Soluble Chloro- and Aryl(phthalocyaninato)indium(III) Complexes: Synthesis and Characterization

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The synthesis of highly soluble chloro(phthalocyaninato)indium(III) complexes $R_xPcInCl$ (**3a**: R^1 = *tert*-butyl, R^2 = H, x = 4 and **4a**: $R^1 = R^2$ = *n*-pentyl, x = 8), and their reactions with R′MgBr [R′ = *p*-trifluoromethylphenyl- (**b**), *m*-trifluoromethylphenyl- (**c**), *p*-fluorophenyl- (**d**), perfluorophenyl- (**e**)] leading to the stable σ-bonded aryl(phthalocyaninato)indium(III) complexes **3b−e**, **4b−e** are described. All compounds were characterized by IR, UV/Vis, MS, ^{1}H, ^{13}C and ^{19}F NMR as well as elemental analyses. Phenyl(phthalocyaninato)indium(III) (**4f**) was prepared by the reaction of $(n\text{-}C_5H_{11})_8PcInCl$ (**4a**) with PhLi. The high solubility of the complexes **3a−e** and **4a−f** is, aside from the influence of the peripheral substituents, considered to be derived from the large dipole moments present which are due to the strongly electron withdrawing axial ligands, and from the lower tendency of axially substituted phthalocyaninato metal complexes to form aggregates.

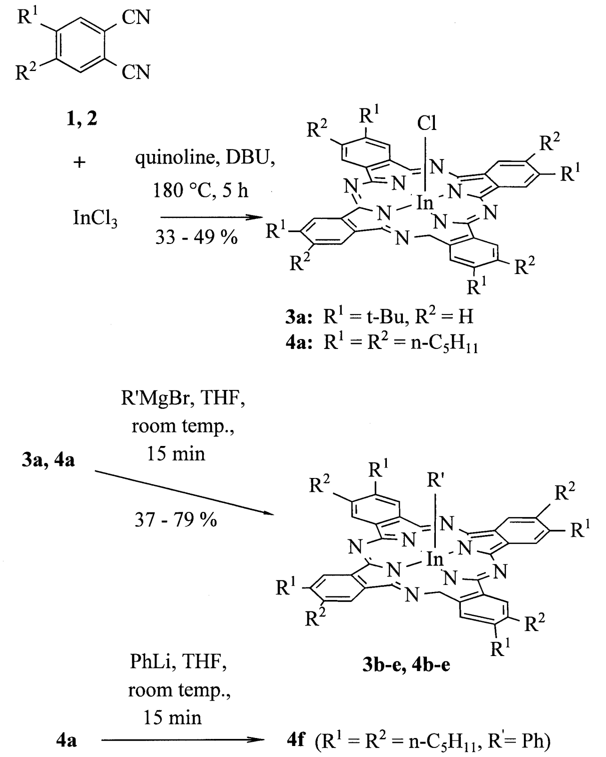
Phthalocyanines and phthalocyaninato metal complexes have been investigated in detail for many years[1], particularly with regard to their properties as dyes[2]. More recently their widespread potential in material sciences[3] has been discovered. Besides numerous other applications these "functional dyes" have also attracted considerable interest in the field of non-linear optics[4]. It is the extensively delocalized π-system in phthalocyanines which gives rise to large optical non-linearities. Furthermore, due to the diversity of the structural features[5] of phthalocyanines, tuning of the optical properties can be achieved by synthetic variations. For example, about 70 different elements have been incorporated into the phthalocyanine core, some of them with different oxidation states, and in addition there are one or two sites which coordinate a variety of axial ligands. The introduction of a diversity of peripheral substituents, with many possibilities to alter the substitution pattern with respect to the number and position of the substituents, has a strong influence[6] on the electronic absorption spectra and optical non-linearities. Other factors[4] which affect optical non-linearities are the length of π-electron conjugation, the crystal structure, and the thin film fabrication techniques employed. The aim of our current research is a systematic study of the effect of axial substitution on non-linear optical (NLO) properties, and specifically on the optical limiting properties of phthalocyanines. Axial substitution will have several effects: it can alter the electronic structure of the phthalocyanine, it can introduce a dipole moment perpendicular to the macrocycle, and, via steric effects, it can also alter the spatial relationships between neighbouring molecules and thus the magnitude of the intermolecular interactions. Large axial substituents can alter the packing of the molecules in the solid state and the tendency to aggregate in solution. Each of these effects can influence the NLO properties. In fact a correlation between the magnitude of the third-order non-linear optical susceptibility tensor $\chi^{(3)}$ for third harmonic generation (THG) experiments[4] and axial substitution has been noted. The reason for this effect may be associated with the fact that there is a permanent dipole moment in these materials.

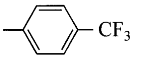
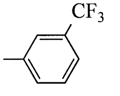
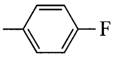
Several axially substituted phthalocyanines have been reported[4][7] to be good non-linear absorbers for optical limiting, but there has been no study of the effect of different axial substitution patterns on the relevant optical properties of these materials.

Our approach here is to investigate the influence of different axial substituents on the reverse saturable absorption, and optical limiting properties, of soluble peripherally alkylsubstituted phthalocyaninatoindium(III) complexes. Among the axially substituted phthalocyanines, $(t\text{Bu})_4$PcInCl[7] has one of the largest positive non-linear absorption coefficients. It has been used to manufacture optical limiting devices.

A comparative study of the optical properties of $(t\text{Bu})_4$PcInCl with several aryl substituted phthalocyaninatoindium(III) complexes (see Scheme 1) is in progress. The aryl ligands are chosen so as to alter both the spatial and electronic properties of the materials. Compared with the chloro ligand, aryl substituents will introduce steric crowding and should reduce the tendency, which is common in phthalocyanines, to form aggregates . Due to the increasing electron withdrawing properties of the aryl ligands, these materials should possess an increasing ground state dipole moment.

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



No.	R^1	R^2	No.	R'	abbreviation
1	t-Bu	H	**a**	-Cl	
2	n-C_5H_{11}	n-C_5H_{11}	**b**		p-TMP
3	t-Bu	H			
4	n-C_5H_{11}	n-C_5H_{11}	**c**		m-TMP
			d		p-FP
			e	-C_6F_5	PFP
			f	-Ph	

We have therefore synthesized a series of monoaxially chloro and aryl substituted phthalocyaninatoindium(III) complexes R_xPcIn(R′) [**3**: R^1 = *tert*-butyl, R^2 = H, x = 4 and **4**: R^1 = R^2 = *n*-pentyl, x = 8; R′ = chloro- (**a**), *p*-trifluoromethylphenyl- (**b**), *m*-trifluoromethylphenyl- (**c**), *p*-fluorophenyl- (**d**), perfluorophenyl- (**e**), phenyl- (**f**); see Scheme 1], which we expect to have similar steric, but different electronic, properties.

Although there are some reports on the preparation of phthalocyaninato[8] as well as porphyrinato[9] metal complexes with metal−alkyl or metal−aryl σ-bonds, to our knowledge nothing is known about complexes of the type PcIn(R′). From studies of alkyl- and aryl(porphyrinato)indium(III) complexes[10] it is known that their stability depends largely on the electron withdrawing properties of the axial ligands. Organometallic complexes containing strongly electron withdrawing perfluoroaryl groups generally show quite different properties than derivatives of the same containing a simple phenyl group[11]. In many cases it was shown that the carbon−metal bond in perfluorophenyl metal complexes is extraordinarily robust for a σ-bond[12].

Coincidentally, the electron withdrawing properties of the ligands which were attached to the indium atom in order to obtain complexes with substantial axial dipole moments are, at the same time, responsible for the stability of these compounds.

Results and Discussion

The complexes (tBu)$_4$PcInCl (**3a**)[7] and (C_5H_{11})$_8$PcInCl (**4a**) were prepared starting from stoichiometric amounts of 4-*tert*-butylphthalonitrile (**1**)[13] or 4,5-bis(*n*-pentyl)-phthalonitrile (**2**)[14] and $InCl_3$ in quinoline in the presence of catalytic amounts of DBU. The aryl(phthalocyaninato)-indium(III) complexes **3b−e** and **4b−e** were synthesized by the reaction of freshly prepared aryl Grignard compounds with the respective R_xPcInCl complexes **3a** or **4a** (see Scheme 1). The complexes **3a−e** and **4a−e** were characterized by IR, UV/Vis, MS, ^{1}H, ^{13}C, and ^{19}F NMR as well as elemental analyses.

In an attempt to synthesize the parent phenyl(phthalocyaninato)indium(III) complexes **3f** and **4f** starting from PhLi and **3a** or **4a,** it became clear that these compounds are less stable than the fluorinated derivatives. Only a few milligrams of **4f** could be isolated by extraction with *n*-hexane from the crude product. The decomposition product R_8PcH_2 showed poor solubility in this solvent. The small amount obtained limited the characterization of **4f** to MS, IR and UV/Vis. However, a satisfactory elemental analysis could be obtained for this complex. Phenyl(phthalocyaninato)indium(III) **3f** could not be separated from (tBu)$_4$PcH$_2$ in the same way due to the high solubility of the latter in *n*-hexane.

The complexes are highly soluble in various organic solvents such as toluene, dichloromethane, and chloroform. The tetrasubstituted compounds **3a−e** exhibit a much higher solubility in acetone than the corresponding octasubstituted compounds, **4a−f**. (tBu)$_4$PcIn(PFP) (**3e**) is even slightly soluble in methanol. In general, the aryl substituted complexes **3b−e** and **4b−f** are more soluble in solvents of medium polarity, such as dichloromethane, than the corresponding chloroindium(III) complexes **3a** and **4a**. The peripherally tetrasubstituted phthalocyanines **3a−e** consist of a mixture of four structural isomers[15], as regards the fact, that the *tert*-butyl groups can occupy either two positions R^1 or R^2 in each of the isoindoline units of the macrocycles. They are more soluble[3a][16] than their structural counterparts that have eight substituents, assuming the same substitution pattern (herein: 2,3). The high solubility of the aryl substituted phthalocyanines **3b−e** and **4b−f** indicates that they possess quite large axial dipole moments. The enhanced solubility of the complexes **3b−e** and **4b−f**, compared to the chloro analogues **3a** and **4a**, shows that the usual tendency of phthalocyanines to form aggregates[17] can be effectively suppressed by axial substitution. The more sterically demanding the axial ligands are, the lower will be the degree of aggregation.

Elemental analyses and mass spectral data of all the investigated phthalocyaninatoindium(III) complexes suggest the molecular formulas R_xPcInCl and R_xPcIn(R′) for the compounds **3a**, **4a** and **3b−e**, **4b−f**, respectively. For each complex a cluster of peaks, almost identical in intensity to that calculated for its respective isotopic composition, was observed in the field desorption mode. Fragmentation was not observed under these conditions.

In Table 1 the IR data of the aryl(phthalocyaninato)indium(III) complexes are reported. Only the additional absorptions, which do not appear in the spectra of the respective chloro substituted phthalocyanines **3a** or **4a**, are listed in Table 1. Characteristic vibrations for aryl groups bound to a metal atom[18] are found in the range 190−1650 cm^{-1}. In the 670−830 cm^{-1} range vibrational frequencies associated with the C−H out of plane deformation modes of the axial aryl groups appear. The intense absorption bands of the C−F stretching mode are found between 900−1460 cm^{-1}. The vibrational frequencies between 1500−1640 cm^{-1} are associated with the ring vibrations of the axial ligands. The weak absorption band of the In−Cl stretching mode at 336 and 327 cm^{-1} appears in the spectra of the chloro derivatives **3a** and **4a**, respectively. The In−C stretching mode can not be unambiguously assigned due to coupling with C−C modes and vibrations of the phthalocyaninic macrocycle.

Table 1. IR data of the investigated R_xPcIn(R′) complexes (KBr pellets)

Axial ligand R′	Phthalocyanine Pc	ṽ [cm^{-1}]												
p-TMP	**3b**		1599			1388		1164	1128		1016	819	678	
	4b		1598			1388		1163	1127	1047	1015	825	677	
m-TMP	**3c**				1466	1315		1165	1127	1060		794	683	
	4c					1316		1164	1126	1060		795	682	
p-FP	**3d**		1578				1228	1164				814		505
	4d		1577			1358	1226	1164				812		506
PFP	**3e**	1635	1531	1506	1463						959			
	4e	1636		1506	1464	1357				1054	958			
Ph	**4f**					1359								

The electronic absorption data of the complexes investigated are summarized in Table 2. The spectra of **3a−e** and **4a−f** show the typical pattern[17a] of phthalocyaninato metal complexes, with an intense Q band absorption and its vibrational satellites Q(1,0) and Q(2,0), as well as lower intensity π-π* transitions within the heteroaromatic π-system [B(0,0), B(1,0)]. Introduction of electron-donating alkyl groups in the periphery of the macrocycle leads to a bathochromic shift of the Q band maximum[6b][6c]. The octasubstituted complexes **4a−e** have their Q band shifted to the red by $\Delta\lambda = 16.0-17.3$ nm, and the tetrasubstituted complexes **3a−e** by $\Delta\lambda = 7.1-7.8$ nm (see Table 2), with respect to the unsubstituted PcInCl[19]. In contrast, the axial ligands introduced have little influence on the wavelength of the Q band maximum. The observed red shifts are only of the order of 1 nm.

Table 2. UV/Vis data of the investigated R_xPcInCl and R_xPcIn(R′) complexes in chloroform

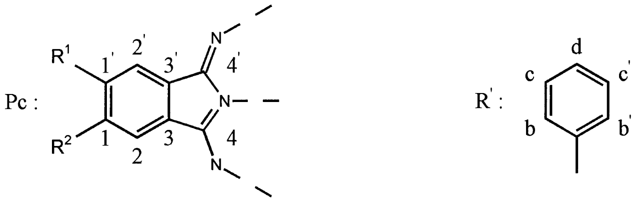
Phthalocyanine Pc	Axial ligand R′	λ_{max} [nm] B(1.0)[a]	B(0.0)	Q(2.0)	Q(1.0)[a]	Q(0.0)
PcInCl (unsubst.)	Cl	337.9	358.2	622.5	656.8	690.2
3a	Cl	339.7	359.5	628.2	667.1	697.3
3b	*p*-TMP	340.9	369.3	628.6	667.3	698.0
3c	*m*-TMP	341.4	368.6	628.5	666.5	697.8
3d	*p*-FP	341.0	368.5	628.2	666.0	697.4
3e	PFP	341.9	365.6	628.7	665.7	697.8
4a	Cl	342.2	361.3	635.4	675.4	706.2
4b	*p*-TMP	353.7	375.3	636.4	675.6	707.2
4c	*m*-TMP	354.0	374.9	636.2	675.9	707.3
4d	*p*-FP	354.6	375.0	635.8	674.9	706.7
4e	PFP	349.3	370.1	636.3	675.7	707.5
4f	Ph	353.6	375.9	635.8	676.2	706.6

[a] All of these bands appear as shoulders.

The ^{1}H-NMR spectrum of (tBu)$_4$PcInCl (**3a**) shows three multiplets in the aromatic region centred at $\delta = 8.30$, 9.30 and 9.45 for the 1-H, 2-H and the 2′-H protons, respectively (see Figure 1). The values for the corresponding protons of all of the aryl substituted complexes **3b−e** are close to those of **3a**, despite the different axial ligands. ^{1}H-NMR data of protons of the macrocycle and peripheral substituents are listed in the experimental section for each compound. The downfield shifts of $\Delta\delta \approx 0.4$, 0.18 and 0.13 for the 1-H, 2-H and 2′-H protons in these compounds point to the fact that the σ-bonded aryl groups lead to stronger deshielding of the aromatic protons, especially of those closer to the heteroaromatic ring system (2-H, 2′-H), than does the chloro ligand. The same can be seen by comparison of $(C_5H_{11})_8$PcInCl (**4a**) and $(C_5H_{11})_8$PcIn(R′) (**4b−e**). In the ^{1}H-NMR spectrum of **4a** the aromatic protons give rise to a singlet at $\delta = 9.10$. The signals of the corresponding protons 2,2′-H of **4b−e** are shifted downfield by $\Delta\delta = 0.16-0.18$.

In contrast, the signals of the axial ligands are considerably shielded by the influence of the large diamagnetic ring-current[20] of the heteroaromatic π-electron system of the phthalocyanine. The shorter the distance between these protons and the centre of the macrocycle, the larger the upfield shift (see Table 3). This is in agreement with the

Figure 1. Notation of the atoms of the macrocycles and axial ligands



proposed structures for the aryl(phthalocyaninato)indium(III) complexes **3b−e** and **4b−e**. The absolute upfield shifts were explicitly calculated by comparing the shifts of corresponding protons for the $R_xPcIn(R')$ complexes and for R′Br, where no influence of a macrocyclic diamagnetic ring-current exists.

Table 3. ^{1}H-NMR data[a] of the protons for the axial ligands in the $R_xPcIn(R')$ complexes and for R′Br[a]

Axial ligand R′	Phthalo-cyanine Pc		Protons of R′ δ	multi/ intens	Protons of R′Br δ	Upfield shift Δδ
p-TMP	**3b**	H-b,b′	4.17	d/2	7.61	−3.44
		H-c,c′	6.17	d/2	7.47	−1.30
	4b	H-b,b′	4.18	d/2	7.61	−3.43
		H-c,c′	6.15	d/2	7.47	−1.32
m-TMP	**3c**	H-b′	4.10	d/1	7.66	−3.56
		H-b	4.41	s/1	7.76	−3.35
		H-c′	6.03−6.09	m/1	7.31−7.37	−1.28
		H-d	6.46	d/1	7.54	−1.08
	4c	H-b′	4.12	d/1	7.66	−3.54
		H-b	4.42	s/1	7.76	−3.34
		H-c′	6.01−6.07	m/1	7.31−7.37	−1.30
		H-d	6.45	d/1	7.54	−1.09
p-FP	**3d**	H-b,b′	3.98−4.04	m/2	7.40−7.45	−3.41
		H-c,c′	5.64−5.71	m/2	6.90-6.97	−1.25
	4d	H-b,b′	4.00−4.06	m/2	7.40−7.45	−3.39
		H-c,c′	5.62−5.70	m/2	6.90−6.97	

[a] Spectra were recorded in $CDCl_3$ at 300K (250.131MHz).

In the ^{13}C-NMR spectra of the compounds synthesized a slight deshielding effect is observed for the carbon atoms close to the indium atom. Again the signals for those carbon atoms in the aryl(phthalocyaninato)indium complexes **3b−e** and **4b−e**, being closer to the phthalocyanine core (C-4 and C-4′), are shifted further downfield than those for C-3 and C-3′ (see Figure 1). Only some of the carbon atom resonances of the axial ligands could be detected. This is due to the C−F coupling leading to split signals of low intensity, the low number of atoms in each set of magnetically equivalent carbon atoms in the ligand compared to the macrocycle, and to the fact that the solubility of the complexes is still too low with regard to the factors limiting the signal intensity which were mentioned previously.

The ^{19}F-NMR data of eight $R_xPcIn(R')$ complexes are given in Table 4. $CDCl_3$ was used as internal standard with $CFCl_3$ as a reference. One narrow singlet was observed for the complexes PcIn(*p*-TMP) (**3b**, **4b**) and PcIn(*m*-TMP) (**3c**, **4c**), all with similar chemical shifts and close to the fluorine signal in α,α,α-trifluorotoluene at −63.9[21]. Due to H−F coupling, multiplets centred at −113.4 and −113.8 are observed for the complexes PcIn(*p*-FP) (**3d**) and (**4d**), respectively. These values are close to that of fluorine in fluorobenzene: −113.1[21]. Three signals are found in the spectra of the perfluorophenyl complexes **3e** (**4e**) at −122.1 (−122.0), −160.9 (−161.2) and −153.3 (−153.7) for the *o*-, *m*-, and *p*-fluorine atoms, respectively. In relation to pentafluorobenzene, whose signals for the same nucleus are at −139.2, −162.7 and −154.5[22a], the *o*-fluorine atoms close to the indium(III) metal are remarkably deshielded. The deshielding of aromatic fluorine atoms in complexes where they are in the *ortho* position of a metal−carbon bond has already been observed and discussed[22]. The spin systems of fluorine in the PcIn(PFP) complexes **3e** and **4e** have typical AA′MM′X patterns[23], which is in agreement with their proposed structures.

Table 4. ^{19}F-NMR data[a] for the $R_xPcIn(R')$ complexes in chloroform

Axial ligand R′	Phthalo cyanine Pc		Fluorine atoms multi/intens	δ
p-TMP	**3b**	*p*-CF_3	s	−64.1
	4b	*p*-CF_3	s	−64.1
m-TMP	**3c**	*m*-CF_3	s	−63.7
	4c	*m*-CF_3	s	−63.6
p-FP	**3d**	*p*-F	m	−113.4[b]
	4d	*p*-F	m	−113.8[b]
PFP	**3e**	*o*-F	m/2	−122.0 − (−122.2)
		m-F	m/2	−160.8 − (−161.1)
		p-F	m/1	−153.2 − (−153.3)
	4e	*o*-F	m/2	−121.8 − (−122.1)
		m-F	m/2	−161.0 − (−161.3)
		p-F	m/1	−153.6 − (−153.8)

[a] Spectra were recorded in $CDCl_3$ at 300K (235.334 MHz). Chemical shifts (δ) upfield from the reference $CFCl_3$ are defined as negative. − [b] With broad-band proton decoupling.

In conclusion stable aryl(phthalocyaninato)indium(III) complexes have been prepared starting from chloro(phthalocyaninato)indium(III) and aryl Grignard reagents or aryl lithium compounds, respectively. Electron withdrawing substituents at the aryl ligands are essential to increase the stability of the complexes obtained. All aryl(phthalocyaninato)indium(III) compounds prepared are highly soluble in common organic solvents. Studies on the non-linear optical properties of these new phthalocyaninato complexes, particularly with regard to their optical limiting properties, are in progress.

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Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl prior to use, quinoline from calcium hydride. *p*-Trifluoromethylbromobenzene, *m*-trifluoromethylbromobenzene, *p*-fluorobromobenzene, perfluorobromobenzene were obtained from commercial sources. 4-*tert*-Butylphthalonitrile (**1**)[13] and 4,5-bis(*n*-pentyl)phthalonitrile (**2**)[14] were prepared according to literature procedures. − FT-IR:

Perkin Elmer Spectrum 1000. − UV/Vis: Shimadzu UV-365. − MS: Varian Mat 711 (FD, temperature of the ion source: 30°C). − ^{1}H, ^{13}C NMR: Bruker AC 250 (^{1}H: 250.131 MHz, ^{13}C: 62.902 MHz). − ^{19}F NMR: Bruker Avance DRX 250 (235.334 MHz). − Elemental Analyses: Carlo-Erba Elemental Analyser 1104, 1106.

General Procedures: The Grignard compounds R′MgBr [R′ = *p*-trifluoromethylphenyl- (**b**), *m*-trifluoromethylphenyl- (**c**), *p*-fluorophenyl- (**d**), perfluorophenyl- (**e**)] were prepared by stirring a mixture of the corresponding substituted bromobenzenes [338 mg (**b**, **c**), 263 mg (**d**), 371 mg (**e**); 1.5 mmol] and Mg turnings (38.9 mg, 1.6 mmol), previously activated by means of an ultrasonic bath, in freshly dried THF (3 ml) at room temp. After most of the magnesium had been consumed, the solution was diluted to a volume of 10 ml by addition of THF. The solution was transferred into a pressure equalizing addition funnel containing a small quantity of glass wool to hold back excess solid magnesium.

Chloro-(tetra-(tert-butyl)phthalocyaninato)indium(III) and Chloro-(octa-(n-pentyl)phthalocyaninato)indium(III) (**3a**, **4a**): A mixture of $InCl_3$ (1.52 g, 6.88 mmol), 4-*tert*-butylphthalonitrile [(**1**), 5.07 g, 27.52 mmol] or 4,5-bis(*n*-pentyl)phthalonitrile [(**2**), 7.38 g, 27.52 mmol], dry quinoline (12 ml), and DBU (1 ml) were stirred at 180°C for 5 h. The solvent was removed by distillation under reduced pressure, leaving a dark green residue, which was chromatographed on silica gel using chloroform as the eluent in order to remove large amounts of the impurities. Then the crude compounds **3a** and **4a** were recrystallized from mixtures of CH_2Cl_2/MeOH (v/v 4:3) or $CHCl_3$/EtOH (v/v 15:7), respectively, by slowly evaporating the more volatile chloromethanes in a rotary evaporator at 40−60°C under slightly reduced pressure. To complete crystallization, the mixtures were kept in a refrigerator overnight. The complexes were collected by filtration, washed twice with methanol and dried at 80°C in vacuo. − $(t\mathrm{Bu})_4$PcInCl (**3a**): Yield 2.98 g (49%), blue-green microcrystals. − IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1} vw, 2957 vs, 2903 m, 2866 m, 1613 vw, 1485 s, 1393 m, 1364 m, 1330 vs, 1280 m, 1256 s, 1199 w, 1147 w, 1087 vs, 1047 m, 922 s, 896 w, 831 m, 761 w, 746 m, 693 w, 671 w, 602 vw, 568 vw, 524 vw, 444 vw, 336 w. − UV/Vis ($CHCl_3$): λ_{max} = 697.3 nm, 667.1 (sh), 628.2, 359.5, 339.7 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.82−1.84 (m, 36 H, *t*Bu), 8.27−8.33 (m, 4 H, 1-H), 9.27−9.33 (m, 4 H, 2-H), 9.42−9.47 (m, 4 H, 2′-H). − ^{13}C NMR ($CDCl_3$): δ = 32.01−32.04 (CH_3), 36.16 (CMe_3), 119.71−119.80 (C-2′), 123.09−123.21 (C-2), 128.48−128.56 (C-1), 135.07−135.23 (C-3), 137.49−137.72 (C-3′), 152.74−153.50 (C-4,4′), 154.55−154.72 (C-1′). − MS (FD); *m/z*: 886.2 [M$^+$]. − $C_{48}H_{48}ClInN_8$ (887.2): calcd. C 64.98; H 5.45; Cl 4.00; N 12.63; found C 65.16; H 5.36; Cl 4.13; N 12.30. − $(C_5H_{11})_8$PcInCl (**4a**): Yield 2.75 g (33%), bluish green needles. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} vs, 2927 vs, 2858 s, 1618 vw, 1483 m, 1465 m, 1460 m, 1451 m, 1401 m, 1377 w, 1335 vs, 1100 vs, 1080 s, 1011 w, 892 w, 873 vw, 744 m, 733 w, 724 w, 327 vw. − UV/Vis ($CHCl_3$): λ_{max} = 706.2 nm, 675.4 (sh), 635.4, 361.3, 342.2 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.04 (t, *J* = 7.0 Hz, 24 H, CH_3), 1.47−1.71 (m, 32 H, γ,δ-CH_2), 1.93−2.05 (m, 16 H, β-CH_2), 3.12−3.18 (m, 16 H, α-CH_2), 9.10 (s, 8 H, 2,2′-H). − ^{13}C NMR ($CDCl_3$): δ = 14.22 (CH_3), 22.79 (δ-CH_2), 31.58, 32.38, 34.05 (α,β,γ-CH_2), 123.41 (C-2), 135.62 (C-3), 144.30 (C-1), 152.93 (C-4). − MS (FD); *m/z*: 1222.3 [M$^+$]. − $C_{72}H_{96}ClInN_8$ (1223.9): calcd. C 70.66; H 7.91; Cl 2.90; N 9.16; found C 70.57; H 8.01; Cl 2.94; N 9.23.

Aryl(tetra-(tert-butyl)phthalocyaninato)indium(III) and Aryl-(octa-(n-pentyl)-phthalocyaninato)indium(III) (**3b−e**, **4b−e**): In a typical reaction, a freshly prepared solution of R′MgBr [R′ = *p*-trifluoromethylphenyl- (**b**), *m*-trifluoromethylphenyl- (**c**), *p*-fluorophenyl- (**d**), perfluorophenyl- (**e**)] in THF (10 ml; 0.15 M R′MgBr), was added dropwise to a stirred solution of **3a** or **4a** (0.3 mmol) in dry THF (25 ml). The reaction was monitored by TLC (silica gel/toluene) and stopped when all of the R_xPcInCl (**3a**, **4a**) had been consumed. The deep green mixture was poured on ice and was extracted several times with diethyl ether. The combined organic layers were washed with water and dried with $MgSO_4$. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel/toluene). Light was strictly excluded during this step. Further purification of the complex was achieved by recrystallization from mixtures of CH_2Cl_2 and methanol, as described above. The pure phthalocyanine was dried in vacuo at 70°C for 3 h. − $(t\mathrm{Bu})_4$PcIn(*p*-TMP) (**3b**): Yield 134.4 mg (45%), bluish green powder. − IR (KBr): $\tilde{\nu}$ = 3076 cm^{-1} vw, 2959 s, 2903 m, 2867 w, 1614 w, 1599 vw, 1487 s, 1388 m, 1365 m, 1327 vs, 1280 m, 1257 s, 1200 w, 1164 m, 1152 m, 1128 s, 1086 vs, 1047 s, 1016 w, 954, 922 m, 897 vw, 831 m, 819 w, 760 w, 747 m, 694 w, 678 w, 671 w, 603 vw, 566 vw, 525 vw, 446 vw. − UV/Vis ($CHCl_3$): λ_{max} = 698.0 nm, 667.3 (sh), 628.6, 369.3, 340.9 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.80 (m, 36 H, *t*Bu), 4.17 (d, *J* = 7.6 Hz, 2 H, H-b,b′), 6.17 (d, *J* = 7.6 Hz, 2 H, H-c,c′), 8.32−8.36 (m, 4 H, 1-H), 9.44−9.52 (m, 4 H, 2-H), 9.57−9.59 (m, 4 H, 2′-H). − ^{13}C NMR ($CDCl_3$): δ = 32.00−32.04 (CH_3), 36.12−36.15 (CMe_3), 119.68 (C-2′), 122.54 (q, *J* = 3.7 Hz, C-c,c′) 123.04 (C-2), 128.29−128.36 (C-1), 134.26 (C-a), 135.40−135.48 (C-3), 137.84−137.92 (C-3′), 153.69−154.24 (C-4,4′), 154.38−154.48 (C-1′). − ^{19}F NMR ($CDCl_3$): δ = −64.1. − MS (FD); *m/z*: 995.9 [M$^+$]. − $C_{55}H_{52}F_3InN_8$ (996.9): calcd. C 66.27; H 5.26; N 11.24; found C 66.43; H 5.29; N 10.95. − $(t\mathrm{Bu})_4$PcIn(*m*-TMP) (**3c**): Yield 132.2 mg (44%), bluish green powder. − IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1} vw, 2959 s, 2905 m, 2868 w, 1613 w, 1487 s, 1466 w, 1394 m, 1365 m, 1327 vs, 1315 vs, 1280 m, 1257 s, 1199 w, 1165 m, 1150 w, 1127 s, 1085 vs, 1060 m, 1047 m, 922 m, 896 vw, 831 m, 794 vw, 760 w, 747 m, 693 w, 683 vw, 671 w, 603 vw, 567 vw, 525 vw, 446 vw. − UV/Vis ($CHCl_3$): λ_{max} = 697.8 nm, 666.5 (sh), 628.5, 368.6, 341.4 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.78−1.80 (m, 36 H, *t*Bu), 4.10 (d, *J* = 7.6 Hz, 1 H, H-b′), 4.41 (s, 1 H, H-b), 6.03−6.09 (m, 1 H, H-c′), 6.46 (d, *J* = 7.6 Hz, 1 H, H-d), 8.32−8.35 (m, 4 H, 1-H), 9.44−9.53 (m, 4 H, 2-H), 9.57−9.60 (m, 4 H, 2′-H). − ^{13}C NMR ($CDCl_3$): δ = 32.00−32.03 (CH_3), 36.12−36.15 (CMe_3), 119.68 (C-2′), 123.05 (C-2), 123.90 (q, 3.7 Hz, C-d), 126.38 (C-b′), 128.31−128.37 (C-1), 130.21 (q, *J* = 3.7 Hz, C-b), 135.39−135.45 (C-3), 137.39−137.41 (C-a), 137.81−137.89 (C-3′), 153.77−154.32 (C-4,4′), 154.44−154.52 (C-1′). − ^{19}F NMR ($CDCl_3$): δ = −63.7. − MS (FD); *m/z*: 995.9 [M$^+$]. − $C_{55}H_{52}F_3InN_8$ (996.9): calcd. C 66.27; H 5.26; N 11.24; found C 66.59; H 5.34; N 11.40. − $(t\mathrm{Bu})_4$PcIn(*p*-FP) (**3d**): Yield 136.3 mg (48%), bluish green powder. − IR (KBr): $\tilde{\nu}$ = 3077 cm^{-1} vw, 2958 vs, 2903 m, 2866 m, 1613 m, 1578 m, 1488 vs, 1393 s, 1364 m, 1329 vs, 1280 s, 1256 s, 1228 m, 1200 w, 1164 m, 1151 m, 1085 vs, 1047 s, 922 s, 896 w, 831 m, 814 m, 760 m, 747 s, 693 w, 672 w, 603 vw, 567 vw, 525 w, 505 vw, 445 vw. − UV/Vis ($CHCl_3$): λ_{max} = 697.4 nm, 666.0 (sh), 628.2, 368.5, 341.0 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.79−1.80 (m, 36 H, *t*Bu), 3.98−4.04 (m, 2 H, H-b,b′), 5.64−5.71 (m, 2 H, H-c,c′), 8.31−8.35 (m, 4 H, 1-H), 9.43−9.51 (m, 4 H, 2-H), 9.57−9.59 (m, 4 H, 2′-H). − ^{13}C NMR ($CDCl_3$): δ = 32.00−32.04 (CH_3), 36.10−36.13 (CMe_3), 113.53 (d, *J* = 19.0 Hz, C-c,c′), 119.63 (C-2′), 123.01 (C-2), 128.20−128.27 (C-1), 135.44−135.53 (C-3), 137.86−137.95 (C-3′), 153.72−154.19 (C-4,4′), 154.27−154.41 (C-1′), 162.05 (d, *J* = 246.9 Hz, C-d). − ^{19}F{^{1}H} NMR ($CDCl_3$): δ = −113.4. − MS (FD); *m/z*: 946.2 [M$^+$]. − $C_{54}H_{52}FInN_8$ (946.9): calcd. C 68.50; H 5.54; N 11.83; found C 67.43; H 5.55; N 11.35. − $(t\mathrm{Bu})_4$PcIn(PFP) (**3e**): Yield 118.5 mg (39%), bluish green powder. − IR (KBr): $\tilde{\nu}$ = 3076 cm^{-1} vw, 2958 s, 2904 m, 2865 m, 1635 vw, 1613 w, 1531 w, 1506 s, 1487 s, 1463 vs, 1394 m, 1364 m, 1330 vs, 1280 m, 1256 s, 1200 w, 1151 w, 1086 vs, 1047 m, 959 m, 922 m, 896 w, 831 m, 761 w, 747 m, 693 w, 672 w, 602 vw, 567 vw, 525 vw, 446 vw. − UV/Vis ($CHCl_3$): λ_{max} = 697.8 nm, 665.7 (sh), 628.7, 365.6, 341.9 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.79−1.81 (m, 36 H, *t*Bu), 8.33−8.37 (m, 4 H, 1-H), 9.44−9.51 (m, 4 H, 2-H), 9.58 (m, 4 H, 2′-H). − ^{13}C NMR ($CDCl_3$): δ = 32.00−32.04 (CH_3), 36.15−36.18 (CMe_3), 119.74 (C-2′), 123.12−123.15 (C-2), 128.42−128.49 (C-1), 135.31−135.39 (C-3), 137.73−137.86 (C-3′), 153.37−154.08 (C-4,4′), 154.52−154.64 (C-1′). − ^{19}F NMR ($CDCl_3$): δ = −122.0 − (−122.2) (F-b,b′), −160.8 − (−161.1) (F-c,c′), −153.2 − (−153.3) (F-d). − MS (FD); *m/z*: 1018.0 [M$^+$]. − $C_{54}H_{48}F_5InN_8$ (1018.8): calcd. C 63.66; H 4.75; N 11.00; found C 64.20; H 4.95; N 10.45. − $(C_5H_{11})_8$PcIn(*p*-TMP) (**4b**): Yield 251.0 mg (63%), dark green powder. − IR (KBr): ṽ = 2956 cm^{-1} vs, 2928 vs, 2859 s, 1618 vw, 1598 vw, 1484 m, 1465 m, 1400 w, 1388 w, 1378 w, 1325 vs, 1163 m, 1127 m, 1098 vs, 1081 s, 1047 m, 1015 w, 894 w, 868 vw, 825 vw, 744 m, 732 w, 677 w. − UV/Vis ($CHCl_3$): λ_{max} = 707.2 nm, 675.6 (sh), 636.4, 375.3, 353.7 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.03 (t, *J* = 7.0 Hz, 24 H, CH_3), 1.46−1.70 (m, 32 H, γ,δ-CH_2), 1.95−2.07 (m, 16 H, β-CH_2), 3.15−3.22 (m, 16 H, α-CH_2), 4.18 (d, *J* = 7.6 Hz, 2 H, H-b,b′), 6.15 (d, *J* = 7.6 Hz, 2 H, H-c,c′), 9.26 (s, 8 H, 2,2′-H). − ^{13}C NMR ($CDCl_3$): δ = 14.19 (CH_3), 22.77 (δ-CH_2), 31.63, 32.35, 34.06 (α,β,γ-CH_2), 122.43 (q, *J* = 3.4 Hz, C-c,c′), 123.41 (C-2), 134.36 (C-a), 135.85 (C-3), 144.14 (C-1), 153.84 (C-4). − ^{19}F NMR ($CDCl_3$): δ = −64.1. − MS (FD); *m/z*: 1332.5 [M$^+$]. − $C_{79}H_{100}F_3InN_8$ (1333.5): calcd. C 71.15; H 7.56; N 8.40; found C 70.92; H 7.45; N 8.29. − $(C_5H_{11})_8$PcIn(*m*-TMP) (**4c**): Yield 317.5 mg (79%), green powder. − IR (KBr): ṽ = 2956 cm^{-1} vs, 2928 vs, 2860 s, 1618 vw, 1484 m, 1466 m, 1452 m, 1401 w, 1378 w, 1334 s, 1316 s, 1164 m, 1126 m, 1099 vs, 1081 s, 1060 w, 1012 w, 894 w, 869 vw, 795 vw, 744 m, 732 w, 682 vw. − UV/Vis ($CHCl_3$): λ_{max} = 707.3 nm, 675.9 (sh), 636.2, 374.9, 354.0 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.03 (t, *J* = 7.0 Hz, 24 H, CH_3), 1.46−1.70 (m, 32 H, γ,δ-CH_2), 1.96−2.08 (m, 16 H, β-CH_2), 3.16−3.22 (m, 16 H, α-CH_2), 4.12 (d, *J* = 7.0 Hz, 1 H, H-b′), 4.42 (s, 1 H, H-b), 6.01−6.07 (m, 1 H, H-c′), 6.45 (d, *J* = 7.7 Hz, 1 H, H-d), 9.28 (s, 8 H, 2,2′-H). − ^{13}C NMR ($CDCl_3$): δ = 14.19 (CH_3), 22.76 (δ-CH_2), 31.62, 32.35, 34.06 (α,β,γ-CH_2), 123.40 (C-2), 123.73 (q, *J* = 3.7 Hz, C-d), 126.26 (C-b′), 130.28 (q, *J* = 3.7 Hz, C-b), 135.84 (C-3), 137.51 (C-a), 144.12 (C-1), 153.89 (C-4). − ^{19}F NMR ($CDCl_3$): δ = −63.6. − MS (FD); *m/z*: 1332.3 [M$^+$]. − $C_{79}H_{100}F_3InN_8$ (1333.5): calcd. C 71.15; H 7.56; N 8.40; found C 71.12; H 7.53; N 8.62. − $(C_5H_{11})_8$PcIn(*p*-FP) (**4d**): Yield 142.4 mg (37%), green powder. − IR (KBr): ṽ = 2955 cm^{-1} vs, 2927 vs, 2858 s, 1617 vw, 1577 w, 1485 s, 1465 m, 1456 m, 1400 w, 1378 w, 1358 m, 1333 vs, 1226 w, 1164 w, 1098 vs, 1012 w, 894 w, 868 w, 812 w, 745 m, 732 w, 506 vw. − UV/Vis ($CHCl_3$): λ_{max} = 706.7 nm, 674.9 (sh), 635.8, 375.0, 354.6 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.03 (t, *J* = 7.0 Hz, 24 H, CH_3), 1.47−1.70 (m, 32 H, γ,δ-CH_2), 1.96−2.08 (m, 16 H, β-CH_2), 3.17−3.23 (m, 16 H, α-CH_2), 4.00−4.06 (m, 2 H, H-b,b′), 5.62−5.70 (m, 2 H, H-c,c′), 9.28 (s, 8 H, 2,2′-H). − ^{13}C NMR ($CDCl_3$): δ = 14.19 (CH_3), 22.77 (δ-CH_2), 31.64, 32.35, 34.06 (α,β,γ-CH_2), 113.42 (d, *J* = 18.5 Hz, C-c,c′), 123.40 (C-2), 135.58 (d, *J* = 6.5 Hz, C-b,b′), 135.91 (C-3), 144.07 (C-1), 153.91 (C-4). − ^{19}F{^{1}H} NMR ($CDCl_3$): δ = −113.8. − MS (FD); *m/z*: 1282.5 [M$^+$]. − $C_{78}H_{100}FInN_8$ (1283.5): calcd. C 72.99; H 7.85; N 8.73; found C 72.71; H 7.66; N 8.71. − $(C_5H_{11})_8$PcIn(PFP) (**4e**): Yield 233.1 mg (57%), green powder. − IR (KBr): ṽ = 2955 cm^{-1} vs, 2927 vs, 2859 vs, 1636 vw, 1617 w, 1506 s, 1483 s, 1464 vs, 1401 m, 1357 vs, 1333 vs, 1098 vs, 1074 vs, 1054 m, 1010 w, 958 vs, 895 m, 871 w, 744 s, 733 m, 725 m. − UV/Vis ($CHCl_3$): λ_{max} = 707.5 nm, 675.7 (sh), 636.3, 370.1, 349.3 (sh). − ^{1}H NMR ($CDCl_3$): δ = 1.04 (t, *J* = 7.1 Hz, 24 H, CH_3), 1.48−1.71 (m, 32 H, γ,δ-CH_2), 1.97−2.09 (m, 16 H, β-CH_2), 3.17−3.23 (m, 16 H, α-CH_2), 9.27 (s, 8 H, 2,2′-H). − ^{13}C NMR ($CDCl_3$): δ = 14.20 (CH_3), 22.78 (δ-CH_2), 31.61, 32.40, 34.09 (α,β,γ-CH_2), 123.40 (C-2), 135.75 (C-3), 144.19 (C-1), 153.39 (C-4). − ^{19}F NMR ($CDCl_3$): δ = −121.8 − (−122.1) (F-b,b′), −161.0 − (−161.3) (F-c,c′), −153.6 − (−153.8) (F-d). − MS (FD); *m/z*: 1353.9 [M$^+$]. − $C_{78}H_{96}F_5InN_8$ (1355.5): calcd. C 69.12; H 7.14; N 8.27; found C 69.10; H 6.83; N 8.21.

First Results in the Preparation of Phenyl(octa-(n-pentyl)phthalocyaninato)indium(III) (**4f**): Phenyllithium in cyclohexane/diethyl ether (0.5 M) at room temp. was added dropwise to a solution of **4a** (122.4 mg, 0.1 mmol) in dry THF (25 ml). The reaction was monitored by TLC (silica gel/toluene) and stopped when all of the R_8PcInCl (**4a**) had been consumed. The deep green mixture obtained was worked up as described above. The complex **4f** was separated from the crude mixture by stirring it in *n*-hexane. Due to the insolubility of the metal free phthalocyanine (formed during the reaction) in this solvent, pure phenyl(phthalocyaninato)indium(III) was obtained after filtration and evaporation of the solvent. − $(C_5H_{11})_8$PcIn(Ph) (**4f**): Green powder. − IR (KBr): ṽ = 2955 cm^{-1} vs, 2926 vs, 2858 s, 1618 vw, 1483 m, 1466 m, 1400 w, 1378 w, 1359 m, 1333 s, 1098 vs, 1079 m, 1011 w, 893 w, 868 vw, 745 m, 732 w, 724 m. − UV/Vis ($CHCl_3$): λ_{max} = 706.6 nm, 676.2 (sh), 635.8, 375.9, 353.6 (sh). − MS (FD); *m/z*: 1263.7 [M$^+$]. − $C_{78}H_{101}InN_8$ (1265.5): calcd. C 74.03; H 8.04; N 8.85; found C 73.97; H 7.91; N 8.96.

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