparently due to a greater propensity for **1** to aggregate in solution. The greater degree of aggregation may well have also led to a shortening of the excited-state lifetime relative to the mononuclear *t*Bu$_4$PcInCl. It is concluded that enlargement of a π-electron system by itself is not sufficient to enhance the optical limiting properties of a Pc. This is because the variations in solubility and excited-state dynamics can result into a less efficient mechanism of excited-state formation when passing from mononuclear to binuclear fused rings.

## Experimental Section

**[2,3,9,10,16,17-Hexa(2-ethylhexyloxy)-23,26-dihydro-23,26-epoxybenzo-phthalocyaninato]magnesium (4):** Magnesium filings (80 mg) were suspended in pentanol (ca. 10 mL). This suspension was heated to 150 °C (reflux) and maintained at that temperature until a slurry was formed (ca. 1 h). Octanol (20 mL) was added to this slurry, followed by 6,7-dicyano-1,4-epoxy-1,4-dihydronaphthalene (**3**)[33] (780 mg, 4.0 mmol) and 4,5-bis(2-ethylhexyloxy)phthalonitrile (**2**) (4.0 g, 10.4 mmol).[33] The suspension was heated to 160 °C and stirred for 24 h. After cooling, the suspension was poured into CH$_3$OH/H$_2$O (5:1) (150 mL). The formed precipitate was isolated by centrifugation and washed several times with CH$_3$OH. The crude mixture of PcMg complexes was separated by chromatography on silica gel, starting with CH$_2$Cl$_2$ as the mobile phase. After elution of fraction 1 complex **4** was obtained as the second fraction, using a mixture of CH$_2$Cl$_2$/THF (50:1) as eluent. The solvent was removed; the green solid was recrystallized from CH$_3$OH to achieve further purification and dried in vacuo at 100 °C. The other products of the statistical condensation were discarded. Yield: 750 mg (15%), green solid. MS (FAB): $m/z$ = 1372.1 [M$^+$], 1258.9 [M$^+$ – C$_8$H$_{17}$], 1146.1 [M – 2C$_8$H$_{17}$]. $^1$H NMR ([D$_8$]THF): $\delta$ = 0.95, 1.00, 1.15 (br., 36 H, CH$_3$), 1.44 (br., 48 H, CH$_2$), 2.05 (br., 6 H, CH), 4.39, 4.49 (br., 12 H, OCH$_2$), 7.83 (s, 2 H, H-2), 8.58 (s, 2 H, H-1), 9.09 (3s, br, 6 H, H-9, H-12, H-17), 10.00 (s, 2 H, H-4) ppm. $^{13}$C NMR ([D$_8$]THF): $\delta$ = 11.7, 11.8, 14.6 (CH$_3$), 23.5, 23.6, 24.1, 24.3, 24.7, 25.1, 25.3, 30.3, 30.5, 31.6, 31.9, 32.8, 32.9 (CH$_2$), 40.8, 41.1, 42.0 (CH), 72.1 (OCH$_2$), 78.3 (C-2), 106.3, 106.6, 106.7, 107.0, 107.2 (C-9, C-12, C-17), 117.3 (C-4), 122.1, 122.8, 123.2 (C-8, C-13, C-16), 127.3 (C-5), 130.6, 133.5, 133.8, 134.0, 135.0 (C-1, C-3, C-7, C-14, C-15), 138.0 (C-5), 150.6 (C-6), 152.4, 152.9, 153.1, 154.0, 154.5 (C-10, C-11, C-18) ppm. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 682.5, 620.0, 359.0 nm.

**[2,3,9,10,16,17-Hexa(2-ethylhexyloxy)-23,26-dihydro-23,26-epoxybenzo-24,25-tetracyclone phthalocyaninato]magnesium Adduct (5):** A mixture of **4** (140 mg, ca. 100 µmol) and tetraphenylcyclopentadien-1-one (40 mg, 103 µmol) was dissolved in dried toluene (30 mL) and stirred at 72 °C for 2 days. The solvent was evaporated and the residue was separated by flash chromatography on SiO$_2$ using CH$_2$Cl$_2$ as eluent (first fraction: Tetracyclone, second fraction: **5**). The solvent was evaporated, the product dried in vacuo at 100 °C and reprecipitated from CH$_3$OH. Yield: 165 mg (92%), green solid. MS (FAB): $m/z$ = 1756.9 [M$^+$], 1346.3 [M$^+$ – C$_{30}$H$_{22}$ – CO]. $^1$H NMR ([D$_8$]THF): $\delta$ = 0.81, 1.04, 1.21 (br., 36 H, CH$_3$), 1.40, 1.62 (br., 48 H, CH$_2$), 2.40 (br., 6 H, CH), 3.40 (s, 2 H, H-1), 4.15, 4.38 (br., 12 H, OCH$_2$), 6.33 (s, 2 H, H-2), 6.94, 7.03, 7.06, 7.20 (br., 10 H, H-40, H-41, H-42), 7.23–7.67 (br., 10 H, H-40′, H-41′, H-42′), 8.91, 9.07 (3 s, br, 6 H, H-9, H-12, H-17), 9.51 (s, 2 H, H-4) ppm. $^{13}$C NMR ([D$_8$]THF): $\delta$ = 11.6, 11.8, 14.5, 14.6 (CH$_3$), 23.6, 24.0, 24.2, 24.7, 25.0, 25.3, 26.0, 30.2, 31.8, 32.0 (CH$_2$), 40.6, 41.0 (CH), 48.6 (C-1), 65.7 (C-37), 68.2, 72.0, 72.2 (OCH$_2$), 82.7 (C-2), 106.1, 106.3, 106.6 (C-9, C-12, C-17), 114.1 (C-4), 127.3, 127.9, 128.3, 128.9, 130.7, 131.2 (C-8, C-13, C-16, C-40–42, C-40′–42′), 136.8, 137.2, 137.9 (C-39, C-39′) 139.6, 139.9 (C-38), 149.2, 150.8, 153.0 (C-3, C-5, C-6, C-7, C-14, C-15), 154.4, 154.9, 155.6, 156.5 (C-10, C-11, C-18), 196.9 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2959, 2926, 1178 (C=O) 1605, 1481, 1462, 1391, 1358, 1275, 1263, 1234, 1105, 1061, 802, 696 cm$^{-1}$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 685.0, 613.0, 359.5 nm.

**[2,3,9,10,16,17-Hexa(2-ethylhexyloxy)-23,26-dihydro-23,26-epoxybenzo-25,26-phthalocyaninato]magnesium Fumaronitrile Adduct (6):** Compound **5** (180 mg, 100 µmol) and fumaronitrile (63 mg, 800 µmol) were dissolved in *o*-xylene (4 mL) and stirred in a sealed tube at 140 °C for 16 hours. The solvent was evaporated and the residue separated by flash chromatography on SiO$_2$. Using CH$_2$Cl$_2$ as eluent 1,2,3,4-tetraphenylbenzene was obtained at the first fraction, whereas the mixture CH$_2$Cl$_2$/THF (5:1) gave **6** in the second fraction. After solvent evaporation the obtained solid was dried in vacuo at 100 °C and reprecipitated from CH$_3$OH. Yield: 135 mg (93%), dark green solid. MS (FAB): $m/z$ = 1424.1 [M$^+$], 1346.1 [M$^+$ – C$_4$H$_2$N$_2$]. $^1$H NMR ([D$_8$]THF): $\delta$ = 1.03, 1.04, 1.16, 1.18 (br., 36 H, CH$_3$),1.31, 1.53, 1.82 (br., 48 H, CH$_2$), 2.05 (br., 6 H, CH), 3.25 (br., 2 H, H-1), 4.51 (br., 12 H, OCH$_2$), 6.35 (br., 2 H, H-3), 8.98 (br. s, 6 H, H-9, H-12, H-17), 9.53 (br., 2 H, H-4) ppm. $^{13}$C NMR ([D$_8$]THF): $\delta$ = 11.9, 14.6 (CH$_3$), 24.1, 30.3, 32.0 (CH$_2$), 41.2 (CH), 72.2 (OCH$_2$), 82.2, 84.8 (C-2), 106.1, 106.3, 106.6, 106.9 (C-9, C-12, C-17), 115.3, 116.7 (C-29), 119.9 (C-4), 133.7, 134.2, 134.3 (C-3, C-5, C-8, C-13, C-16), 139.9, 140.2, 142.5, 144.1 (C-6, C-7, C-14, C-15), 151.9, 153.2, 154.0, 155.4 (C-10, C-11, C-18) ppm. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 686.0, 669.0, 609.5, 426.5, 360.0 nm.

**[25,26-Dicyano-2,3,9,10,16,17-hexa(2-ethylhexyloxy)phthalocyaninato]magnesium (7):** Compound **6** (150 mg, 102 µmol) was dissolved in freshly distilled anhydrous toluene inside an argon-purged vessel and 1.2 mL DBU were added. This mixture was stirred for 2 hours at 100 °C, cooled and then extracted with distilled water to remove the unreacted DBU. Subsequent flash chromatography was performed on SiO$_2$ with CH$_2$Cl$_2$ as eluent to get **7**. After evaporating the solvent, **7** was dried in vacuo at 100 °C. Yield: 135 mg (95%), dark green powder. MS (FAB): $m/z$ = 1406.1 [M$^+$], 1293.0 [M$^+$ – C$_8$H$_{16}$]. $^1$H NMR ([D$_8$]THF): $\delta$ = 1.04, 1.07, 1.09 (br., 18 H, CH$_3$), 1.18, 1.21, 1.24 (br., 18 H, CH$_3$), 1.57, 1.81, 1.84, 1.87 (br., 48 H, CH$_2$), 2.10 (br., 6 H, CH), 4.53, 4.59 (br., 12 H, OCH$_2$), 6.36 (br., 2 H, H-4), 8.56 (br., 2 H, H-2), 8.85 (br., 2 H, H-17), 9.02 (2 s, br, 4 H, H-9, H-12) ppm. $^{13}$C NMR ([D$_8$]THF): $\delta$ = 12.0, 14.6 (CH$_3$), 24.2, 25.3, 30.4, 32.0 (CH$_2$), 41.1, 41.2 (CH), 72.2, 72.4 (OCH$_2$), 106.1, 106.5, 106.9 (C-9, C-12, C-17), 109.7 (C-1), 117.3 (C-29), 122.2 (C-4), 132.3, 133.6, 133.9 (C-3, C-5, C-8, C-13, C-16), 134.1 (C-2), 138.2, 138.8, 142.6, 145.3 (C-6, C-7, C-14, C-15), 150.8, 151.7, 152.1, 152.8 (C-10, C-11, C-18) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 710.5, 682.0, 642.0, 544.5, 363.0 nm.

**Binuclear Mg/Mg Phthalocyanine 8:** Magnesium filings (80 mg) were suspended in ca. 10 mL pentanol. The suspension was heated to 150 °C (reflux) and maintained at this temperature until a slurry was formed (ca. 1 hour). After adding octanol (10 mL) a mixture of **7** (210 mg, 140 µmol) and phthalonitrile (210 mg, 1590 µmol) was suspended in this mixture in an argon-purged vessel. The mixture was stirred and heated to 175 °C for 24 h, cooled and poured into $CH_3OH$ (50 mL). The precipitate formed was isolated by centrifugation and was washed several times with $CH_3OH$. The crude mixture was separated by flash chromatography on silica gel, first with $CH_2Cl_2$ as eluent to remove part of the impurities. The eluent mixture was then changed to $CH_2Cl_2$/THF (50:1) to elute **8**, as second fraction. The third fraction could only be partially eluted with pure THF and was identified as the **AAAA** product of the semi-statistical condensation (MgPc) and discarded. After evaporation of the solvent and drying in vacuo, **8** was reprecipitated from $CH_3OH$. Yield: 90 mg (35%), dark green powder. Elemental analysis: calcd. C 72.64, H 7.09, N 11.17; found C 72.52, H 7.33, N 9.95. MS (FAB): *m*/*z* = 1815 [$M^+$]. $^1H$ NMR ([$D_8$]THF): $\delta$ = 0.90, 1.15 (br., 36 H, $CH_3$), 1.29 (br., 48 H, $CH_2$), 2.12 (br., 6 H, CH), 4.39 (br., 12 H, $OCH_2$), 7.47 (s, 4 H, H-25, H-30, H-33, H-38), 7.70 (s, br., 2 H, H-17), 7.79 (s, br., 2 H, H-15), 7.89, 8.02. 8.25, 8.61 (br., 6 H, H-10, H-8, H-9), 8.86 (br., d, 2 H, H-1) ppm. $^{13}C$ NMR ([$D_8$]-THF): $\delta$ = 11.9, 14.0, 14.6 ($CH_3$), 23.7, 24.1, 30.4, 30.6, 31.2, 32.0, 32.9 ($CH_2$), 40.8, 41.2, 42.2 (CH), 72.3, 72.7 ($OCH_2$), 105.9, 106.3, 107.0 (C-22, C-25, C-30), 122.6, 123.5, 123.7, 124.3 (C-1, C-8, C-9), 125.5 (C-15), 127.1 (C-17), 128.8, 129.7, 129.9 (C-2, C-7, C-10), 131.0–136.7 (C-3, C-6, C-11, C-14, C-16, C-18, C-21, C-26, C-29), 139.4, 140.2, 140.7, 142.0 (C-4, C-5, C-12, C-13, C-19, C-20, C-27, C-28), 151.6, 153.0, 153.9 (C-23, C-24, C-31) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 706.0, 676.0, 652.0, 432.5, 362.0 nm.

**Binuclear Metal Free Phthalocyanine 9:** Compound **8** (50 µmol. 90 mg) was dissolved in freshly dried THF. $CF_3COOH$ (5 mL) was added dropwise at room temperature under argon, and this mixture was heated at 50 °C for 5 hours. After cooling, water (20 mL) was added dropwise to the reaction mixture. The formed precipitate was collected and washed several times with $CH_3OH$. After drying in oven at 90 °C overnight the product was purified by column chromatography on silica gel with $CH_2Cl_2$ as eluent. Compound **9** was collected in the first fraction. The second fraction (unreacted **8**) was eluted afterwards with a mixture of $CH_2Cl_2$/THF (10:1). Compound **9** was reprecipitated from $CH_3OH/CH_2Cl_2$ and dried in vacuo at 100 °C. Yield: 70 mg (65%), dark bluish-green powder. Elemental analyses: calcd. C 71.79, H 7.34, N 10.28; found C 71.42, H 7.20, N 9.85. MS (FAB): *m*/*z* = 1770 [$M^+$], 1346.1 [$M^+$ – 4R + Na], 1120.9 [$M^+$ – 6R + Na], 1006.6 [$M^+$ – 6OR + Na]. $^1H$ NMR ([$D_8$]THF): $\delta$ = 0.86 (br., 36 H, $CH_3$), 1.15 (br., 48 H, $CH_2$), 2.28 (br., 6 H, CH), 4.01, 4.11 (br., 12 H, $OCH_2$), 6.81, 7.08, 7.34, 7.65, 7.77, 8.34 (br., PcH) ppm. $^{13}C$ NMR ([$D_8$]THF): $\delta$ = 1, 11.5, 13.8, 14.2 ($CH_3$), 22.7, 23.2, 24.2, 26.1, 29.3, 29.7, 30.8, 31.9 ($CH_2$), 39.8, 40.8, 45.7, 46.3, 47.3 (CH), 71.9 ($OCH_2$), 103.6, 104.5, 105.7, 108.3 (C-22, C-25, C-30), 112.2 (C-15), 114.1 (C-17), 121.3, 121.7, 122.7 (C-1, C-8, C-9), 126.5, 127.5, 128.3, 129.3 (C-2, C-7, C-10), 132.5, 133.2, 134.2, 138.7, 139.5 (C-3, C-6, C-11, C-14, C-16, C-18, C-21, C-26, C-29), 142.0–145.0 (C-4, C-5, C-12, C-13, C-19, C-20, C-27, C-28), 150.6, 151.6, 152.6, 154.4 (C-23, C-24, C-31) ppm. IR (KBr): $\tilde{\nu}$ = 3298 (NH st), 1607 (NH $\delta$), 801 (NH $\delta$) $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 688.0, 673.0, 667.0, 358.0 nm.

**Binuclear In/In Phthalocyanine 1:** Binuclear Pc **9** (70 mg, 40 µmol) and an excess of $InCl_3$ (90 mg, 400 µmol) were suspended in DMF. After adding quinoline (1 mL) the mixture was heated up to 130 °C and maintained at this temperature. After completing the reaction (in about 4 hours as monitored by UV/Vis spectroscopy), water was added dropwise to the mixture to precipitate the compound (20 mL). After centrifugation **1** was three times reprecipitated from hot $CH_3OH$ and dried in vacuo at 100 °C. Yield: 68 mg (82%), dark green powder. Elemental analyses: calcd. C 64.92, H 6.05, N 10.04; found C 65.72, H 5.57, N 9.19. MS (FAB): *m*/*z* = 2060.5 [$M^+$], 1916.0 [$M^+$ – OR – $CH_3$]. $^1H$ NMR ([$D_8$]THF): $\delta$ = 0.87, 0.89, 1.29 (br., 36 H, $CH_3$), 1.40, 1.60 (br., 48 H, $CH_2$), 2.04 (br., 6 H, CH), 4.01, 4.25, 4.50 (br., 12 H, $OCH_2$), 6.91 (s, 4 H, H-25, H-30, H-33, H-38), 7.17 (s, br., 2 H, H-17), 7.28 (s, br., 2 H, H-15), 7.40, 7.78, 7.82. 7.90 (br., 6 H, H-10, H-8, H-9), 8.20, 8.24 (br., d, 2 H, H-1) ppm. $^{13}C$ NMR ([$D_8$]THF): $\delta$ = 11.5, 11.7, 12.2, 14.6, 14.8 ($CH_3$), 21.4, 23.0, 23.5, 26.9, 27.7, 28.0, 30.3, 30.6, 32.8, 35.1 ($CH_2$), 40.0, 40.4, 40.7 (CH), 71.5, 72.2 ($OCH_2$), 104.9, 105.5, 106.4, 106.9 (C-22, C-25, C-30), 123.6, 123.9, 124.8, 125.9 (C-1, C-8, C-9), 127.5 (C-15), 128.2 (C-17), 128.8, 129.6, 129.9, 130.1, 130.9 (C-2, C-7, C-10), 133.0–138.2 (C-3, C-6, C-11, C-14, C-16, C-18, C-21, C-26, C-29), 140.7, 140.9, 142.0 (C-4, C-5, C-12, C-13, C-19, C-20, C-27, C-28), 152.0, 152.7, 153.5 (C-23, C-24, C-31) ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2927, 2858, 1602, 1494, 1457, 1383, 1276, 1202, 1098, 1049, 892, 740.7, 567 $cm^{-1}$. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ = 724.0, 689.0, 663.0, 353.0 nm.

**Apparatus for Nonlinear Optical Experiments with Nanosecond Pulses:** The experimental apparatus for the nanosecond optical limiting experiments with the Z-scan technique has been described previously in ref.[46]. The nanosecond pulsed laser beam for Z-scan experiments at 532 nm was generated by a doubled Nd:YAG laser with an 8 ns pulse width. The actual beam profile for nanosecond experiments resembled a Gaussian profile with a correlation higher than 95%. The input laser beam is expanded in such a way that only the central 10% was transmitted by a first spatial filter before focussing on the sample. The reason for such an arrangement is to produce an approximately flat (not-peaked) top intensity profile. The repetition rate of incidence on the sample was 10 Hz in the whole range of incident energies. The energy of the incident beam could be modulated through the filtering action of waveplate/polarizer combinations. The optics of collimation for all experiments was f/5, whereas the optics of collection in the open-aperture configuration was f/0.8. The thin layer of the liquid solution of **1** was sandwiched between two $CaF_2$ optical windows. The sample was mounted on a translation stage and moved through the beam focus by means of a piezoelectric driver. The value of the beam radius at the focus is 2.5 µm at 532 nm. The evaluation of the focus location for the positioning of the sample was made possible by measuring the minimum energy transmitted by the system when the value of the incident energy was close to its limiting threshold.[46]

## Acknowledgments

Financial support from EU (contracts HPRN-CT-2000–00020 and HPRN-CT-2002–00323) is gratefully acknowledged. Dr. Sergej Vagin from the University of Ivanovo (Russia) is acknowledged for some useful suggestions.

---

[1] M. Hanack, M. Lang, *Adv. Mater.* **1994**, *6*, 819.
[2] P. Erk, H. Hengelsberg, in: *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Elsevier Science: Amsterdam, **2003**, vol. 19, pp. 105–150.
[3] a) R. F. Parton, I. F. J. Vankelecom, M. Casselman, C. P. Bezoukhanova, J. B. Uytterhoeven, P. A. Jacobs, *Nature* **1994**, *370*, 541; b) N. Sehlotho, T. Nyokong, *J. Mol. Catal. A: Chem.*

**2004**, *209*, 51; c) T. V. Magdesieva, K. P. Butin, T. Yamamoto, D. A. Tryk, A. Fujishima, *J. Electrochem. Soc.* **2003**, *150*, E608; d) A. B. Sorokin, A. Tuel, *Catal. Today* **2000**, *57*, 45; e) M. Kimura, Y. Sugihara, T. Muto, K. Hanabusa, H. Shirai, N. Kobayashi, *Chem. Eur. J.* **1999**, *5*, 3495.

[4] J. J. Simon, H. J. André, *Molecular Semiconductors*, Springer, Berlin, **1985**.

[5] K. Y. Law, *Chem. Rev.* **1993**, *93*, 449.

[6] a) B. Bott, T. A. Jones, *Sensors Actuators* **1984**, *5*, 43; b) R. A. Collins, K. A. Mohammed, *J. Phys. D* **1988**, *21*, 154; c) Y. Sadaoka, T. A. Göpel, W. Jones, *Sensors Actuators B* **1990**, *1*, 148.

[7] H. Yanagi, N. Tamura, S. Taira, H. Furuta, S. Douko, G. Schnurpfeil, D. Woehrle, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1995**, *267*, 435.

[8] M. M. Nicholson, in: *Phthalocyanines: Properties and Applications* (Eds.: C. C. Leznoff, A. J. P. Lever), Wiley-VCH: Weinheim, **1993**, vol. 3, pp. 71–117.

[9] a) M. Hanack, D. Dini, M. Vagin, S. Barthel, *Chem. Rec.* **2002**, *2*, 129; b) D. Dini, M. Barthel, M. Hanack, *Eur. J. Org. Chem.* **2001**, 3759; c) S. R. Flom, in: *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Elsevier Science: Amsterdam, **2003**, vol. 19, pp. 179–190.

[10] R. Hurditch, *Adv. Colour Sci. Technol.* **2001**, *4*, 33.

[11] a) M. J. Cook, *Chem. Rec.* **2002**, *2*, 225; b) S. Palacin, *Adv. Coll. Interf. Sci.* **2000**, *87*, 165.

[12] a) R. Zhou, F. Josse, W. Gopel, Z. Z. Oeztuerk, O. Bekaroglu, *Appl. Organomet. Chem.* **1996**, *10*, 557; b) G. Guillaud, J. Simon, J. P. Germain, *Coord. Chem. Rev.* **1998**, *178–180*, 1433.

[13] a) R. K. Pandey, G. Zheng, in: *Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press: San Diego, **2000**, vol. 6, p. 157; b) E. Ben-Hur, W. S. Chan, in: *Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Elsevier Science: San Diego, **2003**, vol. 19, p. 1.

[14] P. J. Gregory, *J. Porphyrins Phthalocyanines* **2000**, 432.

[15] J. H. Chou, M. E. Kosal, H. S. Nalwa, N. A. Rakow, K. S. Suslick, in: *Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press: San Diego, **2000**, vol. 6, p. 43.

[16] R. Hurditch, *Adv. Colour Sci. Technol.* **2001**, *4*, 33.

[17] D. Dini, M. Hanack, in: *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Elsevier Science: Amsterdam, **2003**, vol. 17, pp. 1–36.

[18] *Phthalocyanines: Properties and Applications* (Eds.: C. C. Leznoff, A. B. P. Lever), VCH: Cambridge, **1989–1996**, vol. 1–4.

[19] Y. R. Shen, *The Principles of Nonlinear Optics*, John Wiley & Sons: New York, **1984**.

[20] B. Sheehy, L. F. Di Mauro, *Ann. Rev. Phys. Chem.* **1996**, *47*, 463–494.

[21] N. B. McKeown, in: *Science of Synthesis* (Houben–Weyle, *Methods of Molecular Transformations-Hetarenes and Related Ring Systems*) (Ed.: S. M. Weinreb), Georg Thieme Verlag: Stuttgart, **2004**, vol. 17, pp. 1237–1368.

[22] M. Hanack, H. Heckmann, R. Polley, in: *Methods of Organic Chemistry (Houben-Weyl -Hetarenes IV: Six-Membered and Larger Hetero-rings with Maximum Insaturation)* (Ed.: E. Schaumann), Georg Thieme Verlag: Stuttgart, **1997**, vol. E9d, pp. 717–842.

[23] M. J. Cook, *Chem. Rec.* **2002**, *2*, 225–236.

[24] M. J. Cook, *J. Mater. Sci. Mater. Electron.* **1994**, *5*, 117–128.

[25] G. Schmid, E. Witke, U. Schlick, S. Knecht, M. Hanack, *J. Mater. Chem.* **1995**, *5*, 855–859.

[26] C. Rager, G. Schmid, M. Hanack, *Chem. Eur. J.* **1999**, *5*, 280–288.

[27] G. Winter, H. Heckmann, P. Haisch, W. Eberhardt, M. Hanack, L. Lueer, H. J. Egelhaaf, D. Oelkrug, *J. Am. Chem. Soc.* **1998**, *120*, 11663–11673.

[28] M. Barthel, M. Hanack, *J. Porphyrins Phthalocyanines* **2000**, *4*, 635–638.

[29] Y. Chen, L. R. Subramanian, M. Barthel, M. Hanack, *Eur. J. Inorg. Chem.* **2002**, 1032–1034.

[30] N. Kobayashi, *Coord. Chem. Rev.* **2002**, *227*, 129–152.

[31] M. J. Cook, *Adv. Mater.* **1995**, *7*, 877–880.

[32] M. Hanack, D. Dini, in: *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Elsevier Science: Amsterdam, **2003**, vol. 18, pp. 215–280.

[33] a) M. Calvete, M. Hanack, *Eur. J. Org. Chem.* **2003**, 2080–2083; b) R. Jung, M. Hanack, *Synthesis* **2001**, *9*, 1386–1394.

[34] N. Kobayashi, Y. Higashi, T. Osa, *J. Chem. Soc. Chem. Commun.* **1994**, 1785–1786.

[35] N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, T. Koyama, A. Monden, H. Shirai, *J. Am. Chem. Soc.* **1994**, *116*, 879–890.

[36] C. C. Leznoff, H. Lam, S. M. Marcuccio, W. A. Nevin, P. Janda, N. Kobayashi, A. B. P. Lever, *J. Chem. Soc. Chem. Commun.* **1987**, 699–701.

[37] J. Yang, M. R. Van de Mark, *Tetrahedron Lett.* **1993**, *34*, 5223–5226.

[38] N. Kobayashi, Y. Higashi, T. Osa, *J. Chem. Soc. Chem. Commun.* **1991**, 1203–1205.

[39] T. Fukuda, J. R. Stork, R. J. Potucek, M. M. Olmstead, B. C. Noll, N. Kobayashi, W. S. Durfee, *Angew. Chem.* **2002**, *114*, 2677–2680.

[40] G. De La Torre, M. V. Martinez-Diaz, T. Torres, *J. Porphyrins Phthalocyanines* **1999**, *3*, 560–568.

[41] G. De La Torre, M. V. Martinez-Diaz, P. R. Ashton, T. Torres, *J. Org. Chem.* **1998**, *63*, 8888–8893.

[42] C. G. Claessens, T. Torres, *Angew. Chem. Int. Ed.* **2002**, *41*, 2561–2565.

[43] K. Ishii, N. Kobayashi, Y. Higashi, T. Osa, D. Lelievre, J. Simon, S. Yamauchi, *Chem. Commun.* **1999**, 969–970.

[44] D. Lelievre, L. Bosio, J. Simon, J. J. Andre, F. Bensebaa, *J. Am. Chem. Soc.* **1992**, *114*, 4475–4479.

[45] D. Lelièvre, O. Damette, J. Simon, *J. Chem. Soc., Chem. Commun.* **1993**, 939–940.

[46] a) J. S. Shirk, R. G. S. Pong, S. R. Flom, H. Heckmann, M. Hanack, *J. Phys. Chem. A* **2000**, *104*, 1438–1449; b) J. S. Shirk, R. G. S. Pong, S. R. Flom, M. E. Boyle, A. W. Snow, *MRS Symp. Proc.* **1995** (volume date **1994**), *374*, 201–209.

[47] L. W. Tutt, T. F. Boggess, *Progr. Quant. Electr.* **1993**, *17*, 299–338.

[48] Y. P. Sun, J. E. Riggs, *Int. Rev. Phys. Chem.* **1999**, *18*, 43–90.

[49] T. Xia, D. J. Hagan, A. Dogariu, A. A. Said, E. W. Van Stryland, *Appl. Opt.* **1997**, *36*, 4110–4122.

[50] J. D. Swalen, F. Kajzar, *Nonlinear Opt.* **2001**, *27*, 13–32.

[51] J. W. Perry, K. Mansour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Marder, P. Miles, *Science* **1996**, *273*, 1533–1536.

[52] Y. Chen, D. Dini, M. Hanack, M. Fujitsuka, O. Ito, *Chem. Commun.* **2004**, 340–341.

[53] Y. Chen, M. Fujitsuka, S. M. O'Flaherty, M. Hanack, O. Ito, W. J. Blau, *Adv. Mater.* **2003**, *15*, 899–902.

[54] M. Hanack, T. Schneider, M. Barthel, J. S. Shirk, S. R. Flom, R. G. S. Pong, *Coord. Chem. Rev.* **2001**, *219–221*, 235–258.

[55] D. R. Coulter, V. M. Miskowski, J. W. Perry, T. H. Wei, E. W. Van Stryland, D. J. Hagan, *SPIE Proc.* **1989**, *1105*, 42–51.

[56] a) S. Vagin, M. Barthel, D. Dini, M. Hanack, *Inorg. Chem.* **2003**, *42*, 2683–2694; b) S. Vagin, M. Hanack, *Eur. J. Org. Chem.* **2002**, 2859–2865.

[57] M. J. F. Calvete, D. Dini, M. Hanack, J. C. Sancho-García, J. Cornil, W. Chen, W. Ji, *J. Mol. Model.*, in press.

[58] B. Hauschel, R. Jung, M. Hanack, *Eur. J. Inorg. Chem.* **1999**, 693–703.

[59] A. W. Snow, in: *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Elsevier Science: Amsterdam, **2003**, vol. 17, pp. 129–176.

[60] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.

[61] E. W. Van Stryland, M. Sheik-Bahae, A. A. Said, D. J. Hagan, *Progr. Cryst. Growth Charact.* **1993**, *27*, 279–311.

[62] a) H. S. Nalwa, J. S. Shirk, in: *Phthalocyanines: Properties and Applications* (Eds.: C. C. Leznoff, A. J. P. Lever), Wiley-VCH: Weinheim, **1996**, vol. 4, pp. 79–181; b) S. M. O'Flaherty, S. V. Hold, M. J. Cook, T. Torres, Y. Chen, M. Hanack, W. J. Blau, *Adv. Mater.* **2003**, *15*, 19–32.

[63] J. I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall: Englewood Cliffs (NJ), **1971**.

[64] T. H. Wei, D. J. Hagan, M. J. Sence, E. W. Van Stryland, J. W. Perry, D. R. Coulther, *Appl. Phys. B* **1992**, *54*, 46–51.

[65] U. Gubler, C. Bosshard, in *Polymers for Photonics Applications I (Advances in Polymer Science Series)* (Ed.: K. S. Lee), Springer: Berlin, **2002**, vol. 158, pp. 123–191.

[66] a) K. J. McEwan, P. A. Fleitz, J. E. Rogers, J. E. Slagle, D. G. McLean, H. Akdas, M. Katterle, I. M. Blake, H. L. Anderson, *Adv. Mater.* **2004**, *16*, 1933–1935; b) D. Kim, A. Osuka, *J. Phys. Chem. A* **2003**, *107*, 8791–8816.

Received: March 9, 2005