Synthesis and Characterization of Soluble Chloro- and Aryl(naphthalocyaninato)indium(III) Complexes and Their Precursors

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Keywords: Indium / Nitrogen heterocycles / Nonlinear optics / Phthalocyanines

The syntheses of highly soluble chloro(naphthalocyaninato)-indium(III) compounds $(R^2)_4(R^4)_4$NcInCl (**5a**: R^2 = H, R^4 = *tert*-butyl; **6a**: R^2 = R^4 = *tert*-butyl; **7a**: R^2 = 2-ethylhexyloxy, R^4 = *tert*-butyl; **8a**: R^2 = R^4 = 2-ethylhexyloxy), and their reactions with R′MgBr [**b**: R′ = *p*-(trifluoromethyl)phenyl; **c**: R′ = pentafluorophenyl] producing the axially substituted aryl(naphthalocyaninato)indium(III) compounds **5b**, **5c**, **6b**, **6c**, **7b**, **7c**, **8b**, and **8c** are described. All compounds were characterized by IR, UV/Vis, MS, and ^{1}H, ^{13}C, and ^{19}F NMR, as well as by elemental analysis. The high solubilities of the octasubstituted naphthalocyanines **6**–**8** and their low tendencies to form aggregates are due to steric crowding arising from the new unsymmetrical peripheral substitution pattern and the bulky, electron-withdrawing axial ligands. These properties make the (naphthalocyaninato)indium compounds very interesting candidates for further investigations concerning their nonlinear optical properties, particularly for optical limiting applications. We also report on the complete syntheses and characterization of the corresponding diiminoisoindoline precursors **2** (R^2 = R^4 = *tert*-butyl), **3** (R^2 = 2-ethylhexyloxy; R^4 = *tert*-butyl) and **4** (R^2 = R^4 = 2-ethylhexyloxy).

Introduction

Phthalocyanines and naphthalocyanines, especially their metal complexes, have been investigated in detail because of their widespread usage not only as dyes but also in the field of materials science.[1−4] In recent years the very interesting nonlinear optical properties of these materials[5−7] have been investigated. Among the nonlinear optical applications of phthalocyanines, optical limiting has been particularly promising.[5] [Tetrakis(cumylphenoxy)phthalocyaninato]-lead [$(CP)_4$PcPb], described by Shirk et al.[8] and a tetra-*tert*-butyl-substituted chloro(phthalocyaninato)indium(III) complex, described by Perry et al.,[9] are known to be very good materials for optical limiting. Recently, our group has made new approaches[10,11] towards optimization of (phthalocyaninato)indium complexes for optical limiting, using different axial and peripheral substituents and expanding the ring to produce naphthalocyanine moieties.

Optical limiters have a transmission that varies with the incident intensity of light. The transmission is high at normal light intensities but low for intense beams. Ideally, this intensity-dependent transmission can limit the transmitted light intensity so that it is always below some maximum value; hence the name. This is useful for protection of elements that are sensitive to sudden high-intensity light, such as optical elements, sensors and, especially, the human eye.

Results

The tetra-*tert*-butyl-substituted chloro(phthalocyaninato)-indium(III) complex (tBu)$_4$PcInCl was found to fit that requirement very effectively.[9] Here, the third coordination site of the indium centre is occupied by a chloro atom. We exchanged this halogen (by means of Grignard reactions described later in this work) for several fluoro-substituted aromatic groups, such as *p*-(trifluoromethyl)phenyl and pentafluorophenyl moieties[10]. These sterically highly demanding groups reduce interactions between neighbouring molecules and so raise the solubility of the complexes in organic solvents, by minimizing the tendency − common for phthalocyanines and naphthalocyanines in solutions − to form aggregates. Aggregation can strongly influence the NLO properties.[12] In phthalocyanines without an axial ligand, such as tetrakis(cumylphenoxy)-substituted phthalocyanines, there are pronounced spectral changes at higher concentrations, such as a substantial absorption band shift of several nm for the 2,(3)-substituted isomer, and a peak extinction change of about an order of magnitude. Higher solubility in thin liquid and solid films, in comparison to that of the axially halogen-substituted species, is even observed. Additionally, electron-withdrawing substituents such as trifluoromethyl or pentafluorophenyl on the axial position alter the electronic properties of the complexes and introduce a ground-state dipole moment perpendicular to the macrocyclic core, which is assumed to increase optical nonlinearity.[13]

In comparison to the chloro compounds, each of the (phthalocyaninato)indium complexes studied showed very promising results, such as higher nonlinear absorption coefficients, lower limiting thresholds, and an earlier onset of the optical limiting behaviour.[11] Excitation of the (phthalocyaninato)indium complexes in the visible region initially gives an excited singlet state that evolves into a triplet state, with a quantum yield approaching unity and an intersystem crossing time of about 300 ps. The triplet state lifetime is much longer than 10 ns. This means that the

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nanosecond nonlinear absorption is dominated by the absorption from an orientationally averaged triplet state. The axial aryl groups did not affect the linear optical properties; in fact the Q- and B-bands in the UV/Vis spectra are shifted only slightly, by a few nanometers, on exchanging the axial ligands.[11]

Extension of the phthalocyanine core by linear benzannellation affords the related group of 2,3-naphthalocyanines (2,3-Ncs). The more extended π-electron system should in theory produce nonlinear optical properties more pronounced than those seen in the phthalocyanine analogues. In addition, the 2,3-Ncs have their Q-bands shifted to the near IR spectral region − around 800 nm − so the hue of the Nc solutions is dominated by the B-band absorption in the blue region at around 400 nm. Dilute naphthalocyanine solutions are therefore yellow to green. This linear optical behaviour of naphthalocyanines offers new applications in fields where the green-blue colour of phthalocyanines might be deleterious. In, for example, an environment in which it is necessary to see normal red light signals or displays, the strongly red-absorbing phthalocyanines would be unsuitable for eye protection, even though their performance in limiting high intensities would be good. Naphthalocyanines are almost transparent in this red light region; they have transmission windows in the yellow and red region (530−650 nm) of the spectrum. We therefore now focused on synthesizing substituted, highly soluble (naphthalocyaninato)indium(III) complexes with different axial ligands, developing a new unsymmetrical peripheral octasubstitution pattern, with alkyl and alkoxy substituents in the 2- and 4-positions of the Ncs (see Figure 1). The resulting compounds are in general more soluble than the known symmetrically octasubstituted 2,3-naphthalocyanines.[14]

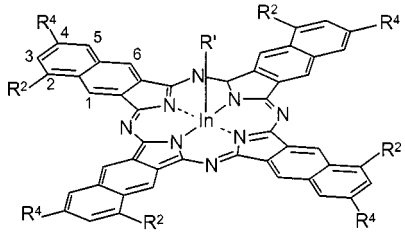
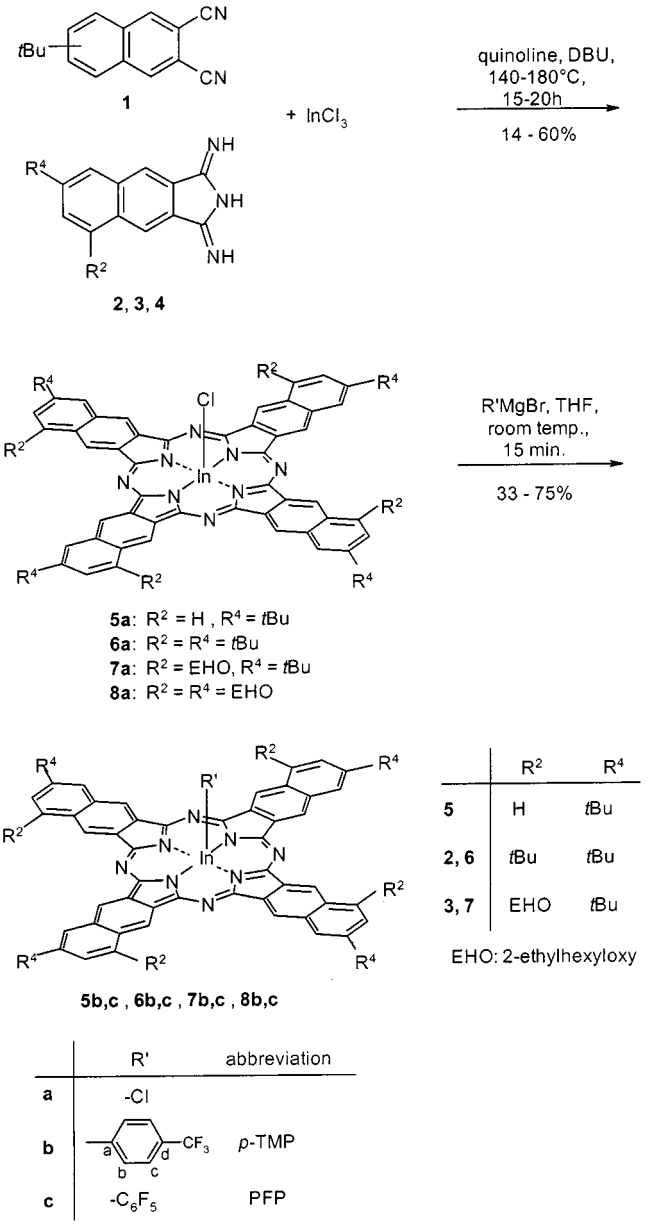


Figure 1. 2,4-Octasubstituted naphthalocyanines

The syntheses of octa-*tert*-butyl-substituted (**6a**), tetra-*tert*-butyltetrakis(2-ethylhexyloxy)-substituted (**7a**), octakis-(2-ethylhexyloxy)-substituted (**8a**), and the tetra-*tert*-butyl-substituted (**5a**) chloro(naphthalocyaninato)indium(III) complexes are shown in Scheme 1 (top). The bulky (*tert*-butyl, *t*Bu) and long-chain (2-ethylhexyloxy, EHO) substituents were chosen because of their known solubilizing character, due to their steric demand. In addition, the electron-donating effects of these groups shift the Q-band absorption further to the near IR.



	R²	R⁴
5	H	*t*Bu
2, 6	*t*Bu	*t*Bu
3, 7	EHO	*t*Bu

	R'	abbreviation
a	-Cl	
b		*p*-TMP
c	$-C_6F_5$	PFP

Scheme 1. Syntheses of different octasubstituted and tetrasubstituted chloro(naphthalocyaninato)indium(III) complexes

The tetra-*tert*-butyl-substituted naphthalocyanine **5a** (mixture of isomers) is a known compound[15] and was used here as a standard with which to compare the different substitution effects of the new synthesized Ncs. Compound **5a** was synthesized starting from the respective naphthalenedicarbonitrile **1**, whereas the octasubstituted chloro(naphthalocyaninato)indium complexes **6a**, **7a**, and **8a** were prepared starting with the isoindoline precursors **2**, **3**, and **4**, respectively. The diiminoisoindolines provide a preformed naphthalocyanine core and are much more reactive than the naphthalenedicarbonitriles. Their total syntheses are described later in this work.

Treatment with indium(III) chloride was carried out in quinoline in the presence of the non-nucleophilic base DBU

as the ring-forming catalyst. No conversion into **6a**, **7a**, and **8a** was observed when the corresponding dinitriles were used as starting materials in place of the diiminoisoindolines. This clearly indicates the lower reactivity of disubstituted naphthalenedicarbonitriles in comparison with the diiminoisoindolines. The resulting chloro(naphthalocyaninato)indium complexes **6a**−**8a** are much more soluble than **5a** in organic solvents such as chloroform or toluene, due to the steric crowding produced by eight bulky substituents.

The chloro(naphthalocyaninato)indium complexes **5a**, **6a**, **7a**, and **8a** were subjected to axial ligand exchange using Grignard methodology. The *p*-(trifluoromethyl)phenyl (pTMP) and pentafluorophenyl (PFP) groups used had previously shown their high potential for reducing the tendency of (phthalocyaninato)indium complexes to aggregate and for enhancing their nonlinear optical properties.[10,11] The Grignard reactions were carried out in dry THF at room temperature and were complete within 15 min, as depicted in the bottom part of Scheme 1. The resulting axially aryl-substituted naphthalocyaninato complexes **5b**, **5c**, **6b**, **6c**, **7b**, **7c**, **8b**, and **8c** do not change very much either in colour or in stability upon ligand exchange. Dilute solutions of the compounds possessing exclusively *tert*-butyl groups (**5b**, **5c**, **6b**, and **6c**) are still greenish yellow while the others, bearing at least one EHO group (**7b**, **7c**, **8b**, and **8c**), are yellow to orange. The ligand exchange apparently has only a very small effect on the electronic properties of the Ncs. UV/Vis spectra of dilute samples of the naphthalocyaninato complexes **5b**, **5c**, **6b**, **6c**, **7b**, **7c**, **8b**, and **8c** show slightly bathochromically shifted B-bands (ca. 3−13 nm) and hypsochromically shifted Q-bands (0.5−4 nm) relative to their chloro analogues. This is depicted in Figure 2 for dilute solutions of **7a** and **7b** as examples.

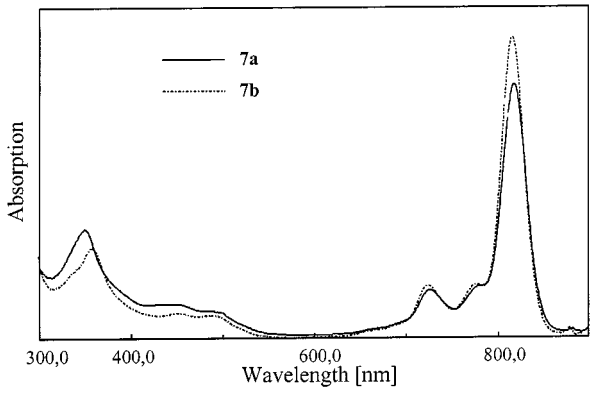


Figure 2. UV/Vis spectra of **7a** and **7b** in $CHCl_3$ (ca. 0.007 mM)

From the UV/Vis spectra, it could be seen that the tetra-*tert*-butyl-substituted Ncs **5a**, **5b**, and **5c** showed a stronger tendency to aggregate than the mixed octasubstituted Ncs **6a**−**8c** did. This is certainly consistent with expectations from steric considerations. For the octasubstituted materials, the *tert*-butyl peripheral substituents were more effective at blocking aggregation than the 2-ethylhexyloxy (EHO) substituents were. The mixed substituent − $(t\mathrm{Bu})_4(\mathrm{EHO})_4$ − materials with large axial substituents showed very little evidence of aggregation even in very concentrated solutions and pure films, as is illustrated by the band shapes and the bathochromic shifts of the Q-band maxima of different concentrated solutions of **7a**−**c**. In the cases of **7a**−**c** it can be seen that neither band broadening nor any redshift of the Q-band was observed.[16] In the infrared spectra of **5b**−**8c** the new indium−carbon bond-stretching vibration is not found, whereas the characteristic vibrations for fluoroaromatics bound to a metal centre can be identified in most cases.

^{1}H and ^{13}C NMR measurements on the peripherally *tert*-butyl- and 2-ethylhexyloxy-substituted naphthalocyaninato complexes **5a**−**c**, **6a**−**c**, **7a**−**c**, and **8a**−**c** show the methyl and methylene proton signals in the δ = 0.5−4.5 region and the aliphatic carbon resonances in the δ = 10−40 region. The signals of the deshielded α-carbon atoms next to the ether oxygen atom of the EHO substituents (in **7a**−**c** and **8a**−**c**) appear at about δ = 70. The aromatic macrocycle proton and carbon signals of all investigated naphthalocyanines are found at δ ≈ 6.5−10.5 and δ ≈ 99−160, respectively. In most cases, the highest deshielding effect is attributable to the macrocyclic protons 2 and 2′ and carbon atoms 4 and 4′ adjacent to the naphthalocyanine core. Structurally related naphthalocyanines, such as the chloro compounds and their two axially aryl-substituted derivatives, have similar NMR spectra in terms of the periphery and core resonances. The additional proton signals of the axial *p*-(trifluoromethyl)phenyl groups are found in the δ = 3.5−6.5 region as two multiplets or as broad singlets. The expected doublet splitting is only observed with the tetra-*tert*-butyl-substituted compound **5b**. For the pTMP-substituted naphthalocyanines, carbon resonances are found only for the atoms *a* bound to the central metal ion and *c*,*c*′ in the positions *meta* to the indium centre, at δ ≈ 122 and 133. PFP-substituted Ncs do not display axial carbon resonances, because the resolution of the split signals is too low, due to C−F coupling.

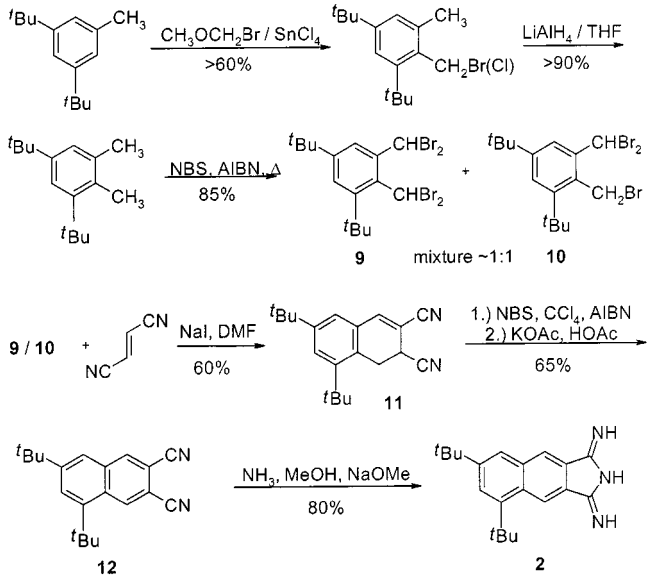
The solubilities in chloroform of the axially substituted naphthalocyanines **7b**, **7c**, **8b**, and **8c** are high, easily exceeding 180 mmol/l. The compounds bearing only *tert*-butyl groups at the periphery − **5b**, **5c**, **6b**, and **6c** − are less soluble. All axially aryl-substituted compounds are much more soluble than their chloro precursors in solvents of medium polarity, because of the steric effects arising from the larger axial aryl substituents. Of the naphthalocyanines discussed, **7b** displays the highest solubility in chloroform, with excellent long-term stability in solution, even at high concentrations. UV/Vis spectra of **7b** do not show any evidence of degradation or aggregation of the compound. Compound **7b** has therefore been selected first for detailed nonlinear optical investigations with regard to optical limiting performance. The results will be reported elsewhere.[16]

The syntheses of the unsymmetrically substituted isoindoline precursors **2**, **3**, and **4**, described in the following section, always first involves the preparation of substituted *o*-xylenes before formation of the naphthalenedicarbonitrile units **11**, **17**, and **21**, respectively. Schemes 2−4 give an overview of the multistep reactions affording each isoindoline.

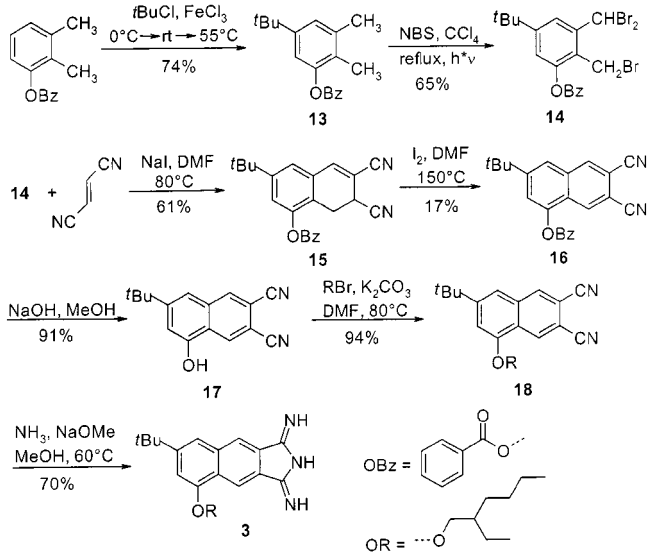
3,5-Di-(*tert*-butyl)toluene (Scheme 2) was bromomethylated[17] (and also chloromethylated, as a side reaction). Halogen-hydrogen exchange yielded the corresponding *o*-xylene, which was brominated at the benzylic positions. The obtained mixture of **9** and **10** reacted with fumarodinitrile to afford the dihydronaphthalenedicarbonitrile **11**, which was aromatized with formation of **12** by bromo substitution and subsequent elimination of 1 equiv. of HBr. Catalytic addition of ammonia to **12** gave the reactive isoindoline **2**.

The mixed substituted isoindoline **3** was obtained in a seven-step reaction (Scheme 3), starting with a Friedel–Crafts alkylation of protected 3-hydroxy-*o*-xylene, followed by bromination and dihydronaphthalenedicarbonitrile formation (**13** → **15**) as described above. This time, molecular iodine was used to oxidize **15**, giving dinitrile **16**. Deprotection of the hydroxy group in **16** and etherification yielded the isoindoline **3** after addition of ammonia.

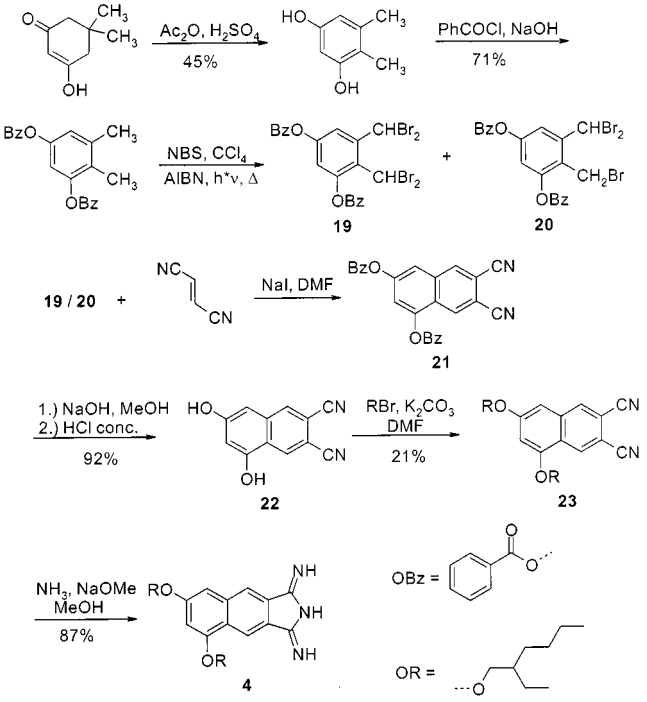
To introduce two hydroxy groups in the 3,5-positions of an *o*-xylene, we started with a rearrangement reaction of dimedone,[18] depicted in Scheme 4. Protection of the phenolic groups, subsequent bromination to form **19** and **20** and fumarodinitrile addition afforded the naphthalenedicarbonitrile **21** directly, without a dihydro intermediate. Saponification of the hydroxy groups in **21**, etherification with 2-ethylhexyl bromide and addition of ammonia gave the isoindoline **4**.



Scheme 2. Synthesis of di-*tert*-butylbenzodiiminoisoindoline (**2**)



Scheme 3. Synthesis of *tert*-butyl-(2-ethylhexyloxy)benzodiiminoisoindoline (**3**)



Scheme 4. Synthesis of bis(2-ethylhexyloxy)benzodiiminoisoindoline (**4**)

Summary

The syntheses of chloro(naphthalocyaninato)indium(III) complexes **6a**, **7a**, and **8a**, unsymmetrically peripherally octasubstituted with *tert*-butyl and/or 2-ethylhexyloxy groups, from the corresponding diiminoisoindoline precursors **2**, **3**, and **4** is reported. We also prepared a tetra-*tert*-butyl-substituted naphthalocyaninato complex **5a**, to compare its properties with those of the octasubstituted Ncs. All chloro(naphthalocyaninato) complexes were subjected to ligand exchange by means of Grignard reactions, to yield the axially *p*-(trifluoromethyl)phenyl- and pentafluorophenyl-substituted species **5b**–**8c**. These generally displayed better solubilities in chloroform than the chloro(naphthalocyaninato) complexes, but did not show any remarkable changes in their UV/Vis spectra. All (naphthalocyaninato)indium complexes described here are undergoing investigation of their nonlinear optical properties, particularly for optical limiting applications.[16] We also describe the multistep syn-

theses of the diiminoisoindolines **2**−**4** (Schemes 2−4), which are the precursors for the chloro(naphthalocyaninato)indium(III) complexes **6a**−**8c**.

Experimental Section

All reactions were carried out under dry nitrogen. THF was distilled from sodium benzophenone ketyl prior to use, quinoline from calcium hydride. *p*-(Trifluoromethyl)bromobenzene, pentafluorobromobenzene, 3,5-di-*tert*-butyltoluene, and dimedone were obtained from commercial sources. 6-*tert*-Butylnaphthalene-2,3-dicarbonitrile (**1**),[19] 2-Bromo(chloro)methyl-3,5-di-*tert*-butyltoluene,[20] di-*tert*-butyl-*o*-xylene,[21] 3-benzoyloxy-*o*-xylene,[22] 3,5-dihydroxy-*o*-xylene,[18] 3,5-dibenzoyloxy-*o*-xylene[23] and [3,(4)-tetra-*tert*-butyl-2,3-naphthalocyaninato]indium(III) chloride[15] (**5a**) 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); Finnigan TSQ 70 MAT (EI, temperature of the ion source: 200 °C, electron energy 70 eV). − ^{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. Owing to the usual difficulties of combustion analysis of phthalocyanines and naphthalocyanines, it was not possible to obtain satisfying elemental analyses for all compounds described.

Precursors

Mixture of α,α,α′,α′-Tetrabromo-3,5-di-*tert*-butyl-*o*-xylene (9) and α,α,α′-Tribromo-3,5-di-*tert*-butyl-*o*-xylene (10): 3,5-Di-*tert*-butyl-*o*-xylene (21.0 g, 0.096 mol), NBS (78.3 g, 0.44 mol), and AIBN (0.5 g) were stirred in dry CCl_4 (300 mL) at reflux for 22 h. The warm solution was filtered and the precipitate was washed with three 50-mL portions of warm CCl_4. After removal of bromine traces with a saturated $NaHSO_3$ solution, the filtrate was dried and concentrated to yield a white solid. Recrystallization from $CHCl_3$/methanol yielded a 1:1 mixture of the triply and quadruply brominated di-*tert*-butyl-*o*-xylenes **9** and **10**, with a melting range of 160−180 °C. The mixture could be used without further purification. Yield 41.0 g (mixture of different products). − IR (KBr): $\tilde{\nu}$ = 3854 cm^{-1} m, 3746 w, 2957 m, 2874 w, 2826 w, 2363 vs, 2338 s, 1653 m, 1576 w, 1558 m, 1522 w, 1458 m, 1394 w, 1240 w, 1217 w, 1078 w, 667 w. − ^{1}H NMR ($CDCl_3$) {chemical shifts of **10** in brackets}: δ = 1.32 {1.34} (s, 9 H, 1′-*t*Bu), 1.46 {1.47} (s, 9 H, 2-*t*Bu), {4.85} [s (br), 2 H, 4-CH_2Br], 7.30 {7.40} (d, ^4J = 2.0 Hz, 1 H, 1-H), 7.47 {7.39} (s, 1 H, 4′-$CHBr_2$), 7.91 (s, 1 H, 4-$CHBr_2$), 8.02 {7.95} (d, ^4J = 2.0 Hz, 1 H, 2′-H). − ^{13}C NMR ($CDCl_3$) {chemical shifts of **10** in brackets}: δ = {28.5} (4-CH_2Br), 30.9 {31.0} (1′-*t*$BuCH_3$), 35.2 {ca. 30−32} (2-CMe_3), 31.9 {32.2} (2-*t*$BuCH_3$), 36.2 (4-$CHBr_2$), 36.1 {36.3} (1′-CMe_3), 39.7 {39.0} (4′-$CHBr_2$), 124.2 {125.3} (C-1), 129.9 {126.7} (C-2′), 131.4 {127.2} (C-3), 143.3 {142.8} (C-3′), 144.4 {147.7} (C-1′), 153.2 {152.2} (C-2). − MS (FD): *m*/*z*: 533.8 [M$^+$ (**9**, $^{81}Br_2$)], 529.9 [M$^+$ (**9**, $^{79}Br_4$)], 455.9 [M$^+$ (**10**, $^{81}Br_2$)], 452.1 [M$^+$ (**10**, $^{79}Br_4$)].

5,7-Di-*tert*-butyl-3,4-dihydronaphthalene-2,3-dicarbonitrile (11): The above mixture of **9** and **10** (29.0 g) was stirred with fumaronitrile (4.9 g, 0.063 mol) and NaI (44.1 g, 0.290 mol) in dry DMF (250 mL) at 70 °C for 24 h. The cold solution was poured into a mixture of $NaHSO_3$ (20.0 g) in water (600 mL) and extracted with diethyl ether. The combined organic layers were washed with water, dried and concentratated to dryness. The residual oil crystallized in vacuo and was recrystallized from methanol. Yield 7.3 g (57% ref. to pure **10**) of **11** with m.p. 140−141 °C. − IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} vs, 2907 m, 2363 w, 2336 w, 1717 w, 1668 m, 1653 m, 1539 s, 1506 m, 1479 w, 1396 m, 1366 m, 1304 w, 1250 w, 1217 w, 1151 w. − ^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 9 H, 5′-*t*Bu), 1.44 (s, 9 H, 6-*t*Bu), 3.20 (dd, ^2J = 15.4, ^3J = 5.7 Hz, 1 H, 2a,b-H), 3.61 (dd, ^2J = 15.4, ^3J = 6.2 Hz, 1 H, 2a,b-H), 3.70 (td, ^3J = 5.6 Hz, 1 H, 3-H), 7.11 (d, ^4J = 1.9 Hz, 1 H, 5-H), 7.39 (s, 1 H, 2′-H), 7.55 (d, ^4J = 2.0 Hz, 1 H, 6′-H). − ^{13}C NMR ($CDCl_3$): δ = 26.9 (C-2), 27.0 (C-3), 29.6 (5′-*t*$BuCH_3$), 31.0 (6-*t*$BuCH_3$), 34.6 (6-CMe_3), 35.7 (5′-CMe_3), 102.7 (C-3′), 117.0; 117.2 (C-4,4′), 119.0 (C-5), 124.8 (C-6′), 127.0 (C-1), 130.6 (C-1′), 146.3 (C-2′), 148.0 (C-6), 150.3 (C-5′). − MS (FD): *m*/*z*: 292.9 [M$^+$]. − $C_{20}H_{24}N_2$ (292.42): calcd. C 82.14, H 8.28, N 9.58; found C 79.26, H 8.00, N 10.42.

5,7-Di-*tert*-butylnaphthalene-2,3-dicarbonitrile (12): Compound **11** (2.0 g, 6.85 mmol), NBS (1.3 g, 7 mmol), and dibenzoyl peroxide (0.5 g) were refluxed in dry CCl_4 (50 mL) for 1 h. Potassium acetate (8.0 g) and conc. acetic acid (5 mL) were added and the mixture was stirred for an additional hour at reflux. The cold mixture was poured into ice water (200 mL) containing NaOH (5.0 g) and $NaHSO_3$ (1.0 g) and extracted several times with $CHCl_3$. The organic layers were dried and concentrated. The crude product was column chromatographed (silica gel/$CHCl_3$, R_f = 0.69). Yield 1.3 g (65%) of **12** as a white powder, m.p. 182−183 °C. − IR (KBr): $\tilde{\nu}$ = 3032 cm^{-1} w, 2964 vs, 2876 m, 2363 m, 2334 m, 2239 w, 1624 m, 1599 w, 1553 w, 1472 m, 1400 w, 1367 m, 1337 w, 1290 w, 1198 w, 1030 w, 1009 w, 935 m, 906 w. − ^{1}H NMR ($CDCl_3$): δ = 1.41 (s, 9 H, 5′-*t*Bu), 1.61 (s, 9 H, 6-*t*Bu), 7.72 [s (br), 1 H, 5-H], 7.87 (d, ^4J = 1.9 Hz, 1 H, 6′-H), 8.30 (s, 1 H, 2′-H), 8.87 (s, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 30.8 (5′-*t*$BuCH_3$), 31.9 (6-*t*$BuCH_3$), 35.4 (6-CMe_3), 36.3 (5′-CMe_3), 107.7 (C-3), 108.6 (C-3′), 115.9; 116.6 (C-4,4′), 123.0 (C-5), 127.1 (C-6′), 129.8 (C-1),134.2 (C-2), 135.5 (C-1′), 137.1 (C-2′), 147.2 (C-6), 153.3 (C-5′). − MS (EI): *m*/*z* (%) = 290.1 (5) [M$^+$], 288.1 (69) [M$^+$ − 2 H], 273.1 (100) [M$^+$ − 2 H − CH_3], 244.9 (20), 231.0 (25), 215.0 (20), 190.0 (10), 114.9 (25), 57.0 (50). − $C_{20}H_{22}N_2$ (290.41): calcd. C 82.71, H 7.64, N 9.65; found C 82.35, H 8.12, N 9.69.

(3′,5′-Di-*tert*-butyl)benzo[*f*]isoindolinediimine (2): Ammonia was bubbled vigorously through a solution of **12** (1.3 g, 4.48 mmol) and NaOMe (100 mg, 1.80 mmol) in anhydrous methanol (50 mL) for 2 h at room temperature. The stream of ammonia was then reduced to a slight current, while the solution was heated to 60 °C. The reaction was monitored by TLC [silica gel/$CHCl_3$, R_f (**2**) = 0] and terminated after most of the naphthalocarbonitrile **12** (R_f = 0.7) had reacted. After evaporation of methanol in vacuo, the residue was column-chromatographed on silica gel with $CHCl_3$ to remove unchanged **12**. The polarity of the eluent was gradually increased by addition of methanol, in order to elute the isoindolinediimine **2**. After evaporation of the solvents, the yellow product **2** was obtained. Yield 1.1 g (80%), m.p. > 160 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3439 cm^{-1} w, 2963 m, 2932 w, 2363 vw, 1728 w, 1620 vw, 1462 vw, 1396 vw, 1379 vw, 1261 vs, 1096 vs, 1024 s, 864 w, 802 vs, 744 vw, 704 vw. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.37 (s, 9 H, 5′-*t*Bu), 1.61 (s, 9 H, 6-*t*Bu), 7.70 (s, 1 H, 5-H), 7.81 (s, 1 H, 6′-H), 8.40 (s, 1 H, 2′-H), 8.92 (s, 1 H, 2-H). − ^{13}C NMR ([D$_6$]DMSO): δ = 30.8 (5′-*t*$BuCH_3$), 31.6 (6-*t*$BuCH_3$), 34.7 (6-CMe_3), 36.1 (5′-CMe_3), 120.0 (C-5), 123.6 (C-6′), 124.0; 124.2 (C-2,2′), 129.9−131.2 (C-1,3,3′), 135.8 (C-1′), 147.5 (C-6), 149.4 (C-5′), 172.3; 172.6 (C-4,4′). − MS (EI): *m*/*z* (%) = 309.2 (3) [(M + 2 H)$^+$], 308.2 (8) [(M + H)$^+$], 307.2 (12) [M$^+$], 292.2 (12) [M$^+$ − CH_3], 288.1 (50) [M$^+$ − 2 H − NH_3], 273.1 (100) [M$^+$ − 2 NH_3], 249.1 (10) [M$^+$ − H − C_4H_9], 245 (15), 231.1 (20), 214.8 (20), 114.7 (22), 57.1 (25) [$C_4H_9^+$]. −

$C_{20}H_{25}N_3$ (307.44): calcd. C 78.12, H 8.20, N 13.67; found C 70.91, H 8.37, N 10.33.

[5′-*tert*-Butyl-3′-(2-ethylhexyloxy)]benzo[*f*]isoindolinediimine (3)

3-Benzoyloxy-5-*tert*-butyl-*o*-xylene (13): A mixture of 3-benzoyloxy-*o*-xylene (22.2 g, 98.10 mmol) and *tert*-butyl chloride (40 mL, 34.0 g, 0.367 mol) was cooled to 0 °C. $FeCl_3$ (17.5 g, 0.108 mol) was added in one portion with vigorous stirring, causing immediate evolution of gaseous HCl. Stirring was continued for 16 h, with the cooling bath slowly warming up to room temperature. The reaction was completed by heating the viscous mass to 35 °C until the evolution of HCl has almost completely stopped. Addition of ice (400 g), and repeated extraction of the product with diethyl ether followed. The organic layers were washed with water, dried with $MgSO_4$, and filtered. The crude product obtained after evaporation of the solvent was purified by column chromatography (SiO_2/toluene, R_f = 0.65) and eluted as the second fraction. Yield 20.4 g (74%) of **13** as pale yellow, viscous oil. − IR (KBr): $\tilde{\nu}$ = 3063 cm^{-1} w, 3034 w, 2964 vs, 2870 m, 1738 vs, 1620 m, 1601 m, 1574 m, 1491 s, 1450 vs, 1406 m, 1364 m, 1313 m, 1261 vs, 1192 s, 1177 vs, 1092 vs, 1070 vs, 1024 s, 1001 w, 933 w, 891 w, 874 m, 708 vs, 631 w. − ^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 9 H, *t*Bu), 2.09 (s, 3 H, 4-CH_3), 2.33 (s, 3 H, 4′-CH_3), 6.99 (d, ^4J = 1.8 Hz, 1 H, 1-H), 7.13 (d, ^4J = 1.5 Hz, 1 H, 2′-H), 7.49−7.55 (m, 2 H, γ-H), 7.64 (tt, ^3J = 7.3, ^4J = 1.7 Hz, 1 H, δ-H), 8.23−8.27 (m, 2 H, β-H). − ^{13}C NMR ($CDCl_3$): δ = 12.2 (4-CH_3), 20.3 (4′-CH_3), 31.2 (*t*BuCH_3), 34.3 (CMe_3), 116.4 (C-1), 124.7 (C-2′), 125.6 (C-3), 128.5 (C-γ), 129.6 (C-α), 130.1 (C-β), 133.4 (C-δ), 137.7 (C-3′), 149.2, 149.5 (C-1′, C-2), 165.1 (COOR). − MS (EI): *m*/*z* (%) = 282.2 (11) [M^+], 276.2 (2) [M^+ − CH_3], 105.1 (100) [$C_6H_5CO^+$], 91.1 (37) [$C_7H_7^+$], 84.9 (43), 82.9 (66), 77.1 (28) [$C_6H_5^+$], 57.1 (7) [$C_4H_9^+$], 47.0 (12). − $C_{19}H_{22}O_2$ (282.38): calcd. C 80.82, H 7.85; found C 80.75, H 7.78.

3-Benzoyloxy-α,α,α′-tribromo-5-*tert*-butyl-*o*-xylene (14): Compound **13** (17.3 g, 61.30 mmol) was dissolved in dry CCl_4 (300 mL). After addition of NBS (67.1 g, 0.377 mol) and the radical starter AIBN (50 mg), the mixture was refluxed for 68 h under irradiation (200-W daylight bulb). The reaction was monitored by TLC (SiO_2/toluene). The deep orange mixture was allowed to cool and filtered, the solid succinimide/NBS residue was washed with CCl_4, and the combined filtrates were washed with 5% aqueous sodium metabisulfite solution in order to remove bromine liberated during the reaction. After phase separation, the organic layer was washed several times with water, dried with $MgSO_4$, and filtered. The crude product obtained after evaporation of the solvent was column-chromatographed (SiO_2/toluene), and the title compound was collected as the main fraction (R_f = 0.72) and recrystallized from *n*-hexane. Yield 22.6 g (71%) of **14** as a white, crystalline powder, m.p.: 127−128 °C. − IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1} vw, 3032 vw, 2964 m, 2868 w, 1738 vs, 1612 w, 1599 w, 1572 w, 1483 w, 1450 m, 1416 m, 1364 w, 1258 vs, 1244 vs, 1229 vs, 1175 s, 1144 m, 1119 m, 1099 m, 1078 s, 1061 vs, 1024 s, 939 w, 889 w, 710 vs, 679 w, 665 w, 642 m. − ^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 9 H, *t*Bu), 4.57 (s, 2 H, 4-CH_2Br), 7.02 (s, 1 H, 4′-$CHBr_2$), 7.23 (d, ^4J = 2.0 Hz, 1 H, 1-H), 7.51−7.57 (m, 2 H, γ-H), 7.67 (tt, ^3J = 7.4, ^4J = 1.7 Hz, 1 H, δ-H), 7.84 (d, ^4J = 1.9 Hz, 1 H, 2′-H), 8.22−8.26 (m, 2 H, β-H). − ^{13}C NMR ($CDCl_3$): δ = 21.8 (4-CH_2Br), 30.9 (*t*BuCH_3), 35.2 (CMe_3), 36.5 (4′-$CHBr_2$), 121.6 (C-1), 122.5 (C-3), 124.7 (C-2′), 128.8 (C-γ), 128.8 (C-α), 130.3 (C-β), 134.0 (C-δ), 140.8 (C-3′), 148.6 (C-1′), 154.0 (C-2), 164.5 (COOR). − MS (EI): *m*/*z* (%) = 520.0 (4) [M^+ ($^{81}Br_2$)], 504.7 (1.5) [M^+ ($^{81}Br_2$) − CH_3], 438.9 (65) [M^+ ($^{81}Br_2$) − ^{81}Br; M^+ (^{81}Br) − ^{79}Br], 254.9 (4), 105.1 (100) [$C_6H_5CO^+$], 77.1 (95) [$C_6H_5^+$], 51.0 (13). − $C_{19}H_{19}Br_3O_2$ (519.07): calcd. C 43.96, H 3.69, Br 46.18; found C 43.57, H 3.59, Br 46.59.

5-Benzoyloxy-7-*tert*-butyl-2,3-dicyano-3,4-dihydronaphthalene (15): Compound **14** (2.13 g, 4.10 mmol), fumaronitrile (395 mg, 5.06 mmol), and anhydrous sodium iodide (4.99 g, 33.30 mmol) in DMF (30 mL) were stirred at 80 °C for 22 h. The dark brown mixture was allowed to cool and stirred into 100 mL of 5% aqueous $NaHSO_3$ solution. The product was extracted with diethyl ether in three portions; the combined organic layers were washed with water, dried with $MgSO_4$, and filtered. Evaporation of the solvent was followed by column chromatography (SiO_2/$CHCl_3$, R_f = 0.58) and recrystallization from ethanol. Yield 886 mg (61%) of **15** as a beige powder, m.p.: 164−166 °C. − IR (KBr): $\tilde{\nu}$ = 3074 cm^{-1} vw, 2964 m, 2908 vw, 2874 vw, 2232 w, 1738 vs, 1624 w, 1599 w, 1568 vw, 1479 vw, 1450 w, 1416 w, 1381 w, 1310 vw, 1248 vs, 1232 vs, 1184 m, 1177 m, 1159 vw, 1138 s, 1097 m, 1080 s, 1069 s, 1024 w, 1005 m, 918 w, 895 w, 710 vs. − ^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 9 H, *t*Bu), 3.04, 3.16 [2 dd, ^2J = 16.5, ^3J = 7.2 Hz; 1 H (1 H), 2^a,2^b-H], 3.71 (td, ^3J = 7.0, ^4J = 1.3 Hz, 1 H, 3-H), 7.21, 7.28 [2d, ^4J = 1.7(2.0) Hz, 1 H (1 H), 5,6′-H], 7.43 (d, ^4J = 1.2 Hz, 1 H, 2′-H), 7.51−7.57 (m, 2 H, γ-H), 7.67 (tt, ^3J = 7.4, ^4J = 1.6 Hz, 1 H, δ-H), 8.18−8.22 (m, 2 H, β-H). − ^{13}C NMR ($CDCl_3$): δ = 25.0 (C-2), 26.8 (C-3), 31.0 (*t*BuCH_3), 34.8 (CMe_3), 104.2 (C-3′), 116.7, 117.2 (4,4′-CN), 121.0 (C-5), 123.2 (C-6′), 124.3 (C-1), 128.4 (C-1′), 128.8 (C-γ), 130.3 (C-β), 130.3 (C-α), 134.2 (C-δ), 144.4 (C-2′), 148.4 (C-5′), 153.0 (C-6), 164.5 (COOR). − MS (EI): *m*/*z* (%) = 356.1 (0.7) [M^+], 341 (0.3) [M^+ − CH_3], 329.1 (2) [M^+ − HCN], 314.1 (0.4) [M^+ − CH_3 − HCN], 193.0 (0.4), 165.9 (0.6), 140.1 (0.5), 105.1 (100) [$C_6H_5CO^+$], 77.0 (30) [$C_6H_5^+$], 51.0 (4). − $C_{23}H_{20}N_2O_2$ (356.42): calcd. C 77.51, H 5.66, N 7.86; found C 77.83, H 4.95, N 7.43.

5-Benzoyloxy-7-*tert*-butylnaphthalene-2,3-dicarbonitrile (16): Compound **15** (1.83 g, 5.13 mmol) and I_2 (2.61 g 10.30 mmol) were stirred at 150 °C in dry DMF (40 mL). The reaction was monitored by TLC (SiO_2/$CHCl_3$), and stopped when all of the dihydronaphthalene **15** (R_f = 0.58) had been oxidized. The dark brown mixture was allowed to cool and stirred into 5% aqueous $NaHSO_3$ solution. The product was extracted with diethyl ether, and the combined organic layers were washed with water, dried with $MgSO_4$, and filtered. Evaporation of the solvent was followed by column chromatography (SiO_2/$CHCl_3$, R_f = 0.53) and recrystallization from ethanol. Yield 310 mg (17%) of **16** as a light brown, crystalline powder, m.p.: 218−220 °C. − IR (KBr): $\tilde{\nu}$ = 3076 cm^{-1} vw, 2964 m, 2907 vw, 2872 vw, 2230 m, 1738 vs, 1624 m, 1593 w, 1568 w, 1479 w, 1450 m, 1381 m, 1248 vs, 1232 vs, 1184 m, 1175 s, 1138 vs, 1097 s, 1080 s, 1069 vs, 1022 m, 1005 s, 918 m, 893 m, 710 vs. − ^{1}H NMR ($CDCl_3$): δ = 1.44 (s, 9 H, *t*Bu), 7.57−7.63 (m, 2 H, γ-H), 7.74 (tt, ^3J = 7.4, ^4J = 1.6 Hz, 1 H, δ-H), 7.75 (d, ^4J = 1.7 Hz, 1 H, 5-H), 7.81−7.82 [d (br), $^4J \approx$ 1.7 Hz, 1 H, 6′-H], 8.28−8.32 (m, 2 H, β-H), 8.35−8.36 (m, 2 H, 2,2′-H). − ^{13}C NMR ($CDCl_3$): δ = 30.8 (*t*BuCH_3), 35.7 (CMe_3), 109.8, 110.6 (C-3,3′), 115.7, 115.9 (4,4′-CN), 121.8 (C-5), 122.4 (C-6′), 125.5 (C-1), 128.2 (C-α), 129.0 (C-γ), 129.7 (C-2), 130.4 (C-β), 134.1 (C-1′), 134.5 (C-δ), 135.9 (C-2′), 146.8 (C-6), 155.3 (C-5′), 164.7 (COOR). − MS (EI): *m*/*z* (%) = 354.1 (0.6) [M^+], 339 (0.4) [M^+ − CH_3], 250.0 (0.8) [(M + H)$^+$ − $C_6H_5CO^+$], 235.0 (2) [(M + H)$^+$ − CH_3 − $C_6H_5CO^+$], 207.0 (0.7), 105.1 (100) [$C_6H_5CO^+$], 77.0 (23) [$C_6H_5^+$], 51.0 (3). − $C_{23}H_{18}N_2O_2$ (354.41): calcd. C 77.95, H 5.12, N 7.90; found C 75.28, H 4.90, N 7.70.

7-*tert*-Butyl-5-hydroxynaphthalene-2,3-dicarbonitrile (17): Compound **16** (1.32 g, 3.72 mmol) was added to a solution of NaOH (1.00 g, 25.00 mmol) in MeOH (50 mL), and stirred for 0.5 h. Acidification of the mixture with 2 N HCl solution (pH = 2) yielded a yellow-brown precipitate, which was collected by filtration, washed

with water until neutral, and recrystallized from $CHCl_3$. Yield 847 mg (91%) of **17** as pale yellow crystals, m.p.: > 250 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3321 (br) cm^{-1} vs, 3059 w, 2970 s, 2910 m, 2876 m, 2241 vs, 1622 s, 1583 m, 1574 s, 1481 w, 1468 w, 1416 vs, 1396 s, 1367 vs, 1298 vs, 1271 m, 1246 s, 1184 s, 1138 s, 1099 s, 947 m, 922 s, 905 w, 868 m, 764 w, 692 w, 663 m. − ^{1}H NMR ([D$_6$]acetone): δ = 1.39 (s, 9 H, *t*Bu), 7.41 (d, ^4J = 1.7 Hz, 1 H, 5-H), 7.65−7.66 (m, 1 H, 6′-H), 8.56 (s, 1 H, 2′-H), 8.71 (s, 1 H, 2-H), 9.98 [s (br), OH]. − ^{13}C NMR ([D$_6$]acetone): δ = 31.1 (*t*BuCH$_3$), 36.0 (CMe$_3$), 108.1 (C-3), 110.6 (C-3′), 112.8 (C-5), 116.4 (C-6′), 117.1, 117.3 (4,4′-CN), 123.8 (C-1), 131.3 (C-2), 135.3 (C-1′), 136.8 (C-2′), 154.3 (C-6), 156.7 (C-5′). − MS (EI): *m*/*z* (%) = 250.1 (35) [M$^+$], 235.1 (100) [M$^+$ − CH$_3$], 207.0 (25) [M$^+$ − CH$_3$ − CO], 194.9 (15), 152.0 (5), 41.1 (10). − $C_{16}H_{14}N_2O$ (250.30): calcd. C 76.78, H 5.64, N 11.19; found C 76.06, H 5.47, N 11.07.

7-*tert*-Butyl-5-(2-ethylhexyloxy)naphthalene-2,3-dicarbonitrile (18): A mixture of **17** (528 mg, 2.11 mmol), 1-bromo-2-ethylhexane (1.1 mL, 1.19 g, 6.16 mmol), and anhydrous potassium carbonate (1.93 g, 14.00 mmol) in dry DMF (13 mL) was stirred at 80 °C for 40 min. With completion of the reaction (TLC, SiO_2/toluene; product spot shows a strong blue fluorescence when excited at 366 nm), the colour of the mixture changed from a bright orange to a duller brown. The mixture was poured into 100 mL of water, and the product was extracted with diethyl ether. The organic layers were washed with water until neutral, dried with $MgSO_4$, and filtered. Evaporation of the solvent was followed by column chromatography (SiO_2/toluene, R_f = 0.40). The waxy solid obtained was thoroughly vacuum-dried overnight at 40 °C. Yield 720 mg (94%) of **18** as a waxy white solid, m.p.: 78−79 °C. − IR (KBr): $\tilde{\nu}$ = 3086 cm^{-1} vw, 2961 vs, 2932 vs, 2874 s, 2860 s, 2232 s, 1624 s, 1591 m, 1574 m, 1477 m, 1466 s, 1454 s, 1414 s, 1400 s, 1379 vs, 1312 s, 1285 s, 1246 s, 1192 s, 1146 s, 1105 m, 1072 m, 1030 vw, 988 w, 908 s, 862 w, 854 w, 660 w. − ^{1}H NMR ($CDCl_3$): δ = 0.91, 0.98 [2 t, ^3J = 6.9 (7.5) Hz, 3H (3 H), δ′,ζ-CH$_3$], 1.34−1.38 (m, 4 H, γ,δ-CH$_2$), 1.41 (s, 9 H, *t*Bu), 1.47-1.66 (m, 4 H, ε,γ′-CH$_2$), 1.83−1.92 (m, 1 H, β-CH), 4.06 (d, ^3J = 5.4 Hz, 2 H, α-CH$_2$), 7.10 (s, 1 H, 5-H), 7.40 (s, 1 H, 6′-H), 8.20 (s, 1 H, 2′-H), 8.63 (s, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 11.2 (CH$_3$-δ′), 14.0 (CH$_3$-ζ), 23.0 (CH$_2$-ε), 24.1 (CH$_2$-γ′), 29.1, 30.7 (CH$_2$-γ,δ), 31.0 (*t*BuCH$_3$), 35.7 (CMe$_3$), 39.4 (CH-β), 71.0 (CH$_2$-α), 108.0 (C-3), 108.0 (C-5), 110.4 (C-3′), 115.6 (C-6′), 116.1, 116.6 (4,4′-CN), 124.1 (C-1), 130.5 (C-2), 134.1 (C-1′), 135.3 (C-2′), 154.9 (C-5′), 155.7 (C-6). − MS (EI): *m*/*z* (%) = 362.2 (10) [M$^+$], 250.1 (100) [M$^+$ − C_8H_{16}], 235.1 (40) [M$^+$ − C_8H_{16} − CH$_3$], 207.1 (7) [M$^+$ − C_8H_{16} − CH$_3$ − CO], 71.0 (52) [$C_5H_{11}^+$], 57.0 (57) [$C_4H_9^+$], 44 (29), 42 (26). − $C_{24}H_{30}N_2O$ (362.52): calcd. C 79.52, H 8.34, N 7.73; found C 79.19, H 8.15, N 7.63.

[5′-*tert*-Butyl-3′-(2-ethylhexyloxy)]benzo[*f*]isoindolinediimine (3): Ammonia was bubbled vigorously through a solution of **18** (5.82 g, 16.10 mmol) and NaOMe (250 mg, 4.63 mmol) in anhydrous methanol (250 mL) at room temperature for 2 h. The stream of ammonia was then reduced to a slight current, while the solution was heated to 60 °C. The reaction was monitored by TLC (silica gel/$CHCl_3$, **3**: R_f = 0) and terminated after most of the naphthalocarbonitrile **18** (R_f = 0.68) had reacted. On cooling, the benzo[*f*]-isoindolinediimine **3** precipitated overnight at ca. −20 °C. The crude product was suction filtered, washed with ice-cold MeOH, and dried. To remove unchanged naphthalocarbonitrile, the product was column chromatographed on silica gel with $CHCl_3$. The polarity of the eluent was gradually increased by addition of methanol, in order to elute the isoindolinediimine **3**. After evaporation of the solvents, the product was recrystallized from a mixture of $CHCl_3$ and *n*-hexane. Yield 4.28 g (70%) of **3** as a yellow powder, m.p.: > 130 °C (dec.). − IR (KBr): $\tilde{\nu}$ = ca. 3200 (br) cm^{-1} w, 2959 vs, 2930 vs, 2872 s, 1661 s, 1636 vs, 1616 vs, 1541 vs, 1460 s, 1398 s, 1377 s, 1327 s, 1275 s, 1242 m, 1202 w, 1151 s, 1096 w, 1038 w, 910 w, 847 w, 771 vw, 725 vw, 663 vw. − ^{1}H NMR ([D$_6$]DMSO): δ = 0.86, 0.94 [2 t, ^3J = 7.0 (7.4) Hz, 3H (3 H), ζ,δ′-CH$_3$], 1.31−1.39 (m, 4 H, γ,δ-CH$_2$), 1.39 (s, 9 H, *t*Bu), 1.45−1.67 (m, 4 H, ε,γ′-CH$_2$), 1.79−1.88 (m, 1 H, β-CH), 4.12 (d, ^3J = 4.9 Hz, 2 H, α-CH$_2$), 7.16 (d, ^4J = 1.4 Hz, 1 H, 5-H), 7.48 [s (br), 1 H, 6′-H], 8.25 (s, 1 H, 2′-H), 8.54 (s, 1 H, 2-H). − ^{13}C NMR ([D$_6$]DMSO): δ = 11.4 (CH$_3$-δ′), 14.3 (CH$_3$-ζ), 22.8 (CH$_2$-ε), 23.9 (CH$_2$-γ′), 28.9, 30.4 (CH$_2$-γ,δ), 31.2 (*t*BuCH$_3$), 35.5 (CMe$_3$), 70.5 (CH$_2$-α), 106.9 (C-5), 116.2 (C-6′), 117.1 (C-2), 122.0 (C-2′), 124.4 (C-1), 131.3, 133.4 (C-3,3′), 135.3 (C-1′), 152.5 (C-5′), 156.0 (C-6), 167.2, 172.2, 172.2, 172.4 (C-4,4′), the CH-β signal is presumably obscured by the solvent peak at δ = 39.5. − MS (EI): *m*/*z* (%) = 380.1 (12) [(M + H)$^+$], 362.3 (5) [M$^+$ − NH$_3$], 267.9 (100) [(M + H)$^+$ − C_8H_{16}], 252.9 (46), 250.1 (57) [M$^+$ − NH$_3$ − C_8H_{16}], 235.0 (25) [M$^+$ − NH$_3$ − C_8H_{16} − CH$_3$], 210 (7), 152.9 (6), 71.0 (37) [$C_5H_{11}^+$], 57.0 (48) [$C_4H_9^+$], 44 (28), 42 (22). − $C_{24}H_{33}N_3O$ (379.55): calcd. C 75.95, H 8.76, N 11.07; found C 73.73, H 8.59, N 10.71.

[3′,5′-Bis(2-ethylhexyloxy)]benzo[*f*]isoindolinediimine (4)

3,5-Dibenzoyloxy-α,α,α′,α′-tetrabromo-*o*-xylene (19): 3,5-Dibenzoyloxy-*o*-xylene (10.0 g, 29.00 mmol) was dissolved in dry CCl_4 (150 mL). NBS (31.0 g, 0.174 mol) and AIBN (1.5 g) were added and the mixture was refluxed for 4 d under irradiation (200-W daylight bulb). The warm solution was suction-filtered and washed with warm CCl_4. After removal of traces of bromine with $NaHSO_3$ and drying with Na_2SO_4, the solvent was removed in vacuo. The crude brown oil was column-chromatographed (SiO_2/toluene/ethyl acetate = 4:1). The first fraction (R_f = 0.7) was collected. It contained **19** as the main compound together with a small amount of the tribromo product **20**. Separation of the products was not necessary. Yield 14.5 g (%) of **19**/**20** as white powder, m.p. 112−114 °C. − IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1} vw, 1589 vs, 1556 s, 1501 m, 1462 s, 1421 s, 1367 w, 1259 vs, 1186 s, 1113 m, 1018 w, 972 w, 943 w, 843 m, 804 w, 744 vw, 723 vw, 665 w. − ^{1}H NMR ([D$_6$]acetone): δ = 4.94 [s, 4-CH$_2$Br (**20**)], 7.58−7.70 (m, γ,γ′-H), 7.71−7.81 (m, δ,δ′,1-H), 8.17−8.23 (m, β,β′-H), 8.41−8.47 (m, 4,4′-CHBr$_2$, 2′-H). − ^{13}C NMR ([D$_6$]acetone): δ = 119.0−119.2 [C-3 (**20**)], 119.6 (C-1), 122.2−122.3 (C-3), 123.0 (C-2′), 129.7−129.7 (C-γ,γ′), 130.9 (C-β,β′), 131.5−131.6 (C-α,α′), 135.0−135.0 (C-δ,δ′), 138.8−138.8 (C-3′), 151.0; 152.3−152.3; 153.0; 154.5 (C-1′,2), 164.3−164.8 (COOR). − MS (FD): *m*/*z*: 662.3 [M$^+$ (^{81}Br$_2$)], 582.0 [M$^+$ (**20**,^{81}Br$_1$)], 556.7 [M$^+$ (^{81}Br$_2$) − C_6H_5CO], 476.8 [M$^+$ (**20**,^{81}Br$_1$) − C_6H_5CO].

5,7-Dibenzoyloxynaphthalene-2,3-dicarbonitrile (21): The mixture of **19**/**20** (8.0 g), fumaronitrile (1.4 g, 0.018 mol) and NaI (12.6 g, 84.00 mmol) were stirred in dry DMF (100 mL) at 70 °C for 4 d. After cooling, the reaction mixture was poured into H_2O (250 mL) containing $NaHSO_3$ (5 g). The precipitate was filtered and washed with H_2O. The crude brown product was then purified by removal of polar impurities with acetone and recrystallization from THF/hexane. Yield 1.8 g (36%) of **21** as a white powder, m.p. 274−275 °C. − IR (KBr): $\tilde{\nu}$ = 3441 cm^{-1} s, 2363 vs, 2338 vs, 1742 s, 1718 m, 1653 s, 1624 w, 1558 m, 1506 m, 1456 w, 1244 s, 1177 w, 1142 w, 1119 w, 1055w, 667 w. − ^{1}H NMR ($CDCl_3$): δ = 7.51−7.64 (2 m, 4 H, γ,γ′-H), 7.66−7.78 (2 tt, $^3J \approx 7$ Hz, $^4J \approx 1.5$ Hz, 2 H, δ,δ′-H), 7.73 (d, ^4J = 2.2 Hz, 1 H, 5-H), 7.85−7.86 [d (br), $^4J \approx 2.2$ Hz, 1 H, 6′-H], 8.20−8.31 (2 m, 4 H, β,β′-H), 8.37 (s, 1 H, 2′-H), 8.48 (s, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 110.4; 111.8 (C-3,3′),

115.3 (C-4,4′), 117.4 (C-6′), 119.3 (C-5), 125.3 (C-1), 127.8; 128.3 (C-α,α′), 128.8; 129.1 (C-γ,γ′), 130.0 (C-2), 130.4; 130.5 (C-β,β′), 134.2 (C-1′), 134.4; 134.8 (C-δ,δ′), 135.5 (C-2′), 147.8 (C-6), 152.1 (C-5′), 164.1; 164.2 (COOR). − MS (FD): *m*/*z*: 417.6 [M^+], 312.7 [$M^+ - C_6H_5CO$]. − $C_{26}H_{14}N_2O_4$ (418.41): calcd. C 74.62, H 3.37, N 6.70; found C 72.20, H 3.55, N 6.47.

5,7-Dihydroxynaphthalene-2,3-dicarbonitrile (22): Compound **21** (5.5 g, 13.00 mmol) was added to a solution of NaOH (5.6 g, 0.140 mol) in MeOH (70 mL) and the mixture was stirred at room temp. for 30 min. The brown solution was acidified with half-conc. HCl and the precipitate was suction-filtered and washed with H_2O until the filtrate was neutral. The crude product was recrystallized from acetone. Yield 2.5 g (92%) of **22** as a yellow-white powder, m.p. > 300 °C. − IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} vs, 2912 m, 2363 m, 2336 w, 2232 s, 1616 s, 1560 vw, 1472 m, 1398 m, 1369 vs, 1315 vw, 1286 w, 1217 w, 1175 w, 1121 w, 1030 vw, 988 vw, 906 m. − ^{1}H NMR ([D$_6$]DMSO): δ = 6.78 (d, ^4J = 2.0 Hz, 1 H, 5-H), 6.82 (d, ^4J = 1.7 Hz, 1 H, 6′-H), 8.44 (s, 1 H, 2′-H), 8.51 (s, 1 H, 2-H). − ^{13}C NMR ([D$_6$]DMSO): δ = 101.9 (C-6′), 102.7 (C-5), 104.8 (C-3), 109.1 (C-3′), 116.7; 117.1 (CN-4,4′), 119.1 (C-1), 130.6 (C-2), 134.2 (C-2′), 135.6 (C-1′), 155.6 (C-6), 161.0 (C-5′). − MS (EI): *m*/*z* (%) = 209.9 (100) [M^+], 180.9 (15) [$M^+ - CO - H$], 152.8 (15) [$M^+ - 2\,CO - H$], 125.9 (15), 105.0 (10) [$C_6H_5CO^+$], 75.1 (5), 50.0 (5). − $C_{12}H_6N_2O_2$ (210.19): calcd. C 68.56, H 2.88, N 13.33; found C 62.69, H 3.37, N 11.88.

5,7-Bis(2-ethylhexyloxy)naphthalene-2,3-dicarbonitrile (23): Compound **22** (5 g, 23.82 mmol), 1-bromo-2-ethylhexane (19.3 g, 100 mmol), and dry K_2CO_3 (13.6 g, 100 mmol) were refluxed in dry DMF (30 mL) for 48 h. After cooling, the solution was poured into H_2O (500 mL) and extracted several times with diethyl ether. The combined organic layers were washed with H_2O until neutral and dried with $MgSO_4$. After removal of the solvent, the residual oil was column-chromatographed (SiO_2/$CHCl_3$, R_f = 0.6) and the product was recrystallized from ethanol. Yield 2.14 g (21%) of **23** as white crystals, m.p. 67 °C. − IR (KBr): $\tilde{\nu}$ = 3373 cm^{-1} s, 3327 vs, 3072 m, 3024 m, 2714 m, 2363 m, 2336 m, 2235 vs, 1632 vs, 1582 m, 1558 w, 1516 w, 1458 m, 1418 s, 1362 m, 1310 m, 1250 m, 1200 m, 1128 w, 922 w, 903 w, 843 m. − ^{1}H NMR ($CDCl_3$): δ = 0.83−1.03 (m, 12 H, ζ,δ′-CH_3), 1.25−1.4 (m, 8 H, γ,δ-CH_2), 1.4−1.65 (m, 8 H, ε,γ′-CH_2), 1.75−1.9 (m, 2 H, β-CH), 3.97; 4.01 (2 d, ^3J = 5.7 Hz (5.4 Hz), 4 H, α-CH_2), 6.67 (d, ^4J = 2.0 Hz, 1 H, 5-H), 6.73 (d, ^4J = 1.9 Hz, 1 H, 6′-H), 8.04 (s, 1 H, 2′-H), 8.53 (s, 1 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 11.0; 11.1 (δ′-CH_3), 14.0 (ζ-CH_3), 22.9; 22.9 (ε-CH_2), 23.8; 24.0 (γ′-CH_2), 29.0; 29.0 (δ-CH_2), 30.4; 30.6 (γ-CH_2), 39.2; 39.2 (β-CH), 71.0; 71.3 (α-CH_2), 98.9 (C-6′), 102.5 (C-5), 105.8 (C-3), 111.1 (C-3′), 116.1; 116.7 (4,4′-CN), 121.7 (C-1), 130.4 (C-2), 133.6 (C-2′), 135.7 (C-1′), 156.2 (C-6), 162.2 (C-5′). − MS (EI): *m*/*z* (%) = 434.3 (8) [M^+], 322.1 (8) [$M^+ - C_8H_{16}$], 223.0 (5), 210.0 (100) [$M^+ - 2\,C_8H_{16}$], 163.8 (4), 148.9 (6), 112.1 (15), 83.0 (10), 70.9 (97) [$C_5H_{11}^+$], 57.0 (90) [$C_4H_9^+$]. − $C_{28}H_{38}O_2N_2$ (434.62): calcd. C 77.37, H 8.82, N 6.45; found C 77.21, H 8.50, N 6.39.

[3′,5′-Bis(2-ethylhexyloxy)]benzo[*f*]isoindolinediimine (4): Ammonia was bubbled vigorously through a solution of **23** (2.0 g, 4.61 mmol) and NaOMe (200 mg, 3.70 mmol) in anhydrous methanol (200 mL) at room temperature for 1 h. The stream of ammonia was then reduced to a slight current, while the solution was heated to 50 °C. The reaction was monitored by TLC (silica gel/$CHCl_3$, **4**: R_f = 0) and terminated after most of the naphthalocarbonitrile **23** (R_f = 0.6) had reacted. After concentration in vacuo, the product was column-chromatographed on silica gel with $CHCl_3$ to remove unchanged naphthalocarbonitrile. The polarity of the eluent was gradually increased by addition of methanol, in order to elute the isoindolinediimine **4**. The solvents were removed to yield 1.8 g (87%) of **4** as yellow powder, m.p. 125−126 °C. − IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} m, 2928 m, 2858 m, 1616 vs, 1541 s, 1462 m, 1429 w, 1385 s, 1325 m, 1269 m, 1223 w, 1171 vs, 1036 m, 827 m, 762 m. − ^{1}H NMR ([D$_6$]DMSO): δ = 0.87−0.92 (m, 12 H, ζ,δ′-CH_3), 1.31−1.47 (m, 16 H, γ,δ,ε,γ′-CH_2), 1.72; 1.82 [2 t, ^3J = 5.1 Hz (4.9 Hz), 2 H, β-CH], 3.99; 4.06 [2 d, ^3J = 5.2 Hz (4.9 Hz), 4 H, α-CH_2], 7.01 [s (br), 1 H, 5-H], 7.16 (s, 1 H, 6′-H), 8.14 (s, 1 H, 2′-H), 8.48 (s, 1 H, 2-H). − ^{13}C NMR ([D$_6$]DMSO): δ = 10.8 (δ′-CH_3), 13.8 (ζ-CH_3), 22.4 (ε-CH_2), 23.3; 23.4 (γ′-CH_2), 28.4 (δ-CH_2), 29.92(γ-CH_2), 38.6 (β-CH), 70.3 (α-CH_2), 100.0 (C-6′), 100.8 (C-5), 115.2 (C-2), 119.7 (C-1), 121.2 (C-2′), 129.8 (C-3), 134.5 (C-3′), 136.1 (C-1′), 156.7 (C-6), 159.2 (C-5′), 171.1−171.3 (C-4,4′). − MS (FD): *m*/*z*: 450.9 [M^+]. − $C_{28}H_{41}N_3O_2$ (451.65): calcd. C 74.45, H 9.16, N 9.31; found C 72.54, H 8.21, N 8.09.

Chloro(naphthalocyaninato)indium(III) Complexes

Chloro(2,4-octa-*tert*-butyl-2,3-naphthalocyaninato)indium(III) (6a): A mixture of indium(III) chloride (180 mg, 0.82 mmol), isoindoline **2** (1.0 g, 3.26 mmol), and DBU (0.5 mL) was stirred in anhydrous quinoline (15 mL) for 20 h at 160 °C. The solvent was removed in vacuo and the residue was column-chromatographed (SiO_2/$CHCl_3$, R_f > 0). The green-brown fraction was eluted and the solvent was evaporated. The crude compound was recrystallized from a mixture of CH_2Cl_2/MeOH (v/v, 1:2) by slowly evaporating the more volatile dichloromethane in a rotary evaporator at 40−60 °C under slightly reduced pressure. To complete crystallization, the mixture was kept in a refrigerator overnight. The complex **6a** was collected by filtration, washed twice with methanol, and vacuum-dried at 50 °C for 6 h. Yield 150 mg (14%) of **6a** as a dark green powder. − IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} m, 2874 m, 1616 m, 1464 m, 1425 m, 1362 vs, 1331 m, 1261 s, 1225 m, 1167 m, 1119 m, 1061 s, 1032 vs, 972 m, 822 m, 806 m. − ^{1}H NMR ($CDCl_3$): δ = 1.63 (s, 36 H, 5′-*t*Bu), 2.10 (s, 36 H, 6-*t*Bu), 8.03 [s (br), 4 H, 5-H], 8.36−8.38 (m, 4 H, 6′-H), 9.84−9.88 (m, 4 H, 2′-H), 10.52−10.63 (m, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 31.3 (5′-*t*BuCH_3), 32.5−32.7 (6-*t*BuCH_3), 35.4−35.4 (6-CMe_3), 37.0−37.1 (5′-CMe_3), 122.0 (C-5), 124.2−124.9 (C-6′,2,2′), 130.4−130.6 (C-1), 132.6−132.9 (C-3,3′), 136.3−136.4 (C-1′), 147.8−147.9 (C-6), 149.2−149.2 (C-5′), 153.1−154.2 (C-4,4′). − MS (FD): *m*/*z*: 1310.2 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 812.5 nm, 772.5 (sh), 722.0, 688.7 (sh), 517.0 (sh), 468.5 (sh), 435.5 (sh), 367.5, 343.0. − $C_{80}H_{88}ClInN_8$ (1311.90): calcd. C 73.25, H 6.77, N 8.55; found C 72.99, H 5.74, N 8.57.

Chloro[3,(4)-tetra-*tert*-butyl-2,(5)-tetrakis(2-ethylhexyloxy)-2,3-naphthalocyaninato]indium(III) (7a): A mixture of indium(III) chloride (146 mg, 0.66 mmol), isoindoline **3** (1.0 g, 2.64 mmol), anhydrous quinoline (9 mL), and DBU (1.0 mL) was stirred at 180 °C for 16 h. After cooling, the mixture was stirred into methanol (400 mL). The precipitate was filtered, washed with methanol, and chromatographed (silica gel/$CHCl_3$; $R_f \geq 0$), in order to remove the greater proportion of polar impurities. The first band (orange-brown) was collected, and the solvent evaporated. The crude compound was recrystallized as above. The complex **7a** was collected by filtration, washed twice with methanol, and vacuum-dried at 70 °C for 2 h. Yield 643 mg (61%) of **7a** as dark brown powder. − IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1} vw, 2956 vs, 2928 s, 2870 m, 2859 m, 1626 w, 1616 w, 1583 vw, 1496 w, 1464 w, 1408 w, 1368 vs, 1357 vs, 1330 m, 1276 m, 1241 m, 1218 w, 1124 w, 1110 s, 1076 vs, 1034 m, 905 w, 875 vw, 842 vw, 740 w, 728 w, 700 vw, 661 vw, 539 vw, 440 vw. − ^{1}H NMR ($CDCl_3$): δ = 0.43−0.50, 0.99−1.06, 1.15−1.28 (3 m, 24 H, δ′,ζ-CH_3), ca. 1.5−2.0 (m, 32 H, γ,γ′,δ, ε-CH_2), 1.64−1.65

(m, 36 H, *t*Bu), 2.24−2.34 (m, 4 H, β-CH), 4.25−4.40 (m, 8 H, α-CH_2), 7.21−7.29 (m, 4 H, 5-H), 7.95−8.08 (m, 4 H, 6′-H), 9.64−9.84 (m, 4 H, 2′-H), 10.00−10.31 (m, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 11.1−11.6 (CH_3-δ′), 14.2−14.4 (CH_3-ζ), 23.1−23.3 (CH_2-ε), 24.4−24.7 (CH_2-γ′), 29.2−29.5, 31.0−31.2 (CH_2-γ,δ), 31.4 (*t*BuCH_3), 35.6−35.6 (CMe_3), 39.6−39.8 (CH-β), 70.8−71.4 (CH_2-α), 104.7−105.0 (C-5), 117.2−117.3 (C-6′), 117.7−117.9 (C-2), 122.5−122.9 (C-2′), 125.1−125.3 (C-1), 132.9−133.1, 133.3−133.4 (C-3,3′), 135.0−135.1 (C-1′), 150.5−150.71 (C-5′), 153.2−154.2 (C-4,4′), 156.4−156.6 (C-6). − MS (FD): *m*/*z*: 1600.2 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 823.0 nm, 781.4 (sh), 730.0, 694.3 (sh), 667.6 (sh), 526.9 (sh), 499.0 (sh), 453.5 (sh), 349.1. − $C_{96}H_{120}ClInN_8O_4$ (1600.33): calcd. C 72.05, H 7.56, N 7.00; found C 72.41, H 7.61, N 6.69.

Chloro[2,4-octakis(2-ethylhexyloxy)-2,3-naphthalocyaninato]-indium(III) (8a): A mixture of indium(III) chloride (102 mg, 0.46 mmol), isoindoline **4** (830 mg, 1.84 mmol), and DBU (0.5 mL) was stirred in anhydrous quinoline (10 mL) at 160 °C for 15 h. The solvent was removed in vacuo and the residue was column-chromatographed (SiO_2/$CHCl_3$, $R_f > 0$). The brown fraction was eluted and the solvent was evaporated. The crude compound was recrystallized as above. The complex **8a** was collected by filtration, washed twice with methanol, and vacuum-dried at 50 °C for 6 h. Yield 170 mg (20%) of **8a** as dark brown powder. − IR (KBr): $\tilde{\nu}$ = 3425 cm^{-1} s, 2974 m, 2912 m, 2363 vw, 2334 vw, 1672 m, 1616 s, 1448 s, 1369 m, 1317 vs, 1080 s, 1022 w, 982 w, 881 w, 814 w, 773 vw, 744 w. − ^{1}H NMR ($CDCl_3$): δ = 0.9−1.3 (2m, 48 H, δ′,ζ-CH_3), 1.3−2.1 (m, 64 H, γ,γ′,δ,ε-CH_2), 2.1−2.4 (m, 8 H, β-CH), 3.6−4.4 (m, 16 H, α-CH_2), 6.1−6.8 (m, 4 H, 5-H), 6.8−7.2 (m, 4 H, 6′-H), 8.6−9.4 (m, 4 H, 2′-H), 9.5−10.1 (m, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 11.3−11.4 (δ′-CH_3), 14.2−14.4 (ζ-CH_3), 23.2 (ε-CH_2), 23.9−24.6 (γ′-CH_2), 29.1−29.3 (δ-CH_2), 30.6−30.7 (γ-CH_2), 39.1−39.42 (β-CH), 70.8−71.3 (α-CH_2), 99.5−99.9 (C-5,6′), 117.3−117.8 (C-2), 120.3−121.1 (C-1), 122.1−122.8 (C-2′), 131.4−131.6 (C-3), 135.3−136.1 (C-1′,3′), 152.2−153.6 (C-4,4′), 157.0−157.7 (C-6), 158.7−159.2 (C-5′). − MS (FD): *m*/*z*: 1888.2 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 825.5 nm, 786.2 (sh), 731.5, 502.5 (sh), 385.0 (sh), 350.0. − $C_{112}H_{152}ClInN_8O_8$ (1888.75): calcd. C 71.22, H 8.11, N 5.93; found C 71.24, H 8.28, N 6.03.

Aryl(naphthalocyaninato)indium(III) Complexes. − General Procedure: The Grignard compounds R′MgBr [R′ = *p*-(trifluoromethyl)-phenyl (**b**), pentafluorophenyl (**c**)] were prepared by stirring a mixture of the corresponding substituted bromobenzene [1.01 g (**b**), 1.10 g (**c**); 1.5 mmol] and Mg turnings (150 mg, 6.25 mmol), previously activated by means of an ultrasonic bath, in freshly dried THF (5 mL) at room temperature. After 5 min, the solution was transferred into a syringe and immediately added dropwise to the chloro(naphthalocyaninato) indium(III) complex in THF through a septum. The reaction was monitored by TLC (SiO_2/toluene) and stopped after all the chloro compound had reacted (typically 15 min). The solution was poured onto ice and extracted with several portions of ether. The organic layers were washed with water and dried. After evaporation of the solvent, the residue was column-chromatographed (SiO_2/toluene) with strict exclusion of light. The crude product was recrystallized from CH_2Cl_2/methanol as described above. The complexes were collected by filtration, washed twice with methanol, and vacuum-dried at 50 °C for 4 h.

[3,(4)-Tetra-*tert*-butyl-2,3-naphthalocyaninato][*p*-(trifluoromethyl)-phenyl]indium(III) (5b): Preparation see General Procedure. Batch: 230 mg (0.21 mmol) of **5a**, chromatography (SiO_2/toluene): R_f = 0.89, yield 129 mg (51%) of **5b** as green powder. − IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1} vw, 2961 vs, 2930 s, 2363 vw, 2108 m, 1744 m, 1651 m, 1643 m, 1564 vw, 1466 w, 1379 w, 1313 m, 1300 m, 1177 w, 1099 vs, 1020 vs, 962 vw, 854 m, 804 vs, 702 vw. − ^{1}H NMR ($CDCl_3$): δ = 1.84−1.87 (m, 36 H, *t*Bu), 3.59 (d, ^3J = 8.02 Hz, 2 H, H-b,b′), 5.71 (d, ^3J = 8.01 Hz, 2 H, H-c,c′), 8.14 (m, 4 H, 5-H), 8.39−8.44 (m, 4 H, 6-H), 8.50−8.60 (m, 4 H, H-6′), 9.05−9.30 (m, 8 H, H-2,2′). − ^{13}C NMR ($CDCl_3$): δ = 31.6 (*t*BuCH_3), 35.5 (CMe_3), 122.0 (q, $^3J_{CF}$ = 3.5 Hz, C-c,c′), 122.4 (C-1), 122.9 (C-1′), 125.2 (C-2′), 126.4 (C-2), 130.0 (C-6′), 132.3 (C-5), 133.4−134.1 (C-6,3,3′), 150.1 (C-5′), 152.4−152.4 (C-4,4′). − ^{19}F NMR ($CDCl_3$): δ = −64.46 (CF_3-d). − MS (FD): *m*/*z*: 1195.3 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 804.5 nm, 763.5 (sh), 716.0, 447.0 (sh), 420.0 (sh), 363.0, 349.5. − $C_{71}H_{60}F_3InN_8$ (1197.12): calcd. C 71.21, H 5.05, N 9.36; found C 70.28, H 4.98, N 9.32.

(Pentafluorophenyl)[3,(4)-tetra-*tert*-butyl-2,3-naphthalocyaninato]-indium(III) (5c): Preparation see General Procedure. Batch: 125 mg (0.12 mmol) of **5a**, chromatography (SiO_2/toluene): R_f = 0.85, yield 60 mg (43%) of **5c** as green powder. − IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1} m, 2874 m, 2804 m, 2363 vs, 2336 s, 1844 w, 1772 w, 1734 w, 1558 w, 1539 w, 1497 w, 1437 w, 1366 m, 1238 w, 1138 w, 1022 w, 982 w, 953 w, 685 w, 667 w. − ^{1}H NMR ($CDCl_3$): δ = 1.90−1.94 (m, 36 H, *t*Bu), 8.18−8.24 (m, 4 H, 5-H), 8.44−8.55 (m, 4 H, 6-H), 8.63−8.66 (m, 4 H, 6′-H), 9.06−9.30 (m, 8 H, 2,2′-H). − ^{13}C NMR ($CDCl_3$): δ = 31.6−31.9 (*t*BuCH_3), 35.6−35.6 (CMe_3), 122.6 (C-1), 123.1 (C-1′), 125.2 (C-2′), 126.4 (C-2), 130.1 (C-6′), 132.3−132.3 (C-5), 133.3−133.5 (C-3), 133.8−134.0 (C-3′), 134.2 (C-6), 150.2 (C-5′), 152.0 (C-4,4′). − ^{19}F NMR ($CDCl_3$): δ = −122.98 to −123.05 (F-b,b′), −153.98 to −154.15 (F-d), −161.42 to −161.57 (F-c,c′). − MS (FD): *m*/*z*: 1218.0 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 806.0 nm, 764.5 (sh), 717.0, 449.0 (sh), 420.0 (sh), 365.0, 342.5. − $C_{70}H_{56}F_5InN_8$ (1219.08): calcd. C 68.95, H 4.63, N 9.19; found C 68.95, H 4.65, N 8.96.

(2,4-Octa-*tert*-butyl-2,3-naphthalocyaninato)[*p*-(trifluoromethyl)-phenyl]indium(III) (6b): Preparation see General Procedure. Batch: 100 mg (0.08 mmol) of **6a**, chromatography (SiO_2/toluene): R_f = 0.89, yield 60 mg (56%) of **6b** as green-brown powder. − IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1} m, 2876 m, 2795 m, 2361 vs, 2336 s, 1558 w, 1539 w, 1394 m, 1366 s, 1246 m, 1229 m, 1178 m, 1124 m, 1042 m, 1022 m, 972 m. − ^{1}H NMR ($CDCl_3$): δ = 1.63−1.64 (m, 36 H, 5′-*t*Bu), 2.10−2.13 (m, 36 H, 6-*t*Bu), 4.67−4.78 (m, 2 H, H-b,b′), 6.34−6.37 (m, 2 H, H-c,c′), 8.02 (s, 4 H, 5-H), 8.41−8.43 (m, 4 H, 6′-H), 9.87−9.96 (m, 4 H, 2′-H), 10.57−10.61 (m, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 31.3 (5′-*t*BuCH_3), 32.5 (6-*t*BuCH_3), 35.4 (6-CMe_3), 37.0 (5′-CMe_3), 121.8−121.8 (C-5), 124.0−124.5 (C-6′,2,2′), 130.4 (C-1), 132.9−133.1 (C-3,3′), 134.8 (C-a), 136.3 (C-1′), 147.8 (C-6), 149.0 (C-5′), 154.2−154.4 (C-4,4′). − ^{19}F NMR ($CDCl_3$): δ = −64.03 (CF_3-d). − MS (FD): *m*/*z*: 1420.5 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 809.0 nm, 769.5 (sh), 720.5, 687.3 (sh), 450.0 (sh), 365.7 (sh), 351.5. − $C_{87}H_{92}F_3InN_8$ (1420.64): calcd. C 73.49, H 6.53, N 7.89; found C 71.48, H 6.00, N 7.11.

(2,4-Octa-*tert*-butyl-2,3-naphthalocyaninato)(pentafluorophenyl)indium(III) (6c): Preparation see General Procedure. Batch: 100 mg (0.08 mmol) of **6a**, chromatography (SiO_2/toluene): R_f = 0.91, yield 53 mg (48%) of **6c** as green-brown powder. − IR (KBr): $\tilde{\nu}$ = 2972 cm^{-1} m, 2878 m, 2804 m, 2363 vs, 2336 s, 1393 m, 1367 s, 1321 m, 1273 m, 1225 m, 1165 m, 1092 m, 1070 m, 991 m, 953 m. − ^{1}H NMR ($CDCl_3$): δ = 1.62−1.64 (m, 36 H, 5′-*t*Bu), 2.12−2.14 (m, 36 H, 6-*t*Bu), 8.03 (s, 4 H, 5-H), 8.43 (s, 4 H, 6′-H), 9.93−10.00 (m, 4 H, 2′-H), 10.62−10.65 (m, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 31.3−31.3 (5′-*t*BuCH_3), 32.6−32.8 (6-*t*BuCH_3), 35.4−35.5 (6-CMe_3), 37.0−37.2 (5′-CMe_3), 121.9 (C-5), 124.1−124.7 (C-6′,2,2′), 130.5−130.6 (C-1), 132.8−133.2 (C-3,3′), 136.3−136.4 (C-1′), 147.8−147.9 (C-6), 149.0−149.1 (C-5′),

153.6−154.5 (C-4,4′). − ^{19}F NMR ($CDCl_3$): δ = −121.57 to −121.64 (F-b,b′), −153.35 (F-d), −160.86 to −161.01 (F-c,c′). − MS (FD): *m/z*: 1442.2 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 812.0 nm, 770.5 (sh), 720.5, 687.5 (sh), 663.0 (sh), 427.0 (sh), 367.5 (sh), 345.5. − $C_{86}H_{88}F_5InN_8$ (1442.61): calcd. C 71.54, H 6.15, N 7.77; found C 70.89, H 5.70, N 7.50.

[4,(3)-Tetra-*tert*-butyl-2,(5)-tetrakis(2-ethylhexyloxy)-2,3-naphthalocyaninato][*p*-(trifluoromethyl)phenyl]indium(III) (7b): Preparation see General Procedure. Batch: 166 mg (0.11 mmol) of **7a**, chromatography (SiO_2/toluene): R_f = 0.85, yield 59.3 mg (33%) of **7b** as brown powder. − IR (KBr): ṽ = 3055 cm^{-1} w, 2957 m, 2905 m, 2833 w, 2363 m, 2336 m, 1506 m, 1464 m, 1393 w, 1356 vs, 1317 w, 1271 m, 1207 w, 1138 w, 1101 s, 1022 m, 995 w, 959 w, 903 m, 812 w. − ^{1}H NMR ($CDCl_3$): δ = 0.8−0.95; 1.0−1.1; 1.14−1.28 (3 m, 24 H, δ′,ζ-CH_3), ca. 1.5−2.0 (m, 32 H, γ,γ′,δ,ε-CH_2), 1.66−1.67 (m, 36 H, *t*Bu), 2.25−2.35 (m, 4 H, β-CH), ca. 4.1−4.45 (m, 8 H, α-CH_2), 4.5−4.7 (m, 2 H, H-b,b′), 6.2−6.35 (m, 2 H, H-c,c′), 7.14−7.28 (m, 4 H, H-5), 7.97−8.10 (m, 4 H, H-6′), 9.6−9.9 (m, 4 H, H-2′), 10.24−10.32 (m, 4 H, H-2). − ^{13}C NMR ($CDCl_3$): δ = 11.1−11.6 (δ′-CH_3), 14.2−14.3 (ζ-CH_3), 23.1−23.3 (ε-CH_2), 24.4−24.6 (γ′-CH_2), 29.3−29.7; 31.0−31.2 (γ,δ-CH_2), 31.4 (*t*BuCH_3), 35.6−35.6 (CMe_3), 39.5−39.7 (β-CH), 70.9−71.4 (α-CH_2), 104.9 (C-5), 117.3 (C-6′), 117.6−117.7 (C-2), 122.3−122.5 (C-c,c′), 122.7 (C-2′), 125.1−125.3 (C-1), 133.0−133.4 (C-3,3′), 134.6−134.7 (C-a), 135.0−135.1 (C-1′), 150.7−150.8 (C-5′), 154.0−154.4 (C-4,4′), 156.4−156.6 (C-6). − ^{19}F NMR ($CDCl_3$): δ = −64.08 (CF_3-d). − MS (FD): *m/z*: 1710.4 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 820.0 nm, 780.0 (sh), 728.5, 490.0 (sh), 453.0 (sh), 360.0. − $C_{103}H_{124}F_3InN_8O_4$ (1709.98): calcd. C 72.35, H 7.31, N 6.55; found C 70.70, H 7.00, N 6.03.

(Pentafluorophenyl)[4,(3)-tetra-*tert*-butyl-2,(5)-tetrakis(2-ethylhexyloxy)-2,3-naphthalocyaninato]indium(III) (7c): Preparation see General Procedure. Batch: 135.5 mg (0.09 mmol) of **7a**, chromatography (SiO_2/toluene): R_f = 0.88, yield 110 mg (75%) of **7c** as brown powder. − IR (KBr): ṽ = 3354 cm^{-1} m, 3126 m, 2916 m, 2847 m, 1711 w, 1680 m, 1641 m, 1564 w, 1547 m, 1468 m, 1385 m, 1367 s, 1319 vs, 1238 m, 1082 m, 1022 w, 1003 w, 962 w, 814 m, 744 w. − ^{1}H NMR ($CDCl_3$): δ = 0.8−0.95; 1.0−1.1; 1.15−1.3 (3 m, 24 H, δ′,ζ-CH_3), ca. 1.5−2.1 (m, 32 H, γ,γ′,δ,ε-CH_2), ca. 1.6−1.8 (m, 36 H, *t*Bu), ca. 2.2−2.4 (m, 4 H, β-CH), 4.25−4.5 (m, 8 H, α-CH_2), 7.24−7.27 (m, 4 H, H-5), 8.0−8.15 (m, 4 H, H-6′), 9.75−9.9 (m, 4 H, H-2′), 10.15−10.35 (m, 4 H, H-2). − ^{13}C NMR ($CDCl_3$): δ = 11.1−11.6 (δ′-CH_3), 14.2−14.4 (ζ-CH_3), 23.2 (ε-CH_2), 24.4−24.3 (γ′-CH_2), 29.5−29.7; 31.1 (γ,δ-CH_2), 31.4 (*t*BuCH_3), 35.6−35.6 (CMe_3), 39.4−39.82 (β-CH), 70.9−71.4 (α-CH_2), 104.9 (C-5), 117.3 (C-6′), 117.9 (C-2), 122.8 (C-2′), 125.3 (C-1), 133.2−133.3 (C-3,3′), 134.9−135.2 (C-1′), 150.8 (C-5′), 153.8−154.2 (C-4,4′), 156.6 (C-6). − ^{19}F NMR ($CDCl_3$): δ = −121.87 to −122.10 (F-b,b′), −153.64 to −153.72 (F-d), −161.00 to −161.14 (F-c,c′). − MS (FD): *m/z*: 1730.5 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 822.5 nm, 783.5 (sh), 729.5, 493.0 (sh), 454.0 (sh), 355.0. − $C_{102}H_{120}F_5InN_8O_4$ (1731.93): calcd. C 70.74, H 6.98, N 6.47; found C 70.78, H 6.24, N 6.38.

[2,4-Octakis(2-ethylhexyloxy)-2,3-naphthalocyaninato][*p*-(trifluoromethyl)phenyl]indium(III) (8b): Preparation see General Procedure. Batch: 199 mg (0.11 mmol) of **8a**, chromatography (SiO_2/toluene): R_f = 0.84, yield 151 mg (71%) of **8b** as dark brown powder. − IR (KBr): ṽ = 2957 cm^{-1} m, 2924 m, 2363 m, 2336 m, 1616 s, 1585 m, 1558 m, 1506 m, 1425 m, 1362 vs, 1269 m, 1204 m, 1153 m, 1094 m, 1030 m, 932 w, 903 w, 822 w, 737 w. − ^{1}H NMR ($CDCl_3$): δ = 0.95−1.3 (m, 48 H, δ′,ζ-CH_3), 1.35−2.05 (2 m, 64 H, γ,γ′,δ,ε-CH_2), 2.2−2.3 (m, 8 H, β-CH), 4.1−4.4 (m, 16 H, α-CH_2), 4.61 [s (br), 2 H, H-b,b′], 6.25 [s (br), 2 H, H-c,c′], 6.7−6.9 (m, 4 H, 5-H), 7.2−7.4 (m, 4 H, 6′-H), 9.5−9.7 (m, 4 H, 2′-H), 10.0−10.25 (m, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 10.8−11.4 (δ′-CH_3), 14.2−14.4 (ζ-CH_3), 23.0−23.2 (ε-CH_2), 24.0−24.5 (γ′-CH_2), 29.2−29.4 (δ-CH_2), 30.4−30.9 (γ-CH_2), 39.2−39.4 (β-CH), 70.8−71.6 (α-CH_2), 99.8−100.1 (C-5,6′), 117.6−117.9 (C-2), 120.7−121.0 (C-1), 122.2−122.8 (C-2′,c,c′), ca. 131.5−132.5 (C-3), 134.6 (C-a), 135.6−135.9 (C-1′,3′), ca. 152.5−154.5 (C-4,4′), ca. 157.0−158.0 (C-6), 158.9−159.2 (C-5′). − ^{19}F NMR ($CDCl_3$): δ = −64.1 (CF_3-d). − MS (FD): *m/z*: 1998.4 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 821.5 nm, 782.0 (sh), 728.5, 497.5 (sh), 449.0 (sh), 363.5. − $C_{119}H_{156}F_3InN_8O_8$ (1998.41): calcd. C 71.50, H 7.87, N 5.61; found C 68.75, H 7.54, N 5.30.

[2,4-Octakis(2-ethylhexyloxy)-2,3-naphthalocyaninato](pentafluorophenyl)indium(III) (8c): Preparation see General Procedure. Batch: 94 mg (0.05 mmol) of **8a**, chromatography (SiO_2/toluene) R_f = 0.86, yield 73 mg (72%) of **8c** as dark brown powder. − IR (KBr): ṽ = 2959 cm^{-1} m, 2916 m, 2361 s, 2336 m, 1616 s, 1587 m, 1558 m, 1506 m, 1425 m, 1385 m, 1325 m, 1261 s, 1221 w, 1159 m, 1090 s, 1030 s, 903 w, 804 m. − ^{1}H NMR ($CDCl_3$): δ = 0.9−1.3 (m, 48 H, δ′,ζ-CH_3), 1.35−2.05 (2 m, 64 H, γ,γ′,δ,ε-CH_2), 2.15−2.35 (m, 8 H, β-CH), 4.1−4.4 (m, 16 H, α-CH_2), 6.7−6.9 (m, 4 H, 5-H), 7.2−7.4 (m, 4 H, 6′-H), 9.5−9.7 (m, 4 H, 2′-H), 10.0−10.25 (m, 4 H, 2-H). − ^{13}C NMR ($CDCl_3$): δ = 10.5−11.5 (δ′-CH_3), 14.4−14.4 (ζ-CH_3), 22.5−23.5 (ε-CH_2), 23.9−24.0 (γ′-CH_2), 29.0−29.5 (δ-CH_2), 30.6−30.9 (γ-CH_2), 39.4−39.4 (β-CH), 70.8−72.0 (α-CH_2), 99.7−100.3 (C-5,6′), 117.9−118.2 (C-2), 121.0−121.2 (C-1), 122.7−122.8 (C-2′), 131.7 (C-3), ca. 135.0−136.5 (C-1′,3′), ca. 152.0−154.5 (C-4,4′), 157.8 (C-6), 159.3−159.4 (C-5′). − ^{19}F NMR ($CDCl_3$): δ = -121.93 to −122.04 (F-b,b′), −153.91 to −154.07 (F-d), −161.25 to −161.54 (F-c,c′). − MS (FD): *m/z:* 2019.7 [M^+]. − UV/Vis ($CHCl_3$): λ_{max} = 824.0 nm, 784.6 (sh), 730.0, 500.0 (sh), 452.5 (sh), 356.5. − $C_{118}H_{152}F_5InN_8O_8$ (2020.36): calcd. C 70.13, H 7.59, N 5.55; found C 68.83, H 7.80, N 5.25.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft ("Phthalocyanine und Naphthalocyanine des Indiums und Titans für Optical Limiting-Experimente", Ha 280/65-1) and the Fonds der Chemischen Industrie for financial support.

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Received January 26, 2001
[O01034]