Phthalocyaninatoindium(III) Acetylacetonates for Nonlinear Optics

Tamer Ezzat Youssef,[a] Sean O'Flaherty,[b] Werner Blau,[b] and Michael Hanack*[a]

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The monomeric octaethylhexyl- and tetra-*tert*-butyl-substituted phthalocyanines **3** and **12** with axial acetylacetonate as ligands were synthesized and characterized, in order to compare their optical limiting properties with the state-of-the-art molecule [tetra-(*tert*-butyl)phthalocyaninato]indium chloride ($(t\mathrm{Bu})_4$PcInCl (**1a**) and the phthalocyanines **1b**–**f**. In addition, the trimer **17** was also synthesized (as a mixture of isomers). The synthesis of **3**, **12** and **17** was carried out by refluxing the corresponding metal-free phthalocyanines, $(t\mathrm{Bu})_4\mathrm{PcH}_2$ (**2**), $(\mathrm{RO})_8\mathrm{PcH}_2$ (**6**) (R = 2-ethylhexyl) and the trimer **16** with an excess of $\mathrm{In(acac)}_3$ in DMF.

Introduction

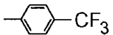
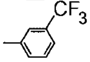
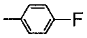
Phthalocyanines (Pcs) and phthalocyaninatometal compounds (PcMs) have attracted considerable attention as a consequence of their diverse optical, electrical and coordination properties, which have led to wide-ranging research.[1] Pcs and many of their derivatives exhibit interesting properties for applications in material science;[2–5] in particular, they have been extensively investigated recently for their nonlinear optical (NLO) properties of which optical limiting (OL) is closest to practical application.[6,7]

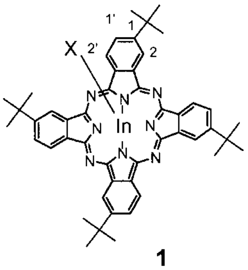
Optical limiters have a transmission that varies with the intensity of the incident light. The transmission is high at normal light intensities but low for intense beams. Ideally, the incident light intensity can limit the transmitted light intensity so that it is always below some maximum value; hence the name. This is useful for protection of elements that are sensitive to sudden high-intensity light, such as optical elements, sensors and, especially, the human eye. Phthalocyanines with a planar π-conjugated system are best suited for OL owing to their good nonlinear optical (NLO) response and high stability against photoirradiation.[8]

[Tetrakis(cumylphenoxy)phthalocyaninato]lead [$(\mathrm{CP})_4$PcPb] described by Shirk et al.[9] and (tetra-*tert*-butylphthalocyaninato)indium(III) chloride $(t\mathrm{Bu})_4$PcInCl, described by Perry et al.[10] and by our group[7,11] are known to be very good optical limiters.

We have previously synthesized the soluble axially substituted (arylphthalocyaninato)indium complexes listed in Table 1, and studied the effect of the axial substituent X on the optical limiting behavior.[7,11] Pcs **1b**–**e** were found to be better optical limiters than the chloro compound **1a**.[7a] Axial substitution alters the electronic structure of the Pc through the presence of an additional dipole moment oriented perpendicularly to the macrocycle.[12] Axial substitution also diminishes aggregation in solution. Both effects strongly influence the OL properties of these compounds.[6,7,13]

Table 1. (Chloro- and arylphthalocyaninato)indium(III) compounds

1	X	abbreviation
a	–Cl	
b		*p*-TMP
c		*m*-TMP
d		*p*- FP
e	$-\mathrm{C_6F_5}$	PFP
f	–Ph	



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We also prepared the corresponding (Pc)gallium $(t\mathrm{Bu})_4$PcGaX (X = Cl, *p*-TMP) and μ-oxo-bridged (Pc)gallium compounds $[\mathrm{R}_n\mathrm{PcGa}]_2\mathrm{O}$[14] and investigated their OL properties.

In continuation of our studies of the synthesis of new Pcs with axial ligands and investigation of their OL properties, we describe here for the first time the synthesis of soluble (phthalocyaninato)indium compounds **3**, **12** and the trimer **17** with acetylacetonate (acac) as the axial ligand. The optical limiting properties of **3**, **12** and **17** are compared with

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[a] Institut für Organische Chemie, Universität Tübingen,
Auf der Morgenstelle 18, 72076 Tübingen, Germany
Fax: (internat.) + 49-(0)7071-295268
E-mail: hanack@uni-tuebingen.de
[b] Department of Physics, Trinity College Dublin,
Dublin 2, Republic of Ireland

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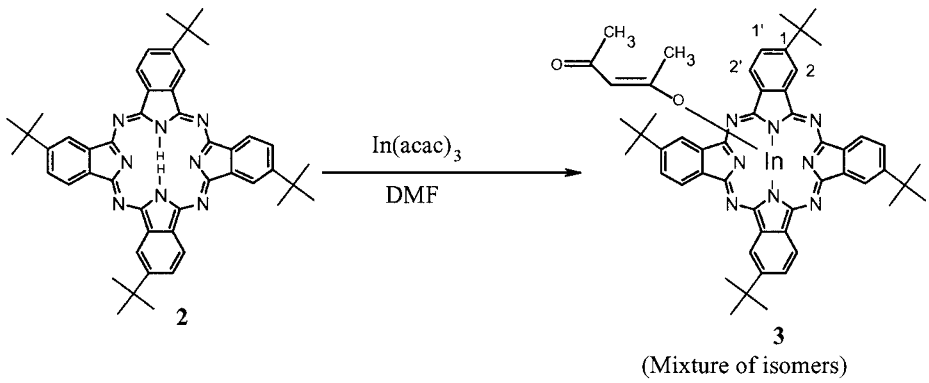


Scheme 1. Synthesis of (tBu)$_4$PcIn(acac) (**3**)

the "state-of-the-art" molecule,[7a,10] (tetra-*tert*-butylphthalocyaninato)indium(III) chloride (**1a**).

Results and Discussion

(Tetra-*tert*-butylphthalocyaninato)indium(III) acetylacetonate (tBu)$_4$PcInacac (**3**) was obtained in good yield by treating the metal-free (tBu)$_4$PcH$_2$ (**2**)[15] with an excess of In(acac)$_3$ in refluxing DMF (Scheme 1).

Pc **3** is much more soluble in organic solvents such as chloroform and toluene than the series of (chloro- and arylphthalocyaninato)indium(III) compounds **1a**−**f**. The structure of **3** was confirmed by spectral methods. The FD mass spectrum of **3** shows a cluster of peaks centered at m/z (%) = 950.8 (100) [M$^+$]. The ^{1}H NMR spectrum of **3** exhibits three multiplets in the aromatic region at δ = 8.38, 9.41 and 9.46 ppm for the 1′-, 2- and the 2′-protons, respectively (see Exp. Sect.).

The UV/Vis spectra of a dilute sample of metal-free (tBu)$_4$PcInH$_2$ (**2**) (recorded in toluene) shows the split Q-bands of the metal-free phthalocyanine centered at 663 and 700 nm.[15] For (tBu)$_4$PcInacac (**3**) the Q-band appears without shifting at 671 nm (Figure 1). The axial (acac) ligand has little influence on the position of the nonsplit Q-band maximum in comparison with the chlorine ligand in **1a**[7b] (697 nm) (Figure 1).

(RO)$_8$PcIn(acac) (**12**) (R = 2-ethylhexyl) was prepared by treating (RO)$_8$PcH$_2$ (**6**) (R = 2-ethylhexyl) with In(acac)$_3$ in DMF at 140 °C (Scheme 2). Compound **6** was isolated from the mixture of Pcs obtained from the reaction between 1 equiv. of 1,2-dicyano-4,5-bis(2-ethylhexyloxy)benzene (**4**)[16] and 6,7-dicyano-1,4-dihydro-1,4-epoxy-1,4-dimethylnaphthalene (**5**)[17] in pentanol at 145 °C in the presence of catalytic amounts of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (Scheme 3).

No NH proton signals could be seen in the ^{1}H NMR spectrum of a pure sample of Pc **12**. The FD mass spectrum

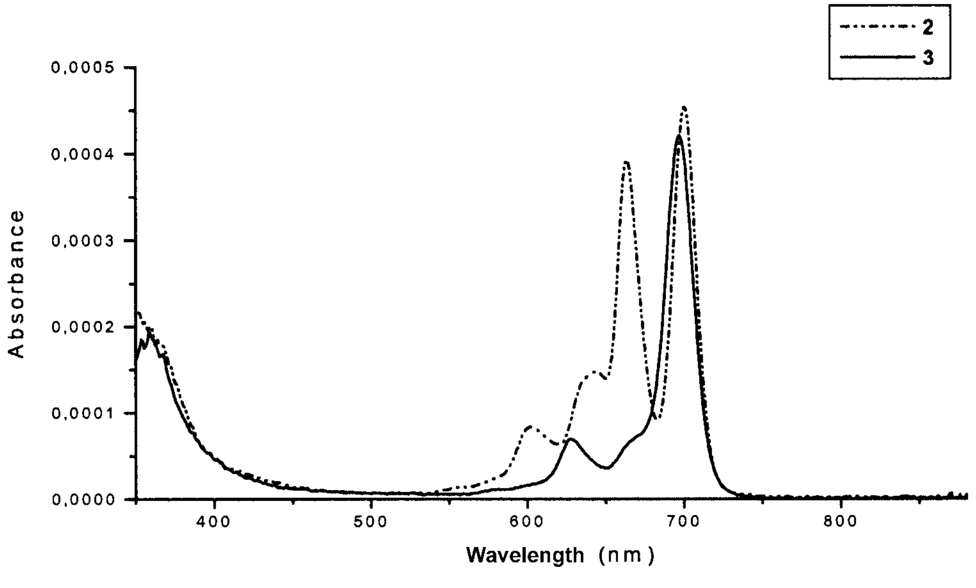
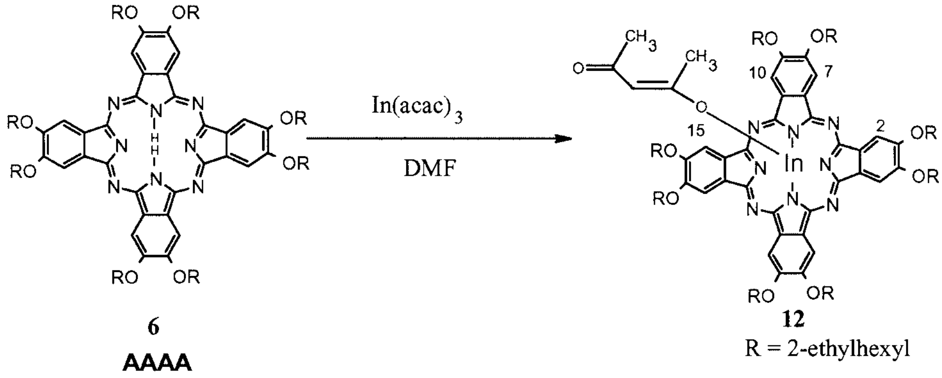
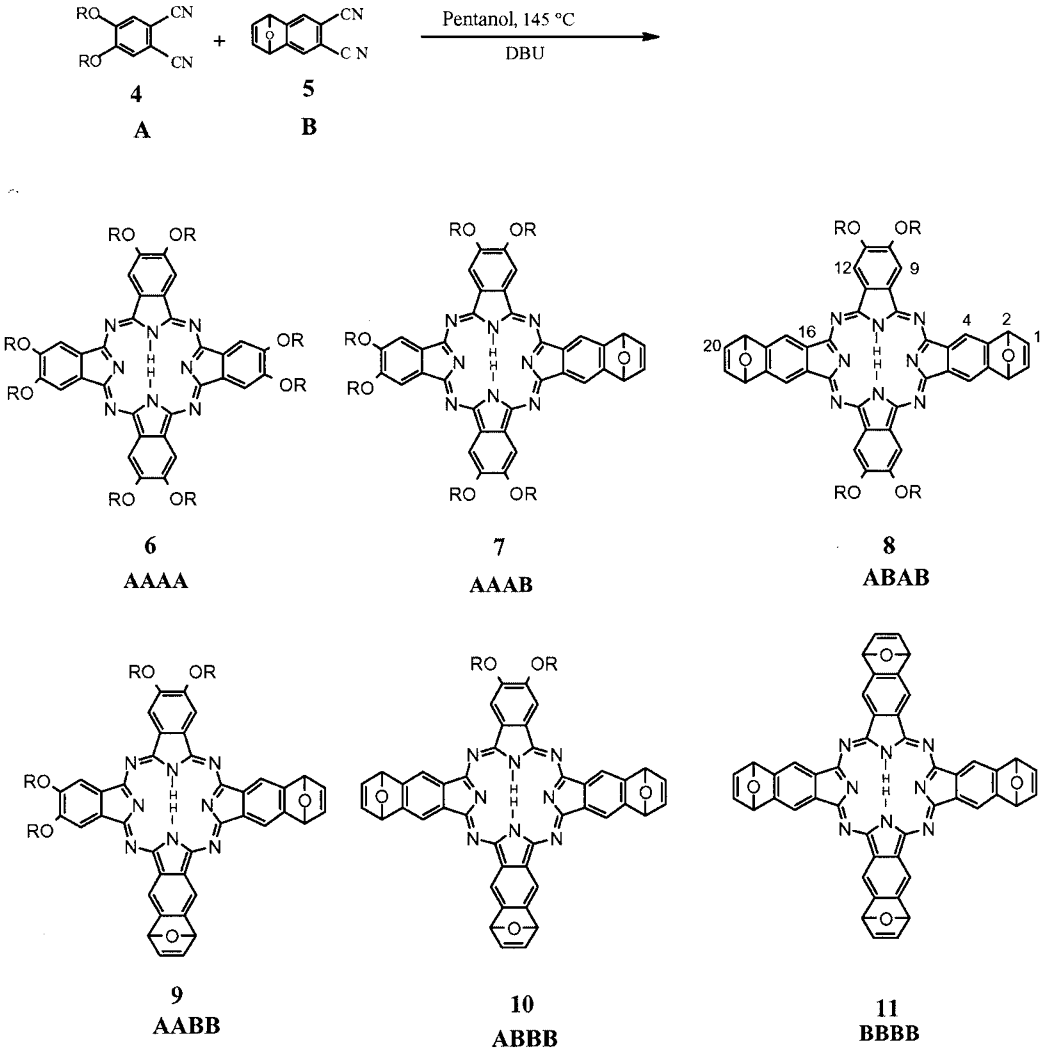


Figure 1. UV/Vis spectra of (tBu)$_4$PcH$_2$ (**2**) and (tBu)$_4$PcInacac (**3**)



Scheme 2. Synthesis of $(RO)_8PcIn(acac)$ (**12**)



Scheme 3. Synthesis of the Pcs **6** and **8**

shows the molecular ion peak [M^+] centered at m/z (%) = 1754.2 (100). In the IR spectrum of **12** the carbonyl band absorption appears at 1775 cm^{-1} (see Exp. Sect.).

The split Q-band in the UV/Vis spectra of a dilute sample of $(RO)_8PcH_2$ (**6**) (toluene) is centered at 662 and 700 nm, the single Q-band of $(RO)_8PcIn(acac)$ (**12**) appears at 696 nm.

For the first time we also investigated the trimeric PcIn compound **17** in order to check whether or not the OL properties of a linear system containing three PcInacac substructures would lead to a considerable increase of the OL properties in comparison to the monomers **3** and **12**, respectively

Trimeric Pcs with a linear structure have previously been prepared by our group.[18]

For the synthesis of trimer **17** we used a repetitive Diels−Alder reaction (DA) along the isobenzofuran route [18] which we have described earlier,[16,19] starting with the bis(dienophilic) Pc **8**.

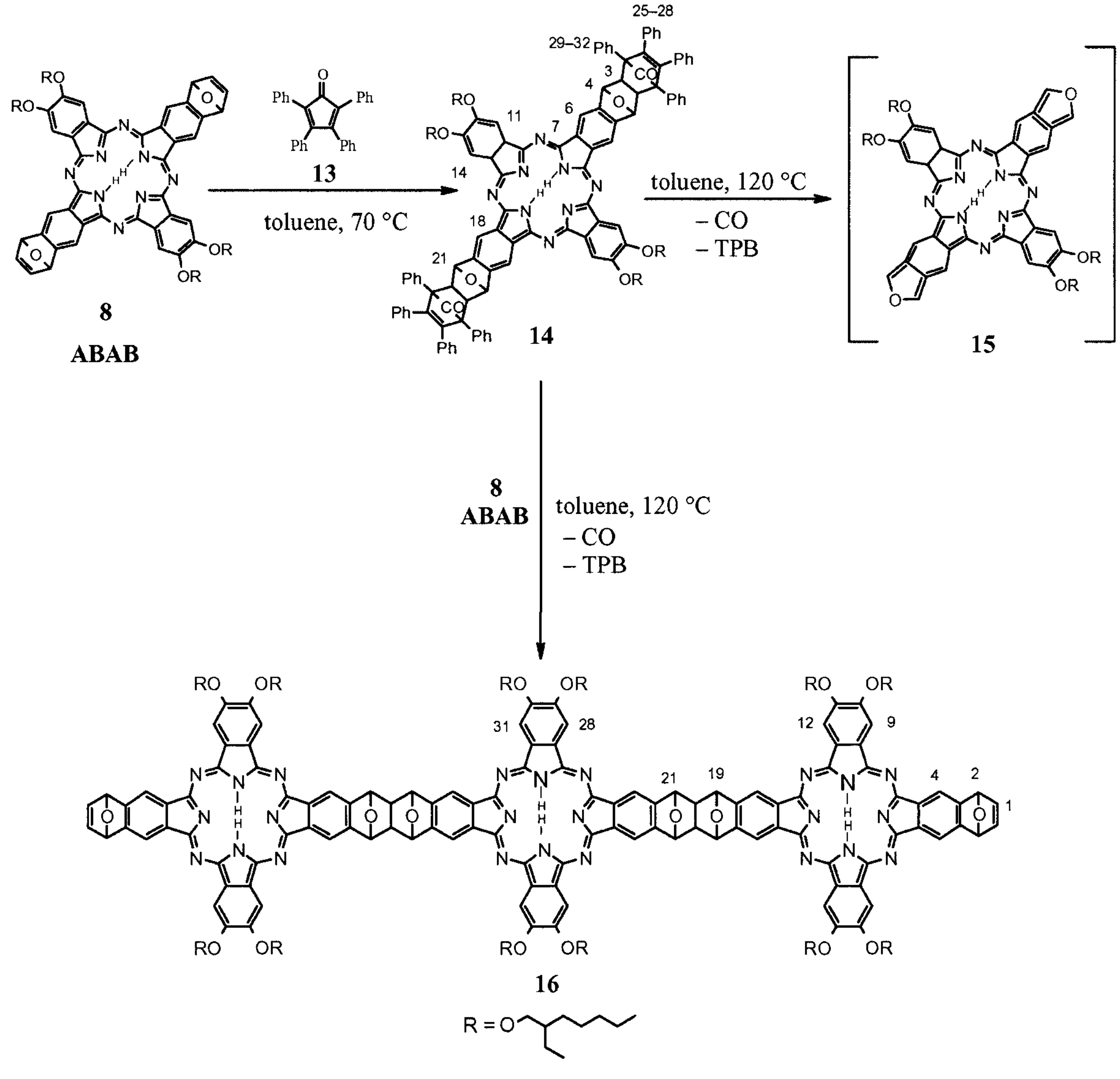
Unsymmetrically substituted Pcs such as, for example, **8** are generally accessible by a statistical condensation of equimolar amounts of two differently substituted phthalonitriles **4** (**A**) and **5** (**B**) which results in the formation of six phthalocyanines, viz. **AAAA** (**6**) (self-condensation of **4**), **AAAB** (**7**), **ABAB** (**8**), **AABB** (**9**), **ABBB** (**10**) and **BBBB** (**11**) (self-condensation of **5**) (Scheme 3).[20]

In the reaction of **4** with **5**, the main products isolated were **8** and **9**; other products are Pcs **6** and **11**.[16,21] Pc **7** and **10** (Scheme 3) were also isolated during the chromatographic workup. The blue-green compounds **6** and **7** were separated from **8**, **9**, **10** and **11** by flash chromatography starting with CH_2Cl_2/hexane (2:1) and ending with CH_2Cl_2/ethyl acetate (2:1) as the mobile phase (see Exp. Sect.). Pc **8** was obtained in yields of up to 17 %.

Compounds **8** and **9** were distinguished by their ^1H NMR and UV/Vis spectra. Pcs **6**, **7**, **10** and **11** were characterized by their FD or FAB mass spectra which showed the peaks for the corresponding molecular ion [M^+].

The ^1H NMR spectrum of **8** exhibits two singlets for the protons of the epoxybenzo units 2-H and 1-H at $\delta = 6.2$ and 7.30−7.38 ppm, respectively, in addition to sharp singlets of the NH at $\delta = -2.4, -2.5$ ppm (see Exp. Sect.). Aggregation of **8** in solution leads to broad resonances in its ^1H NMR spectra.

Pc **8** was converted into the tetracyclone bis(adduct) **14** (Scheme 4) in 70−80 % yield by heating with 1 equiv. of tetraphenylcyclopentadienone (tetracyclone, **13**) in toluene at 70 °C (3−4 d). A small amount of the tetracyclone



Scheme 4. Preparation of trimer **16**

monoadduct was also formed. Separation of the bis(adduct) **14** was achieved by preparative TLC.

By addition of tetracyclone (**13**) to the isolated double bonds in **8**, the signals of the vinylic protons 1-H at δ = 7.30−7.38 ppm disappear and singlets for the methine protons 3-H are found at δ = 3.4 ppm. The appearance of singlets for 3-H in **14** is in agreement with the expected *exo* orientation of the tetracyclone adduct.[16,18] Additional signals for the aromatic protons of the phenyl substituents in **14** are at δ = 7.1−7.67 ppm. The MALDI-TOF MS of **14** shows two fragment peaks at *m*/*z* = 1929.7 and 1107.6 [M^+ − isobenzofuran]. These peaks are due to the loss of CO and 1,2,3,4-tetraphenylbenzene (TPB).

Thermolysis of **14** at 120 °C in toluene leads to loss of CO and 1,2,3,4-tetraphenylbenzene (TBP) with in situ generation of the reactive intermediate **15**, which reacts with a threefold excess of the bis(dienophile) **8** to form the trimer **16** in 25 % yield (Scheme 4).

Trimer **16** was isolated and purified by Soxhlet extraction with ethyl acetate and methanol to remove TPB and excess of **8**. Further purification by column chromatography on silica gel, Al_2O_3 or reversed-phase silica gel was not possible owing to very strong adsorption on the phases used. **16** is soluble in common organic solvents.

Trimer **16** is a mixture of isomers with respect to the position of the oxygen bridges. We did not attempt to separate the isomers; according to earlier results the separation of these kinds of isomers is very difficult.[18]

In **16**, the characteristic resonance of δ = 3.5 ppm (20-H) (the linkage between the macrocycles) and the other signals are in agreement with the ^1H NMR spectroscopic data of the macrocyclic monomer **8**. The ^1H NMR spectrum exhibits broad signals due to aggregation; in particular the resonances of the NH protons are scarcely visible flat broad signals. The MALDI-TOF spectra of **16** showed the molecular ion peak [M^+] at *m*/*z* = 3426.5.

Trimer **17** was obtained by treating the metal-free PcH_2 **16** with an excess of $In(acac)_3$ in refluxing DMF (Scheme 5).

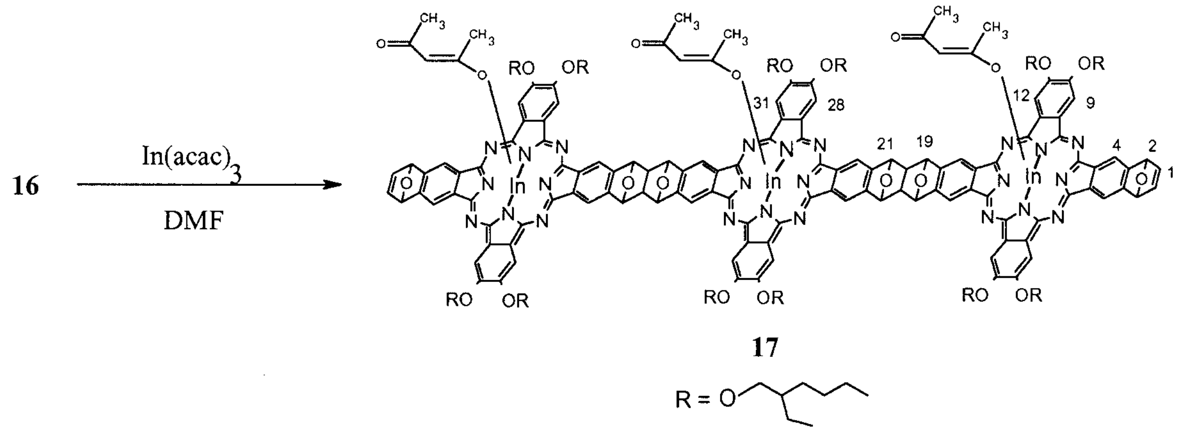
The solubility of **17** in organic solvents is comparatively low, the structure of **17** was established by ^{13}C CP/MAS spectroscopy. The characteristic signal resulting from the Diels−Alder addition is found at δ = 51.00 ppm (C-20). Other signals are in agreement with the ^1H NMR spectroscopic data of the macrocyclic monomer **8** (see Exp. Sect.). MALDI-TOF spectra of **17** (in CF_3COOH) showed the molecular ion peak of the resulting trimer **17** at *m*/*z* = 4062.5. The UV/Vis spectrum of **16** in toluene shows the split Q-band centered at 661 and 699 nm, in **17** the nonsplit Q-band is observed at 686 nm (Figure 2).

From the obtained spectroscopic data, the relative positions of the acac groups (*syn* or *anti* to each other) in **17** cannot be determined; the shown *syn* positions in **17** are arbitrary. As in the case of trimer **16** the oxygen bridges in **17** can be also arranged *syn* or *anti* to each other.

NLO Properties

The open aperture of a Z-scan experiment[23] was used to measure the optical limiting response in the samples. All experiments described in this study were performed using 6-ns 532-nm laser light pulses from a Q-switched frequency-doubled Nd:YAG laser with a pulse repetition rate of 10 Hz. The beam was spatially filtered to remove the higher order modes and tightly focused using a 9-cm focal length lens. All samples were measured in quartz cells with a 1-mm optical path, and at concentrations of 0.5 g/L in spectroscopic grade toluene purchased from Aldrich.

All Z-scans performed exhibit a decrease of transmittance about the focus typical of an induced positive nonlinear absorption of incident light. The nonlinear absorption coefficient, β_I, experienced by the incident pulses was determined from these spectra as a function of the on-focus intensity. Recently, we have adopted this approach in determining effective values of β_I of (phthalocyaninato)gallium and -indium compounds.[24,25] The values of β_I for compounds **1a**, **3**, **12** and **17** as a function of the on-focus intensity (I_0) are plotted in Figure 3. It can clearly be seen that as I_0 increases β_I tends to decrease in magnitude for all samples except for compound **1a** which was measured over a larger intensity range.[24] At intensities beyond those in the figure its β_I coefficient also decreases with increasing intensity. It can be seen that, over the intensity region pre-



Scheme 5. Preparation of trimer **17**

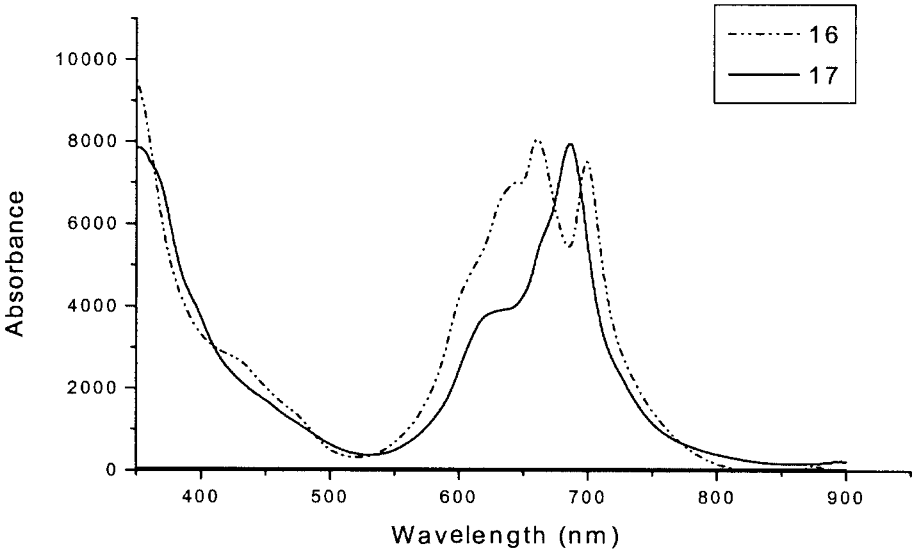


Figure 2. UV/Vis spectra of **16** and **17**

sented in the plot, the magnitude of the nonlinear absorption coefficient is largest for the compounds in the order **12** > **1a** > **3** > **17**. The nonlinear absorption coefficient in all cases is of the order of 10^{-8} to 10^{-7} cm·W^{-1}.

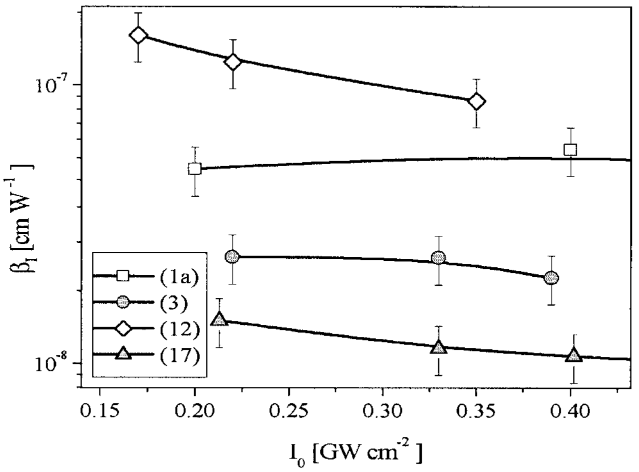


Figure 3. Plots of effective β_I against the on-focus beam intensity I_0 for compounds **1a**, **3**, **12** and **17**; each data point represents an independent open aperture Z-scan, the solid lines are intended as guides to the eye

The optical limiting data plotted with the normalized transmission (T_{Norm}) against the incident energy density per pulse (J·cm^{-2}) are depicted in Figure 4. The nonlinear absorption coefficient $\alpha(F, F_{Sat}, \kappa)$[26] where $\alpha(F, F_{Sat}, \kappa) \approx \alpha_0(1 + F/F_{Sat})^{-1}(1 + \kappa F/F_{Sat})$ derived from laser rate equations in the static state was used to fit the normalized transmission as a function of this energy density to a superposition of all open aperture datasets for each compound. In this expression F represents the energy density, F_{Sat} the saturation energy density and κ the ratio of the excited to ground state absorption cross-sections σ_{ex}/σ_0. The parameters κ (realistically σ_{ex} as α_0 was measured) and F_{Sat} were treated as free constants in the fitting algorithm. The plots of normalized transmission against pulse energy density for compounds **1a**, **3**, **12** and **17** are shown in Figure 4 (a), where the solid lines are theoretical fits to the experimental data. The plot is expanded for clarity in Figure 4 (b) about the section where the data almost overlaps. The α_0, κ and F_{Sat} values for each compound are presented in Table 2.

The F_{Sat} value for the axially substituted (acetylacetonato)indium monomer **3** is reduced significantly compared to that of compound **1a**. The addition of the acetylacetonate group reduced the magnitude of the saturation energy density by a factor of approximately 2.1. This effect was made far more dramatic by modification of the (tBu)$_4$PcInCl (**1a**). The magnitude of the saturation energy density was reduced by more than one order of magnitude when **1a** was modified to **12**. Compound **17** has a far less dramatic effect, reducing the F_{Sat} value by a factor of about 1.2 over compound **1a**. The ratio of the excited to ground state absorption cross-sections $\kappa = \sigma_{ex}/\sigma_0$ was reduced from that exhibited by **1a** to each of the modified species presented here. The κ coefficient was reduced by a factor of 2.5 for modifications to **1a** producing **17** and by a factor of approximately 3.1 for **3**.

Conclusion

Syntheses of the monomeric Pcs **3** and **12** axially substituted with acac, and of the trimer **17**, are described. These (phthalocyaninato)indium compounds with 2-ethylhexyl

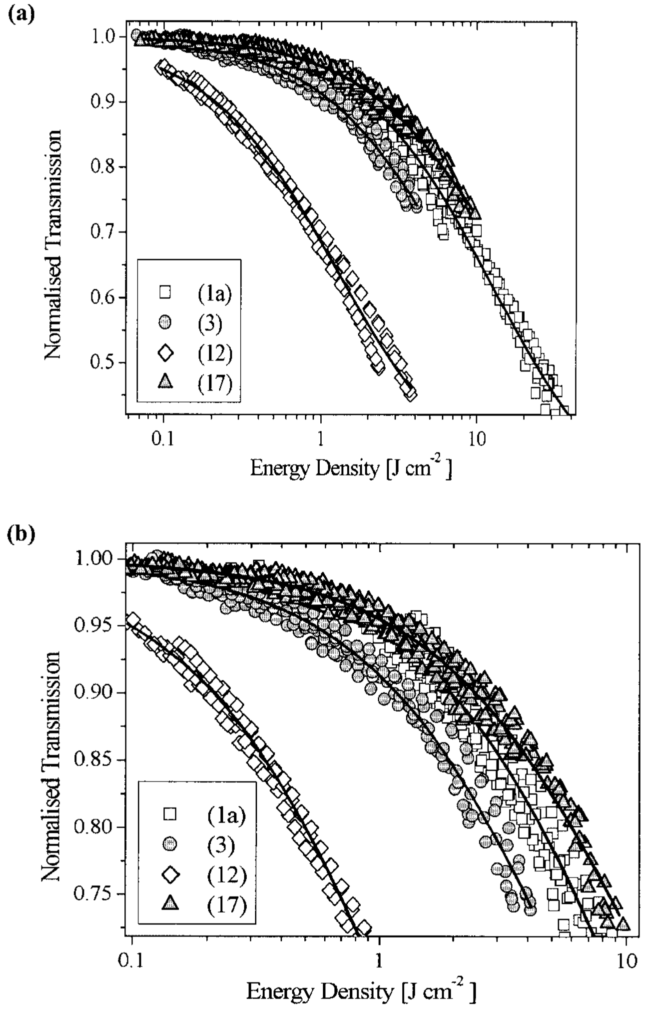


Figure 4. Plots of normalized transmission against pulse energy density for compounds **1a**, **3**, **12** and **17** at 0.5 g/L in toluene where the solid lines are theoretical fits to the experimental data; the fitting parameters are given in Table 2

Table 2. Summary of the nonlinear optical properties for compounds **1a**, **3**, **12** and **17**; all measurements were performed with the compound dissolved in spectroscopic grade toluene at 532 nm

Sample	C [g ·L^{-1}]	α_0 [cm^{-1}]	κ [σ_{ex}/σ_0]	F_{Sat} [J·cm^{-2}]
1a	0.5	0.53	27.4 ± 0.6	24.2 ± 0.8
3	0.5	1.5	8.7 ± 0.7	11.6 ± 1.4
12	0.5	1.3	10.8 ± 0.3	2.3 ± 0.1
17	0.5	0.99	11.0 ± 0.6	20.6 ± 1.5

peripheral substituents are sufficiently soluble to be investigated for their optical limiting properties.

The (phthalocyaninato)indium compounds **3** and **12** with the axially acac ligand show optical limiting properties comparable to the earlier described compounds **1b−f**; however, their κ values are lower than the κ value of **1a**.

No conclusion can be drawn about the symmetry of trimer **17**, which is a mixture of isomers. The κ value and the saturation energy density F_{Sat} of **17**, see Table 2, is the largest of the investigated compounds.

Experimental Section

Instrumentation: FT-IR spectra were recorded with a Bruker IFS 48 spectrophotometer using KBr pellets. The UV/Vis spectra were taken in toluene using a Perkin−Elmer Lambda 2 spectrophotometer. EI mass spectra were obtained with a Finnigan ISQ 70 (200 °C, 70 eV) mass spectrometer, the FD spectra with a Varian MAT 711 A mass spectrometer and reported as mass/charge (*m*/*z*) ratios. NMR spectra were measured with a Bruker 250 ARX spectrometer. The ^{1}H NMR spectra were recorded at 250.1 MHz and the ^{13}C NMR spectra at 62.9 MHz, respectively. The chemical shifts of these spectra were measured relative to partially deuterated solvents and are recorded relative to TMS. The ^{13}C CP/MAS (cross polarization/magic angle spinning) solid-state NMR spectra were recorded with a Bruker ASX 300 multinuclear spectrometer equipped with wide bore magnets (field strength h = 4.7, 7.05 T). Magic angle spinning was applied at 10 kHz.

(tBu)$_4$PcIn(acac) (3): A mixture of (tBu)$_4$PcH$_2$ (**2**)[15] (0.73 g, 1 mmol) and In(acac)$_3$ (acac = acetylacetonate) (0.12 g, 0.3 mmol) was refluxed in anhydrous DMF (15 mL) for 2 h under nitrogen. The mixture was cooled and methanol was added to precipitate the product. The crude Pc **3** was separated and purified by Soxhlet extraction with methanol several times and dried in vacuo to yield a green powder (0.8 g, 84 %). IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 1726 (C=O), 1589, 1488, 1391, 1279, 1086, 831, 761, 672, 500. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ = 700, 663, 602 nm. ^{1}H NMR (TDF): δ = 0.90 (br., 6 H, methyl groups of acac), 1.4−1.72 (m, 36 H, tBu), 2.8 (s, 1 H, CH), 8.34−8.38 (m, 4 H, 1-H′), 9.41−9.44 (m, 4 H, 2-H), 9.46−9.6 (m, 4 H, 2′-H) ppm. FD MS: *m*/*z* (%) = 950.8 (100) [M^{+}].

Pcs 6 and 8: A mixture of 6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalene (**5**)[17] (3.9 mg, 20 mmol), and 1,2-dicyano-4,5-bis(2-ethylhexyloxy)benzene (**4**)[21] (7.6 mg, 20 mmol) was suspended in pentanol (50 mL) in a nitrogen-purged vessel and DBU (0.1 mL) was added. The mixture was heated to 145 °C and stirred for 19 h, cooled and poured into MeOH (200 mL). The precipitate formed was isolated by centrifugation and washed several times with MeOH. The crude mixture of the Pc complexes was separated by flash chromatography on silica gel starting with CH$_2$Cl$_2$ as the mobile phase. After complete elution of fraction 1 to obtain **6** and **7**, CH$_2$Cl$_2$/hexane (2:1) was used as eluent to collect **8** and **9** as the second fraction. After complete elution of **8** and **9**, a mixture of CH$_2$Cl$_2$/EtOAc (2:1) was used as eluent to obtain **10** as the third fraction followed by EtOAC to obtain **11**. The solvent was removed and the blue-green solids were extracted several times with acetone for further purification. Drying in vacuo furnished average yields of **8** (1.9 mg, 17 %) and **9** (2.9 mg, 26 %), **6** (0.7 mg, 6 %) **7** (2.4 mg, 25 %), and **11** (0.71 mg, 6 %).

Pc 8: IR (KBr): $\tilde{\nu}$ = 3420.7 cm^{-1} (NH), 2957, 2923, 2855, 2215, 1604, 1455, 1382, 1275, 1208, 1092, 867, 847, 744, 691, 629, 414. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ = 695, 657, 641, 349 nm. ^{1}H NMR (CDCl$_3$): δ = −2.4, −2.5 (br., 2 H, NH), 1.04−1.2 (br., 24 H, CH$_3$), 1.48, 1.52 (br., 32 H, CH$_2$), 2.05, 2.1 (br., 4 H, CH), 4.3, 4.4 (br., 8 H, OCH$_2$), 6.2 (br., 2-H, 3-H), 7.3−7.38 (br., 4 H, 1-H, 21-H), 8.3, 8.4, 8.7(br., 4 H, 9-H, 12-H), 8.79, 8.87 (br., 4 H, 4-H) ppm. FAB MS: *m*/*z* (%) = 1159.5 (50) [M^{+}].

(RO)$_8$PcIn(acac) (12): A mixture of PcH$_2$ **6** (616 mg, 0.4 mmol) and In(acac)$_3$ (0.06 g, 0.15 mmol) was refluxed in anhydrous DMF

(15 mL) under nitrogen for 3 h. The mixture was cooled and methanol was added to precipitate the product. The crude product **12** was separated and purified by Soxhlet extraction with methanol several times and drying in vacuo to yield a greenish-blue powder (510 mg, 73 %). IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 1726 (C=O), 1609, 1470, 1429, 1389, 1217, 1180, 752. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ = 696, 627, 404 nm. ^1H NMR ($CDCl_3$): δ = 0.80 (br., 6 H, methyl groups of acac), 1.2−1.3(br., 48 H, CH_3), 1.54(br., 64 H, CH_2), 1.69(br., 9 H, CH), 4.15(br., 16 H, OCH_2), 8.92 (s, 8 H, 2-H, 7-H, 10-H, 15-H) ppm. FD MS: *m/z* (%) = 1748.12 (100) [M^+].

Tetracyclone Bis(adduct) 14: A solution of **8** (23.2 mg, 20 mmol) and tetraphenylcyclopentadienone (**13**) (38.5 mg, 100 mmol) in toluene (30 mL) was stirred at 70 °C under nitrogen for 3−4 d. After evaporation of the solvent, the crude material was purified by preparative TLC on silica gel with chloroform in order to remove the unchanged excess of tetracyclone. The resulting green fraction was separated by PTLC (silica gel) with a mixture of dichloromethane/toluene (5:1) into two green fractions consisting of the tetracyclone bis(adduct) **14** and the tetracyclone monoadduct. Yield 31.4 mg (84 %) of **14** and 2.8 mg (9 %) of tetracyclone monoadduct. R_f (silica gel; dichloromethane): 0.8 (**14**), 0.51 (monoadduct). IR (KBr): $\tilde{\nu}$ = 3424 cm^{-1} (NH), 3076, 1772 (C=O), 1652, 1558, 1496, 1417, 1398, 1350, 1271, 1218, 1159, 1105, 1074, 962, 792, 740, 678. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ = 696, 661, 346 nm. ^1H NMR ($CDCl_3$): δ = −0.74 (s, 2 H, NH), 1.01−1.02 (br., 24 H, CH_3), 1.5 (br., 32 H, CH_2), 2.09 (br., 4 H, CH), 3.4, 3.5 (br., 4 H, 3-H, 22-H), 4.36, 4.49 (br., 8 H, OCH_2), 6.34 (br., 4 H, 4-H), 7.1−7.52 (br., 20 H, 25−28 H), 7.62−7.67 (br., 20 H, 29−32 H), 8.84(br., 4 H, 11-H), 9.45(br., 4 H, 6-H) ppm. MALDI-TOF MS: *m/z* (%) = 1928.46 (100) [M^+].

Trimer 16: A solution of the tetracyclone bis(adduct) **14** (38.6 mg, 20 mmol) and a threefold excess of PcH_2 **8** (69.6 mg, 60 mmol) in anhydrous toluene (25 mL) was stirred at 120 °C under nitrogen for 2 d. After evaporation of the solvent, the trimer obtained was isolated and purified by Soxhlet extraction with methanol and acetone to remove TPB and excess of **8**. Trimer **16** was obtained as a green powder (57.2 mg, 83 %). IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1} (NH), 2956, 2924, 2361, 2336, 1717, 1652, 1558, 1456, 1381, 1085, 863, 702, 419. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ = 699, 661, 645, 343 nm. ^1H NMR (TDF): δ = −0.40, −0.46, −0.49 (br., 3 H, NH), 1.16, 1.2 (br., 72 H, CH_3), 1.71, 1.77 (br., 96 H, CH_2), 2.4 (br., 12 H, CH), 3.5 (s, 4 H, 20-H), 5.61 (br., 24 H, OCH_2), 6.97 (s, 12 H, 2-H, 19-H, 21-H), 7.5 (s,4 H, 1-H), 7.9 (s, 12 H, 12-H, 31-H), 8.2 (s, 12 H, 4-H, 17-H, 23-H) ppm. MALDI-TOF MS: *m/z* (%) = 3426.4 (100) [M^+].

Trimer 17: A mixture of trimer **16** (17.1 mg, 5 mmol) and $In(acac)_3$ (0.18 g, 0.4 mmol) was refluxed in anhydrous DMF (15 mL) under nitrogen for 3 h. The mixture was cooled and methanol was added to precipitate the product, which was purified by Soxhlet extraction with methanol and ethyl acetate to remove the rest of the metal-free trimer **16**. Trimer **17** was obtained as a blue-green powder (17.3 mg, 84 %). IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 1726 (C=O), 1455, 1383, 1377, 1282, 1217, 1119, 752. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ = 686, 350 nm. ^{13}C CP/MAS NMR: δ = 10.68 (CH_3), 24.42 (CH_2), 29.47 (CH_2), 40 (CH), 51 (C-20), 73.71(C-2, C−OCH_2), 83.64(C-21, C-19), 108.61 (C-31, C-28, C-12, C-9, C-4), 124.18 (C-23, C-17), 149.72 (C-32, C-27, C-24, C-22, C-18, C-16, C-11, C-8, C-5, C-3, C-1), 179.2 (C-33, C-26, C-25, C-15, C-14, C-7, C-6), 166.06 (C-11, C-10, C-29, C-30), 193.4 (C=O) ppm. MALDI-TOF MS: *m/z* (%) = 4062.24 (100) [M^+].

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