Synthesis and Characterization of Soluble Axially Substituted Tetra-(*tert*-butyl)gallium(III)phthalocyanines

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The synthesis and characterization of the highly soluble tetra(*tert*-butyl)gallium(III) phthalocyanines ($(t\mathrm{Bu})_4$PcGaCl (**2**) and $(t\mathrm{Bu})_4$PcGa(*p*-TMP) (**3**) is described. They were characterized by IR, UV/Vis, MS, and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

Introduction

Phthalocyanines (Pcs) and their analogs have been intensively investigated for many technological applications due to their remarkable photophysical, optoelectronic, conductive properties, and biological activities, as well as their wide variety of architectural flexibility.[1−3] In recent years we have concentrated our efforts on studying the influence of different axial substituents on the nonlinear optical (NLO) properties, particularly on the optical limiting (OL) properties of soluble peripherally alkyl-substituted phthalocyaninato-and naphthalocyaninatoindium(III) complexes. We have synthesized, for example, a series of soluble axially substituted indium(III)phthalocyanines $(t\mathrm{Bu})_4$PcInX with X = Cl, Br, I, *p*-trifluoromethylphenyl (*p*-TMP), *m*-TMP, *p*-fluorophenyl, and pentafluorophenyl, amongst others.[4−6]

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 behavior.[5,7,8] Furthermore, soluble axially substituted indium naphthalocyanines have been prepared[9] that show a similar optical limiting behavior.[10]

Peripherally unsubstituted gallium phthalocyanines with an axial chloro, fluoro or hydroxy ligand (PcGaX, X = Cl, F, OH) were the first phthalocyanines to be investigated for their third order (χ^3) nonlinear behavior;[11] values of the order of 10^{-11} esu were found. The greatest disadvantage of peripherally unsubstituted phthalocyanines is their poor solubility in organic solvents. For this reason, we report here the synthesis of the highly soluble chlorogallium(III) 2,(3)-tetra(*tert*-butyl)phthalocyanine [$(t\mathrm{Bu})_4$PcGaCl] (**2**), and its reaction with R′MgBr (R′ = *p*-TMP) leading to the σ-bonded aryl(phthalocyaninato)gallium(III) complex $(t\mathrm{Bu})_4$PcGa(*p*-TMP) (**3**). The aryl substituent should introduce greater steric crowding than the chloro ligand and should reduce the tendency, which is common in Pc's, to form aggregates.[12]

Results and Discussion

The synthetic pathway to **2** and **3**, together with the numbering of the atoms of the macrocycles and the axial *p*-TMP ligand, is shown in Scheme 1. Compound **2** was obtained by the reaction of 4-*tert*-butylphthalonitrile with anhydrous $GaCl_3$ (molar ratio, 4:1.05) in doubly distilled, deoxygenated quinoline at 180 °C in the presence of catalytic amounts of the nonnucleophilic base 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU). Compound **3** was synthesized by the reaction of a freshly prepared 10-fold excess of *p*-TMP Grignard reagent with $(t\mathrm{Bu})_4$PcGaCl. Products **2** and **3** were further purified by column chromatography and recrystallization; they are highly soluble in common organic solvents.

The UV/Vis spectra of **2** and **3** in $CHCl_3$ are shown in Figure 1; it can clearly be seen that they are almost identical. The introduction of electron-donating *tert*-butyl groups in the periphery of the macrocycle of **2** leads to a red-shift of about 8 nm of the Q-band maximum with respect to the unsubstituted PcGaCl (Fluka product). The axial *p*-TMP ligand has little influence on the position of the Q-band maximum in comparison with compound **2**. The observed red-shift is only of the order of 1.5 nm. Similar results with $(t\mathrm{Bu})_4$PcInCl and $(t\mathrm{Bu})_4$PcIn(*p*-TMP) have been reported by us earlier.[4] The UV/Vis spectra of $(t\mathrm{Bu})_4$PcGaCl (**2**) and $(t\mathrm{Bu})_4$PcInCl are almost identical, with a Δλ value of 2−3 nm. $(t\mathrm{Bu})_4$PcIn(*p*-TMP), on the

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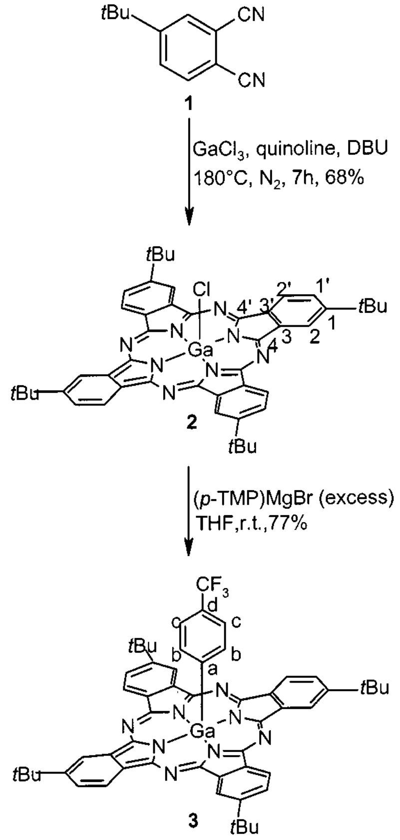

Scheme 1

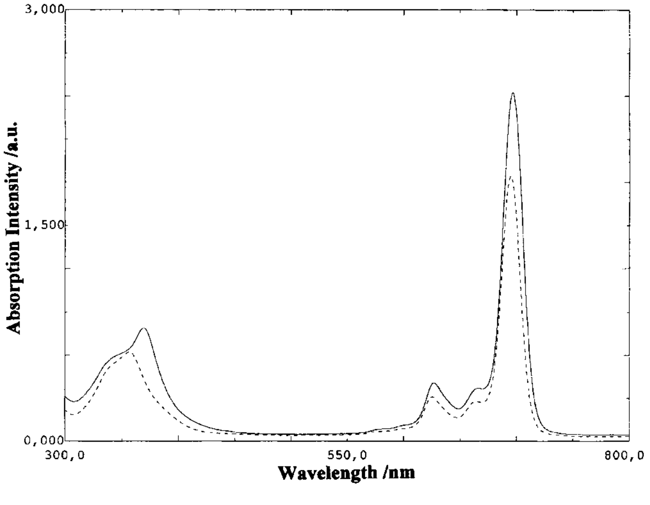

Figure 1. The UV/Vis spectra of $(tBu)_4PcGaCl$ (dashed line) and $(tBu)_4PcGa(p\text{-}TMP)$ (solid line) in $CHCl_3$.

other hand, shows a bathochromically shifted Q-band (1.5 nm) relative to the gallium compound **3**.

The greater solubility of compound **3** than of the chloro analog **2** shows that the usual tendency of phthalocyanines to form aggregates can be effectively suppressed by axial substitution.[4] Similar to the aryl axially substituted indium(III)phthalocyanines,[5] the shape of the UV/Vis spectrum of **3** is almost independent of the concentration of the solution and shows no aggregation. However, for the chlorogallium phthalocyanine **2**, a concentration-dependent increase of the absorption on the red side of the Q-band indicates a somewhat larger degree of aggregation. A comparison of the UV/Vis absorption spectra of thin film and dilute solutions of **2** and **3** in $CHCl_3$ shows that the absorption spectra of thin films of **2** and **3** are broader. Upon comparing the thin film and dilute solution UV/Vis spectra of **2**, it is observed that the position of the Q-band maximum is shifted slightly by about 2.5 nm towards longer wavelength. In the case of **3**, the same comparison shows that the position of the Q-band maximum is almost unchanged, which is consistent with relatively weak aggregation of **3** in solution.

The field desorption (FD) mass spectrum of **2** shows a cluster of peaks centered at m/z (%) = 842.3 (100), assigned to the molecular peak, which is almost identical to the calculated intensity pattern for **2** [m/z (%) = 840.3 (90), 841.3 (50), 842.3 (100), 843.3 (52), 844.3 (33) and 845.3 (12)]. Likewise, the molecular peak of **3** at m/z (%) = 951.4 (100) is also detected in the FD mode. The mass spectrum of **3** measured in the FAB modes shows a peak at m/z = 958 which is assigned to an $[M^+ + Li]$ peak.

The IR spectrum of **2** is similar to that of $(tBu)_4PcInCl$.[4] The Ga−Cl stretching vibration is shifted from 431 cm^{-1} in unsubstituted PcGaCl[13] to 351 cm^{-1} in **2**, while the ν_{In-Cl} band in $(tBu)_4PcInCl$ appears at 336 cm^{-1}.[4] For **3**, some new absorption bands, which do not appear in the spectrum of $(tBu)_4PcGaCl$ (**2**), were observed (see Exp. Sect.).

The ^1H NMR spectra of **2** and **3** in $CDCl_3$ confirm the presence of the expected mixtures of structural isomers of tetrasubstituted phthalocyanines. The numbering of the atoms of the macrocycle and the axial *p*-TMP ligand is shown in Scheme 1. In **2** the aromatic signals appear as two broad multiplets [δ = 9.4−8.9 (8 H, H-2,2′) and δ = 8.4−8.2 (4 H, H-1)], the singlet of the *tert*-butyl group appears at δ = 1.9 (36 H) and is split because of the structural isomers; the signals are located almost in the same range as those of $(tBu)_4PcInCl$.[4,5] For compound **3**, the σ-bonded *p*-TMP ligand causes a slightly stronger deshielding of the aromatic protons, especially those closer to the heteroaromatic 18-π-electron system (H-2,2′), than does the chloro ligand in **2**. The proton signals of the *p*-TMP ligand are shifted upfield due to the diamagnetic ring-current of the phthalocyanine macrocycle. They appear at δ = 7.1 (d, ^3J = 8.9 Hz, 2 H, H-c,c′) and 6.8 (d, ^3J = 8.7 Hz, 2 H, H-b,b′), compared to δ = 7.5(H-c,c′) and 7.6 (H-b,b′) in pure *p*-trifluoromethylphenyl bromide (*p*-TMPBr). This is a smaller upfield shift than in $(tBu)_4PcIn(p\text{-}TMP)$ due to the different central metal atom.[4,5]

The ^{13}C NMR spectra of **2** and **3** are also similar to the ^{13}C NMR spectra of $(tBu)_4PcInCl$ and $(tBu)_4PcIn(p\text{-}TMP)$,[4] and show seven signals for the aromatic carbon atoms and two signals for the *tert*-butyl group. The aromatic signals are broadened due to the structural isomers, and the carbon signals of the *p*-TMP ligand are split on account of C−F coupling and are of very low intensity. However, additional signals can be observed at δ = 113.9, 127.5−127.8 and 133.3, and are assigned to C-d, C-c,c′ and C-a of the axial ligand, respectively.

The ^{19}F NMR spectrum of **3** provides evidence for the attachment of the *p*-TMP ligand at the gallium atom: only one narrow singlet at $\delta = -62.8$ was observed for the axial ligand, whereas the ^{19}F signal of pure α,α,α-trifluorotoluene appears at $\delta = -63.9$.[5] Similarly to **3**, the ^{19}F signal of (tBu)$_4$PcIn(*p*-TMP) appears at $\delta = -64.1$.[4,5] The difference in chemical shifts of the fluorine atoms in (tBu)$_4$PcIn(*p*-TMP) and (tBu)$_4$PcGa(*p*-TMP) **3** is due to the different electronic effects of indium(III) and gallium(III).

Experimental Section

General: The operations for synthesis prior to the termination reaction were carried out under purified dry nitrogen. Solvents were purified, dried and distilled under dry nitrogen. FT-IR: Perkin−Elmer Spectrum 1000. UV/Vis: Shimadzu UV-365. MS: Varian Mat 711(FD: temperature of the ion source 30 °C; FAB: temperature of the ion source 50 °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.

Chlorogallium(III) 2,(3)-Tetra(*tert*-butyl)phthalocyanine [(tBu)$_4$PcGaCl] (2): A mixture of anhydrous gallium(III) chloride (0.75 g, 4.26 mmol), 4-*tert*-butylphthalonitrile (**1**; 3 g, 16.3 mmol), quinoline (15 mL, doubly distilled over CaH_2), and DBU (1 mL) was stirred at 180 °C for 7 h. The solvent was then removed by distillation under reduced pressure, leaving a dark green residue, which was chromatographed on silica gel using a gradient of toluene and chloroform 100:0 to 0:100 in order to remove metal-free phthalocyanine and a large portion of polar impurities. The blackish green fraction ($R_f \geq 0$) was collected, the solvent evaporated, and the crude compound recrystallized from a mixture of CH_2Cl_2/MeOH (v/v 4:3) by slowly evaporating the more volatile dichloromethane in a rotary evaporator at 40−60 °C under slightly reduced pressure. To complete the crystallization, the mixture was kept in a refrigerator overnight. The complex was collected by filtration, washed twice with methanol and dried at 80 °C in vacuum for 10 h. Yield 2.35 g (68.5%) of **2** as a blackish green powder. FD-MS ($C_{48}H_{48}ClGaN_8$): calcd. 842.14; found 842.3(100). UV/Vis ($CHCl_3$): λ_{max} (nm) = 695, 664.5 (sh), 625, 356. FT-IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1} vw, 2958 s, 2866 m, 1734 w, 1682 w, 1615 m, 1507 m, 1483 m, 1406 m, 1394 m, 1364 m, 1334 vs, 1281 m, 1258 s, 1201 m, 1149 m, 1087 vs, 1052 m, 1024 w, 967 w, 929 s, 895 w, 831 m, 765 m, 750 s, 694 m, 670 m, 602 vw, 566 vw, 532 m, 444 vw, 350.5 w [ν(Ga-Cl)]. ^{1}H NMR ($CDCl_3$): δ = 1.9 (m, 36 H, tBu), 8.2−8.4 (m, 4 H, H-1), 8.9−9.4 (m, 8 H, H-2, -2′). ^{13}C NMR ($CDCl_3$): δ = 31.1−32.1 (tBuCH$_3$), 36.2 (CMe$_3$), 119.1−119.6 (C-2′), 122.6−122.9 (C-2), 128.5−128.6 (C-1), 133.7−133.9 (C-3), 135.9−136.2 (C-3′), 150.4−151.1 (C-4, -4′), 154.2−154.6 (C-1′). $C_{48}H_{48}ClGaN_8$ (842.1): calcd. C 68.46, H 5.74, N 13.31, Cl 4.21; found C 66.50, H 5.63, N 12.36, Cl 4.15.

***p*-(Trifluoromethyl)phenylgallium(III) 2,(3)-Tetra(*tert*-butyl)phthalocyanine [(tBu)$_4$PcGa(*p*-TMP)] (3):** A freshly prepared solution of R′MgBr (R′ = *p*-trifluoromethylphenyl) in THF (20 mL, 0.18 M R′MgBr) was added dropwise to a stirred solution of (tBu)$_4$PcGaCl (**2**; 300 mg, 0.356 mmol) in dry THF (25 mL). The reaction was monitored by TLC and stopped when all of the chloro complex **2** had been consumed. The deep green mixture was poured onto ice and then 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 rapidly subjected to column chromatography (silica gel/toluene). Light was strictly excluded during this step. Further purification of the complex was achieved by recrystallization from a mixture of CH_2Cl_2/MeOH (v/v 1:1) 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 was collected by filtration, washed twice with methanol and dried at 70 °C in vacuum for 6 h. Yield 260 mg (77%) of **3** as a green powder. FD-MS ($C_{52}H_{52}F_3GaN_8$): calcd. 951.14; found 951.4 (100). FAB-MS (*m/z*): 958 [M$^+$ + Li], 864, 857, 842, 823, 805 [(tBu)$_4$PcGa$^+$], 789, 749, 637, 539, 489, 481, 469, 385, 342, 281, 269, 253. UV/Vis ($CHCl_3$): λ_{max} (nm) = 696.5, 666 (sh), 626.5, 369.5. FT-IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} s, 2870 m, 1737 m, 1668 m, 1617 m, 1548 s,1516 vs, 1486 m, 1465 m, 1399 w, 1376 m, 1365 m, 1325 s (C−F), 1284 w, 1258 m, 1233 w, 1199 w, 1163 m (C−F), 1146 vw, 1123 ms, 1088 m, 1067 m, 1048 m, 1037 m, 1017 m, 929 w, 902 w, 842 m, 796 w, 750 m, 697 w, 687 w, 665 w, 521 w. ^{1}H NMR ($CDCl_3$): δ = 1.9 (m, 36 H, tBu), 6.8 (d, ^{3}J = 8.7 Hz, 2 H, H-b,b′), 7.1 (d, ^{3}J = 8.9 Hz, 2 H, H-c,c′), 8.2−8.3 (m, 4 H, H-1), 9.0−9.4 (m, 8 H, H-2,2′). ^{13}C NMR ($CDCl_3$): δ = 31.0−33.3 (tBuCH$_3$), 36.2 (CMe$_3$), 113.9 (-c-d), 119.2−119.6 (C-2′), 122.8 −123.0 (C-2), 127.5−127.8 (C-c,c′), 128.6 (C-1), 133.3 (C-a), 133.9−134.3 (C-3), 136.5−136.8 (C-3′), 151.7 (C-4,4′), 154.4−154.6 (C-1′). ^{19}F NMR($CDCl_3$): $\delta = -62.8$. $C_{52}H_{52}F_3GaN_8$ (915.8): calcd. C 69.41, H 5.51, N 11.77, F 5.99; found C 68.95, H 5.34, N 10.44, F 8.31.

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