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Synthesis and Characterization of (Octaaryltetraazaporphyrinato)indium(III) Complexes for Optical Limiting

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The preparation of (octaaryltetraazaporphyrinato)indium(III) chlorides [aryl = phenyl (**5a**), *p*-*tert*-butylphenyl (**6a**), *p*-(trifluoromethyl)phenyl (**7a**), *m*-(trifluoromethyl)phenyl (**8a**)] and their reactions with aryl Grignard reagents XMgBr to give **5b**–**8b** [X = *p*-(trifluoromethyl)phenyl] and **5c** (R = 3,5-difluorophenyl) are described. The characterization of all compounds by UV–vis, FT-IR, and ^{1}H and ^{13}C NMR spectroscopy was performed. The hypsochromic shift of all bands in the absorption spectra of complexes **5a**–**8a** is observed in the sequence **6a** < **5a** < **7a** ≈ **8a**. This is associated with the increasing electron-withdrawing character of the aryl substituents in the periphery of the tetraazaporphyrin macrocycle. Compounds **8a,b** are very good soluble in organic solvents with **8a** exhibiting the higher photochemical stability among the various synthesized species. The optical limiting (OL) properties of the complexes have been studied and correlated with the structure of the (tetraazaporphyrinato)indium(III) complexes and the electronic nature of the different substituents. In particular, the OL effect at 532 nm increases on going from the series of compounds **5** to the series **8**.

Introduction

Conjugated macrocycles such as metallophthalocyanines (PcM's), metallonaphthalocyanines (NcM's) and metallotetraazaporphyrins (TAPM's) have been extensively studied due to their widespread usage in various important fields of material science.[1] The recognition of the importance of these classes of materials as far as nonlinear optics is concerned is relatively recent.[2] In fact, PcM's, NcM's, TAPM's, and their derivatives are new functional compounds which constitute the active materials in advanced devices based on nonlinear optical properties.[3] In particular, it has been proved that PcM's and analogous species produce strong optical limiting (OL) effects,[2a−e] which can be profitably exploited for the protection of light-sensitive elements against accidental or hostile intense radiations.[2f,4] The reasons for that have to be found in the presence of an extended network of π-electrons which infer a high electrical polarizability to the

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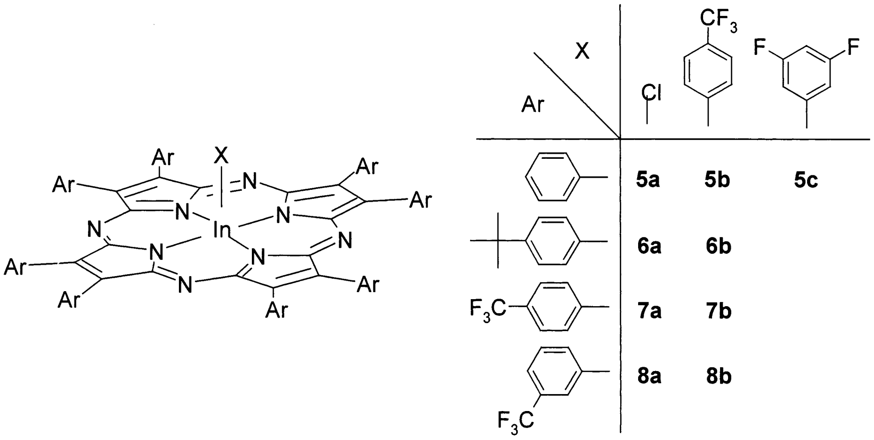

Figure 1. Structure and designation of synthesized indium complexes.

molecule[5] and, in addition, take part in a number of fast transitions in the spectral regions of OL interest.[6] Moreover, the versatility of the synthetic methods offers the possibility of modifying the skeleton of these conjugated macrocycles in a plethora of ways by modulating all the various constituents according to predefined molecular structures.[7]

Indium phthalo- and naphthalocyanines are well-known as active materials for OL applications.[2e,8] In these complexes the trivalent nature of the coordinated central In atom requires the presence of a monovalent axial ligand which is approximately oriented in a perpendicular direction with respect to the plane defined by the coordinating macrocycle.[9] The nature of the peripheral substituents and axial ligands in these indium−macrocycle complexes influences the stability and the relative OL performance. The introduction of sterically large axial substituents leads to a decrease of the aggregation tendency of the complexes. Aggregates are mostly coplanar-associated arrangements driven by enhanced van der Waals attractive forces of the Pc rings. For an OL material this aggregation must be avoided, since strong intermolecular interactions open additional relaxation pathways and, thereby, shorten the exited-state lifetime which reduces the effective nonlinear absorption.[8a] The presence of peripheral substituents facilitates the solubilization of the substituted compounds as well, but in some cases these can lead to a decrease of the photochemical stability of the substituted compounds under the conditions at which OL is required.[10]

The OL effect is a photoinduced change of light transmission through a material or a device, which consists of the decrease of the transmittance when the light intensity exceeds a system-dependent threshold value.[4c] An appropriate equation describing the OL effect is

$$-(\mathrm{d}I_{\mathrm{in}}/\mathrm{d}z) = [\alpha(I_{\mathrm{in}})]I_{\mathrm{in}} = \alpha_0 I_{\mathrm{in}} + \beta_0 I_{\mathrm{in}}^{2} \qquad (1)$$

with I_{in} being the intensity of the incident light, z the direction of light propagation, $\alpha(I_{\mathrm{in}})$ the general intensity-dependent absorption coefficient, α_0 the linear absorption coefficient, and β_0 the nonlinear absorption coefficient. In eq 1, the effective intensity-dependent absorption coefficient $\alpha(I_{\mathrm{in}})$ is expressed in the form $\alpha_0 + \beta_0 I_{\mathrm{in}}$, thus showing the nonlinearity of the optical properties of the irradiated material.[4d]

Studies on the OL effect produced by indium tetraazaporphyrins have not been reported up to now, and only few indium(III) complexes of octaphenyltetraazaporphyrin are known.[11]

In this work we report on the synthesis and the OL properties of a series of new axially coordinated indium(III) octaaryltetraazaporphyrins (see Figure 1) of the general formula $[(\mathrm{Ar})_8\mathrm{TAP}]\mathrm{In(X)}$, with Ar = phenyl (Ph, series **5**), *p-tert*-butylphenyl (*p-t*-BuPh, series **6**), *p*-(trifluoromethyl)phenyl, (*p*-$\mathrm{CF_3Ph}$, series **7**), and *m*-(trifluoromethyl)phenyl (*m*-$\mathrm{CF_3Ph}$, series **8**) and X = Cl (series **a**), *p*-(trifluoromethyl)phenyl (*p*-TMP, series **b**), and 3,5-difluorophenyl (DFP, series **c**).

Experimental Section

Diphenylfumaronitrile (**1**) was prepared from benzyl cyanide (purity 98%, Fluka) according to a reported procedure[12] and purified additionally by vacuum distillation. Bis(*p-tert*-butylphenyl)fumaronitrile (**2**) was obtained from *p-tert*-butylbenzyl bromide (purity 90%, Fluka) by the combination of methods described in the literature.[13,14]

Solvents for synthesis, chromatography, and spectroscopic characterization of compounds were pure chemicals (Aldrich, Fluka).

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THF for Grignard reactions was thoroughly dried by refluxing with sodium and distilled. All reactions with Grignard reagents were carried out under nitrogen atmosphere. Quinoline was additionally purified by vacuum distillation under nitrogen.

The following equipment was used for characterization: UV-vis, Shimadzu UV-365; FT-IR, Bruker IFS-48; ^{1}H and ^{13}C-NMR, Bruker AC 250 (^{1}H, 250.131 MHz; ^{13}C, 62.902 MHz); mass, Varian Mat 711; elemental analyses, Carlo-Erba elemental analyzer 1104, 1106.

Optical Limiting Measurements. The OL effect for the various octaaryltetraazaporphyrins has been studied with the *Z*-scan technique in the open aperture and closed aperture configurations.[15] The samples are solutions of octaaryltetraazaporphyrins in toluene with concentrations $(0.5-5) \times 10^{-4}$ M. The optical cell was a quartz cuvette with optical path thickness equal to 0.1 cm. The sample irradiation was realized with a pulsed Nd:YAG laser (from Continuum Minilite, Edinburgh, Scotland) emitting at the second harmonic ($\lambda = 532$ nm). Samples linear transmittance at the wavelength of laser irradiation ranged in the interval 70−90%. The maximum energy per laser pulse was 100 mJ. The pulse duration ranged in the interval 3−7 ns. The frequency of sample irradiation was 10 pulses/s. The Nd:YAG laser beam was focused with a neutral lens having the focal distance equal to 10 cm. During the *Z*-scan determinations the sample spanned a total length of 3.5 cm centered at the beam focus. The displacement of the sample along the *Z*-scan direction was controlled by means of a piezoelectric driver. The laser beam radius was approximately 0.5 cm before lens focusing. The recording of sample transmittance was taken every 0.05 cm along the spanned length. The reported values of transmittance were averaged on a basis of 20 determinations/analyzed *Z*-position.

Bis(*m*-(trifluoromethyl)phenyl)fumaronitrile (3). *m*-(Trifluoromethyl)benzyl cyanide (10 g, 52.4 mmol; purity 97%, Aldrich) and resublimed I_2 (13.4 g, 0.105 mol) were dissolved in 130 mL of diethyl ether and cooled to 0 °C. A cooled solution of Na (2.4 g, 0.104 mol) in 35 mL of methanol was added to this mixture dropwise over 20−30 min, maintaining the temperature of reaction mixture strictly in the range of 0 to −5 °C. After all of the sodium methoxide solution had been added, the reaction mixture was stirred at this temperature for 10 min and then poured into 200 mL of ice water. The organic phase was separated and washed consecutively with 100 mL of aqueous solution of sodium thiosulfate (3%) and 100 mL of distilled water. *n*-Hexane (50 mL) was added to the obtained slightly yellowish diethyl ether phase, and the solvents were removed under vacuum until 30 mL remained. The precipitated colorless crystals were immediately filtered off, washed with a small portion of *n*-hexane, and dried in vacuo (0.1 bar) at 80−90 °C. Yield: 5.7 g (15.6 mmol, 58%). Mp: 164−165 °C. FT-IR (KBr) (ν, cm^{-1}): 3090 w; 2228 (ν CN) m; 1614 w; 1489 w; 1443 m; 1333 vs; 1290 w; 1236 s; 1196 s; 1173 s; 1134 vs; 1103 m; 1076 s; 1040 w; 1001 w; 916 m; 881 m; 814 m; 802 s; 766 w; 698 s; 673 m; 656 m. ^{1}H NMR (CDCl$_3$) (δ, ppm): 8.02−8.07 (m, 4H); 7.84 (d, 2H, $^3J \approx 8.0$ Hz); 7.71 (t, 2H, $^3J \approx 7.8$ Hz). ^{13}C NMR (CDCl$_3$) (δ, ppm): 132.2 (s); 132.1 (q, $^2J \approx 33$ Hz); 131.8 (q, $^4J \approx 0.9$ Hz); 130.2 (s); ≈130.2 (q, covered); 128.7 (q, $^3J \approx 3.5$ Hz); 125.7 (q, $^3J \approx 3.8$ Hz); 123.2 (q, $^1J \approx 272.8$ Hz); 115.6 (s). Mass (FD): $m/z = 366.1$ (M$^+$). Anal. Calcd for $C_{18}H_8F_6N_2$, $M = 366.3$ g/mol: C, 59.03; H, 2.20; N, 7.65. Found: C, 58.90; H, 2.06; N, 7.69.

Bis(*p*-(trifluoromethyl)phenyl)fumaronitrile (4). *p*-(Trifluoromethyl)benzyl cyanide (4 g, 21.2 mmol; purity 98%, Aldrich), I_2 (5.4 g, 42.5 mmol), Na (0.97 g, 42.2 mmol), methanol (16 mL), and diethyl ether (70 mL) were used by applying the similar method of preparation as described for the *meta*-precursor **3**. The formation of precipitate was observed during the reaction. After the reaction mixture was poured into 100 mL of cold water, the diethyl ether was added until complete dissolution of the precipitate. The organic phase was treated further as described above for the *meta*-derivative. Yield: 2.7 g (7.4 mmol, 69%) of colorless crystals. Mp: 234−236 °C. FT-IR (KBr) (ν, cm^{-1}): 3111 vw; 2226 (ν_{CN}) w; 1929 vw; 1618 w; 1410 m; 1323 vs; 1234 w; 1202 m; 1188 m; 1165 s; 1130 vs; 1070 s; 1018 m; 860 m; 833 s; 764 m; 660 m; 638 w; 604 m; 492 w; 424 w. ^{1}H NMR (CDCl$_3$) (δ, ppm): 7.96 (d, 4H, $^3J \approx 8.0$ Hz); 7.82 (d, 4H, $^3J \approx 8.0$ Hz). ^{13}C NMR (CDCl$_3$) (δ, ppm): 134.7 (q, $^5J \approx 1.4$ Hz); 133.8 (q, $^2J \approx 33.3$ Hz); 129.2 (s); 126.5 (q, $^3J \approx 3.7$ Hz); 125.8 (s); 123.2 (q, $^1J \approx 272.8$ Hz); 115.6 (s). Mass (FD): $m/z = 365.9$ (M$^+$). Anal. Calcd for $C_{18}H_8F_6N_2$, $M = 366.3$ g/mol: C, 59.03; H, 2.20; N, 7.65. Found: C, 59.00; H, 2.13; N, 7.77.

(Octaphenyltetraazaporphyrinato)indium(III) chloride (5a). InCl$_3$ (1 g, 4.5 mmol) and **1** (4 g, 17.4 mmol) were heated in 20 mL of quinoline in the presence of 5 drops of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU, purity 99%, Fluka) at 230 °C for 6 h. The quinoline was distilled off in a vacuum, and the crude product was washed with methanol by Soxhlet extraction and finally dried in a vacuum (0.1 bar, 60 °C, 24 h.). Yield: 2 g (1.87 mmol, 43%) of dark greenish-brown crystalline powder. UV−vis (CH$_2$Cl$_2$) (λ_{max}, nm/rel intens): 378/0.773; 475/0.227; 590/0.218; 642 /1.00. FT-IR (KBr) (ν, cm^{-1}): 3053 w; 1456 m; 1367 m; 1300 w; 1198 w; 1186 w; 1140 m; 1003 s; 986 vs; 920 w; 876 m; 822 w; 800 w; 787 w; 773 w; 756 m; 746 m; 729 m; 712 w; 692 s; 604 m; 534 m; 517 w. Anal. Calcd for $C_{64}H_{40}N_8ClIn$, $M = 1071.4$ g/mol: C, 71.75; H, 3.76; N, 10.46. Found: C, 71.95; H, 3.50; N, 10.74.

(Octakis(*p*-*tert*-butylphenyl)tetraazaporphyrinato)indium(III) chloride (6a). InCl$_3$ (0.5 g, 2.26 mmol) and **2** (3 g, 8.77 mmol) were heated (240 °C, 7 h) in 10 mL of 1-chloronaphthalene in the presence of DBU (5 drops). The reaction mixture was cooled slowly to induce crystallization and poured into 100 mL of methanol. The precipitate was centrifuged and washed with methanol in a Soxhlet. For further purification, the product was dissolved in CH$_2$Cl$_2$ and filtered and an equal amount of methanol was added to the filtrate. Dichloromethane was partially removed from the obtained solution using a rotary evaporator, and the formed precipitate was filtered off and dried in a vacuum (0.1 bar, 60 °C, 24 h). Yield: 1.3 g (0.86 mmol, 39%) of red-brown powder. UV−vis (CH$_2$Cl$_2$) [λ_{max}, nm /log(ϵ)]: 383/4.94; 500/4.50; 602/4.42; 653/5.07. FT-IR (KBr) (ν, cm^{-1}): 3082 vw; 3038 vw; 2964 vs; 2905 m; 2868 w; 1610 w; 1493 w; 1460 m; 1425 vw; 1393 w; 1369 m; 1300 w; 1269 m; 1194 w; 1146 w; 1109 m; 1016 w; 989 vs; 881 w; 839 m; 806 w; 775 vw; 748 w. ^{1}H NMR (CDCl$_3$) (δ, ppm): 8.32 (d, 16H, $^3J \approx 8.4$ Hz); 7.61 (d, 16H, $^3J \approx 8.4$ Hz); 1.51 (s, 72H). ^{13}C NMR (CDCl$_3$) (δ, ppm): 156.8 (s); 151.3 (s); 142.6 (s); 132.7 (s); 130.5 (s); 125.3 (s); 34.9 (s); 31.6 (s). Mass (FD): $m/z = 1519.9$ (M$^+$). Anal. Calcd for $C_{96}H_{104}N_8ClIn$, $M = 1520.2$ g/mol: C, 75.85; H, 6.90; N, 7.37. Found: C, 75.43; H, 7.13; N, 7.73.

(Octakis(*p*-(trifluoromethyl)phenyl)tetraazaporphyrinato)-indium(III) chloride (7a). InCl$_3$ (0.3 g, 1.35 mmol), **4** (1.5 g, 4.10 mmol), and DBU (4 drops) were heated in 5 mL of quinoline at 230 °C for 8 h. After cooling, to wash the product, methanol (50 mL) was added to the reaction mixture. The mixture was intensively stirred for 10 min, and water (5 mL) was added dropwise to complete the precipitation of the product. The precipitate was

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centrifuged, the methanol solution was removed, and the same washing procedure was repeated twice. The solid was dissolved in CH_2Cl_2 and filtered through a glass filter G4. Methanol (50 mL) was added to the obtained solution, and the solvents were partially removed using a rotary evaporator. The precipitation of the product was completed by addition of few drops of water, and the precipitate was filtered off. After drying in a vacuum (0.1 bar) at 90 °C, the product was continuously washed with hexane in a Soxhlet, dried again, and chromatographed on silica gel (CH_2Cl_2, the green fraction was collected). Yield: 0.50 g (0.31 mmol, 30%) of dark greenish powder. UV−vis (CH_2Cl_2) [λ_{max}, nm/log(ϵ)]: 379/5.03; 457/4.30; 585/4.37; 638/5.16. FT-IR (KBr) (ν, cm^{-1}): 1618 m; 1464 w; 1408 w; 1371 w; 1325 vs; 1175 s; 1134 s; 1069 s; 1018 m; 988 s; 881 w; 847 m; 810 vw; 777 w; 683 m; 623 w; 603 w; 432 w. ^{1}H NMR ($CDCl_3$) (δ, ppm): 8.30 (d, 16H, $^3J \approx 8.2$ Hz); 7.85 (d, 16H, $^3J \approx 8.4$ Hz). ^{13}C NMR (THF-d_8) (δ, ppm): 158.1 (s); 143.4 (s); 137.3 (s); 134.3 (s); 131.6 (q, $^2J \approx 32.4$ Hz); 126.4 (q, nonresolved); 125.5 (q, $^1J \approx 271.9$ Hz). Mass (FD): $m/z = 1614.5$ (M$^+$). Mass (FAB): $m/z = 1578.8$ (M$^+$ $-$ Cl). Anal. Calcd for $C_{72}H_{32}N_8F_{24}ClIn$, $M = 1615.3$ g/mol: C, 53.54; H, 2.00; N, 6.94. Found: C, 53.65; H, 2.05; N, 7.07.

Octakis(*m*-(trifluoromethyl)phenyl)tetraazaporphyrin (8). Na (0.2 g, 8.70 mmol) was dissolved in methanol (20 mL), and the solution was cooled in ice−water bath. Compound **3** (1.5 g, 4.17 mmol) was added to this solution with stirring. A stream of dry ammonia was bubbled through the reaction mixture for 1 h at ice bath temperature and then for 1 h at room temperature. Completion of reaction was monitored by TLC, until no traces of starting material were detected. The greenish-yellow reaction mixture was poured into 50 mL of cold water, and the organic phase was extracted with three 50 mL portions of chloroform. The chloroform solution was washed with 100 mL of water, dried over anhydrous Na_2SO_4, and filtered, and the solvent was evaporated. The residual viscous material was dissolved in *n*-pentanol (7 mL) and heated at 140 °C for 16 h. The reaction mixture was slowly cooled and then filtered. The precipitate was washed with small portions of hexane or methanol and dried in a vacuum at 60 °C. Yield: 0.82 g (0.56 mmol, 54%) of crystalline powder with violet reflection. UV−vis (CH_2Cl_2) [λ_{max}, nm/log(ϵ)]: 365/4.98; 422 sh; 552 sh; 590/4.78; 658/5.00. FT-IR (KBr) (ν, cm^{-1}): 3300 vw; 1489 vw; 1435 vw; 1331 vs; 1313 s; 1279 w; 1184 s; 1167 s; 1126 s; 1097 m; 1076 m; 1036 vw; 988 w; 906 w; 885 w; 804 m; 758 w; 698 s; 654 w. ^{1}H NMR ($CDCl_3$) (δ, ppm): 8.38 (d, 8H, $^3J \approx 7.7$ Hz); 8.27 (s, 8H); 7.86 (d, 8H, $^3J \approx 8.1$ Hz); 7.71 (t, 8H, $^3J \approx 7.7$ Hz); −1.76 (s, 2H). ^{13}C NMR ($CDCl_3$) (δ, ppm): 153.6 (s); 141.4 (s); 135.6 (s); 133.0 (s); 131.2 (q, $^2J \approx 32.5$ Hz); 129.3 (q, $^3J \approx 4.1$ Hz); 129.2 (s); 125.6 (q, $^3J \approx 3.7$ Hz); 123.4 (q, $^1J \approx 272.5$). Mass (FD): $m/z = 1467.1$ (M$^+$). Anal. Calcd for $C_{72}H_{34}N_8F_{24}$, $M = 1467.1$ g/mol: C, 58.95; H, 2.34; N, 7.64. Found: C, 58.88; H, 2.21; N, 7.73.

Octakis(*p*-(trifluoromethyl)phenyl)tetraazaporphyrin (7) was prepared identically to **8**. Yield: 53% of dark-green insoluble powder. UV−vis [solid state, poly(chlorotrifluoroethylene)] [λ_{max}, nm]: 376; 464; 610; 680. FT-IR (KBr) (ν, cm^{-1}): 3296 vw; 1618 w; 1491 vw; 1412 vw; 1328 vs; 1169 s; 1132 s; 1114 m; 1070 s; 1034 w; 1019 m; 968 m; 849 m; 839 m; 778 w; 764 w; 725 vw; 677 w; 616 w; 431 w. Anal. Calcd for $C_{72}H_{34}N_8F_{24}$, $M = 1467.1$ g/mol: C, 58.95; H, 2.34; N, 7.64. Found: C, 58.80; H, 2.05; N, 7.62.

(Octakis(*m*-(trifluoromethyl)phenyl)tetraazaporphyrinato)-indium(III) chloride (8a). $InCl_3$ (0.2 g, 0.9 mmol) and **8** (0.2 g, 0.136 mmol) were refluxed in DMF (15 mL) for 2 h. After the reaction mixture was cooled to room temperature, water (10 mL) was added. The formed precipitate was centrifuged, dissolved in 50 mL of methanol, crystallized by dropwise addition of water, and centrifuged again. After the sample was dried in a vacuum at 80 °C, 180 mg (0.112 mmol) of dark-green powder was obtained. Yield: 82%. UV−vis (CH_2Cl_2) [λ_{max}, nm /log(ϵ)]: 378/5.05; 458/4.31; 584/4.38; 636/5.15. FT-IR (KBr) (ν, cm^{-1}): 1373 w; 1331 vs; 1312 s; 1279 m; 1198 m; 1169 s; 1128 s; 1097 m; 1076 m; 1009 m; 914 m; 808 m; 744 vw; 719 m; 698 m; 687 w; 654 vw. ^{1}H NMR ($CDCl_3$) (δ, ppm): 8.35 (d, 8H, $^3J \approx 8.1$ Hz); 8.27 (s, 8H); 7.87 (d, 8H, $^3J \approx 8.1$ Hz); 7.72 (t, 8H, $^3J \approx 7.9$ Hz). ^{13}C NMR ($CDCl_3$) (δ, ppm): 156.6 (s); 143.0 (s); 135.5 (s); 132.6 (s); 131.3 (q, $^2J \approx 32.8$ Hz); 129.4 (q, $^3J \approx 4.1$ Hz); 129.3 (s); 125.9 (q, $^3J \approx 3.7$ Hz); 123.9 (q, $^1J \approx 272.8$ Hz). Mass (FD): $m/z = 1614.9$ (M$^+$). Anal. Calcd for $C_{72}H_{32}N_8F_{24}ClIn$, $M = 1615.3$ g/mol: C, 53.54; H, 2.00; N, 6.94. Found: C, 52.73; H, 2.11; N, 6.87.

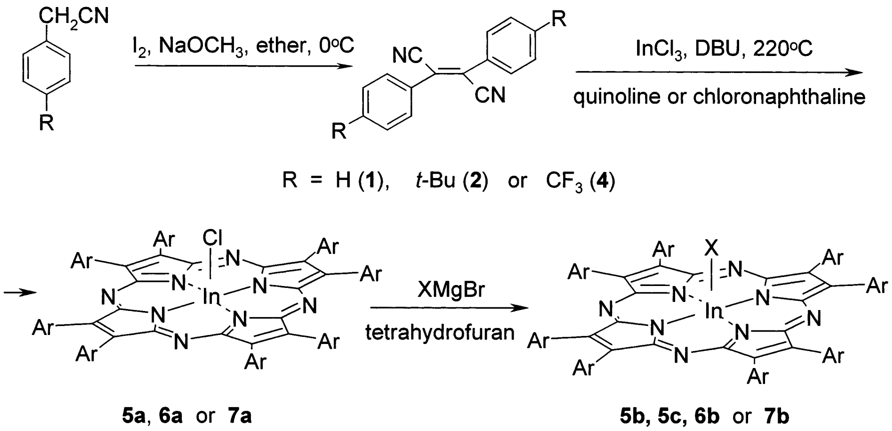
***p*-(Trifluoromethyl)phenylmagnesium bromide** [(*p*-TMP)-MgBr] in a THF solution was prepared by stirring magnesium turnings (25 mg, 1.1 mmol) with *p*-(trifluoromethyl)phenyl bromide (0.15 mL, 1.0 mmol) in 2 mL of dry THF at room temperature.

(*p*-(Trifluoromethyl)phenyl)(octaphenyltetraazaporphyrinato)-indium(III) (5b). Compound **5a** (150 mg, 0.14 mmol) was suspended in dry THF (15 mL) at room temperature. The freshly prepared THF solution of (*p*-TMP)MgBr was added dropwise to this mixture using a syringe. The reaction mixture was stirred for 17 h and then poured into 100 mL of an ice−methanol mixture (approximately 1:1) and centrifuged. The obtained precipitate was washed with methanol, dried, and chromatographed (silica gel/ CH_2Cl_2, the first fraction was taken). Yield: 83 mg (0.070 mmol, 50%). UV−vis (CH_2Cl_2) [λ_{max}, nm/log(ϵ)]: 395/5.01; 483/4.16; 591/4.39; 643/5.15. FT-IR (KBr) (ν, cm^{-1}): 3055 w; 1599 vw; 1460 m; 1387 w; 1367 m; 1325 s; 1300 vw; 1200 vw; 1182 w; 1163 m; 1138 m; 1126 m; 1049 m; 1003 m; 984 vs; 914 w; 876 m; 822 m; 773 m; 744 m; 692 s; 604 m. ^{1}H NMR ($CDCl_3$) (δ, ppm): 8.28−8.32 (m, 16H); 7.54−7.57 (m, 24H); 6.33 (d, 2H, $^3J \approx 8.0$ Hz); 4.22 (d, 2H, $^3J \approx 8.0$ Hz). ^{13}C NMR ($CDCl_3$) (δ, ppm): 157.5 (s); 142.4 (s); 134.5 (s); 133.4 (s); 133.0 (s); 128.4 (s); 128.2 (s). Anal. Calcd for $C_{71}H_{44}N_8F_3In$, $M = 1181.0$ g/mol: C, 72.21; H, 3.76; N, 9.49. Found: C, 71.89; H, 3.69; N, 9.43.

(*p*-(Trifluoromethyl)phenyl)[octakis(*p*-tert-butylphenyl)tetraazaporphyrinato]indium(III) (6b). Compound **6a** (160 mg, 0.105 mmol) in 15 mL of THF was used for the reaction similar to the preparation of **5b**. After the addition of (*p*-TMP)MgBr the reaction mixture was stirred for 1 h and treated further as described for **5b**. Yield: 125 mg (0.077 mmol, 73%) of a dark violet powder. UV−vis (CH_2Cl_2) [λ_{max}, nm/log(ϵ)]: 402/4.98; 504/4.31; 600/4.41; 653/5.10. FT-IR (KBr) (ν, cm^{-1}): 2964 vs; 2905 m; 2868 m; 1610 m; 1493 m; 1462 s; 1423 w; 1389 m; 1367 s; 1325 s; 1298 w; 1269 m; 1196 m; 1165 m; 1144 m; 1130 m; 1109 s; 1047 m; 1016 m; 988 vs; 881 m; 847 m; 839 s; 820 m; 806 m; 746 m; 679 w. ^{1}H NMR ($CDCl_3$) (δ, ppm): 8.33 (d, 16H, $^3J \approx 8.4$ Hz); 7.60 (d, 16H, $^3J \approx 8.4$ Hz); 6.28 (d, 2H, $^3J \approx 7.5$ Hz); 4.15 (d, 2H, $^3J \approx 7.5$ Hz); 1.51 (s, 72H). ^{13}C NMR ($CDCl_3$) (δ, ppm): 157.5 (s); 151.0 (s); 142.2 (s); 134.6 (s); 132.7 (s); 130.7 (s); 125.3 (s); 122.6 (q, $^3J \approx 3.7$ Hz); 34.9 (s); 31.6 (s). Mass (FD): $m/z = 1629.6$ (M$^+$). Anal. Calcd for $C_{103}H_{108}N_8F_3In$, $M = 1629.9$ g/mol: C, 75.90; H, 6.68; N, 6.87. Found: C, 76.22; H, 6.86; N, 6.89.

(*p*-(Trifluoromethyl)phenyl)[octakis(*p*-(trifluoromethyl)-phenyl)tetraazaporphyrinato]indium(III) (7b). A freshly prepared solution of (*p*-TMP)MgBr in THF was added dropwise to a solution of **7a** (100 mg, 0.062 mmol) in 10 mL of THF and stirred for 1 h at room temperature. The reaction mixture was poured into 100 mL of ice−methanol mixture (1:1) and centrifuged. The precipitate

Scheme 1. Preparation of **5a**−**c**, **6a**,**b**, and **7a**,**b**



was washed with aqueous methanol, dried, and chromatographed (silica gel/CH_2Cl_2, the first fraction). Yield: 53 mg (0.031 mmol, 50%) of dark green powder. UV−vis (CH_2Cl_2) [λ_{max}, nm/log(ϵ)]: 393/4.96; 587/4.34; 639/5.12. FT-IR (KBr) (ν, cm^{-1}): 1618 m; 1474 vw; 1410 vw; 1327 vs; 1169 s; 1128 s; 1069 s; 1018 m; 986 s; 881 w; 845 m; 820 vw; 777 vw; 729 vw; 683 w; 623 w; 602 vw; 430 w. ^1H NMR ($CDCl_3$) (δ, ppm): 8.29 (d, 16H, $^3J \approx 8.2$ Hz); 7.83 (d, 16H, $^3J \approx 8.4$ Hz); 6.39 (d, 2H, $^3J \approx 7.5$ Hz); 4.24 (d, 2H, $^3J \approx 7.7$ Hz). ^{13}C NMR (THF-d_8) (δ, ppm): 158.6 (s); 143.1 (s); 137.5 (s); 135.3 (s); 134.3 (s); 131.4 (q, $^2J \approx 32.8$ Hz); 126.3 (q, nonresolved); 125.5 (q, $^1J \approx 271.9$ Hz); 123.6 (q, $^3J \approx 3.7$ Hz). Mass (FD): m/z = 1723.9 (M^+). Anal. Calcd for $C_{79}H_{36}N_8F_{27}In$, M = 1725.0 g/mol: C, 55.01; H, 2.10; N, 6.50. Found: C, 55.23; H, 2.12; N, 6.37.

(*p*-(Trifluoromethyl)phenyl)[octakis(m-(trifluoromethyl)-phenyl)tetraazaporphyrinato]indium(III) (8b). A freshly prepared solution of (*p*-TMP)MgBr in THF was added dropwise to a solution of **8a** (100 mg, 0.062 mmol) in 10 mL of THF and stirred for 1 h at room temperature. The reaction mixture was poured into 100 mL of ice−methanol mixture (1:1) and centrifuged. The precipitate was thoroughly washed with aqueous methanol to remove the violet byproduct, dried, and chromatographed (silica gel/CH_2Cl_2, the first fraction). Yield: 60 mg (0.035 mmol, 56%) of dark green powder. UV−vis (CH_2Cl_2) [λ_{max}, nm/log(ϵ)]: 394/5.03; 585/4.38; 637/5.17. FT-IR (KBr) (ν, cm^{-1}): 1599 vw; 1466 vw; 1447 w; 1391 vw; 1371 w; 1331 vs; 1312 s; 1279 m; 1198 m; 1167 s; 1126 s; 1097 m; 1076 m; 1049 w; 1015 w; 1007 m; 914 m; 806 m; 764 w; 716 m; 698 m; 687 w; 654 w; 596 vw; 532 vw. ^1H NMR ($CDCl_3$) (δ, ppm): 8.35 (d, 8H, $^3J \approx 7.7$ Hz); 8.27 (s, 8H); 7.85 (d, 8H, $^3J \approx 7.7$ Hz); 7.69 (t, 8H, $^3J \approx 7.7$ Hz); 6.42 (d, 2H, $^3J \approx 7.7$ Hz); 4.25 (d, 2H, $^3J \approx 7.7$ Hz). ^{13}C NMR ($CDCl_3$) (δ, ppm): 157.3 (s); 142.6 (s); 135.6 (s); 134.4 (s); 133.0 (s); 131.2 (q, $^2J \approx 32.8$ Hz); 129.4 (q, $^3J \approx 3.7$ Hz); 129.2 (s); 127.6 (s); 125.6 (q, $^3J \approx 3.7$ Hz); 123.9 (q, $^1J \approx 272.4$ Hz); 123.2 (q, $^3J \approx 3.7$ Hz). Mass (FD): m/z = 1725.3 (M^+). Anal. Calcd for $C_{79}H_{36}N_8F_{27}In$, M = 1725.0 g/mol: C, 55.01; H, 2.10; N, 6.50. Found: C, 54.73; H, 2.06; N, 6.32.

(3,5-Difluorophenyl)(octaphenyltetraazaporphyrinato)indium(III) (5c). Mg (50 mg, 2.1 mmol) and 3,5-difluorophenyl bromide (0.23 mL, 2.0 mmol) in 3 mL of THF was stirred at room temperature until most of the magnesium turnings were dissolved. The obtained solution of (3,5-difluorophenyl)magnesium bromide was added dropwise using a syringe to a suspension of **5a** (165 mg, 0.154 mmol) in 30 mL of dry THF. The reaction mixture was stirred at room temperature for 18 h, poured into 50 mL of ice water, and centrifuged. The precipitate was washed with methanol, dried, and chromatographed (silica gel/CH_2Cl_2, the first fraction). Yield: 85 mg (0.074 mmol, 48%). UV−vis (CH_2Cl_2) [λ_{max}, nm/log(ϵ)]: 392/5.00; 481/4.19; 591/4.38; 643/5.13. FT-IR (KBr) (ν, cm^{-1}): 3055 w; 1597 w; 1583 m; 1458 m; 1408 m; 1369 m; 1300 w; 1271 w; 1202 w; 1184 w; 1140 m; 1119 w; 1028 vw; 1003 m; 984 vs; 914 w; 876 m; 849 w; 822 m; 787 vw; 773 m; 744 m; 692 s; 604 m. ^1H NMR ($CDCl_3$) (δ, ppm): 8.28−8.32 (m, 16H); 7.54−7.57 (m, 24H); 5.71−5.80 (m, 1H); 3.59−3.63 (m, 2H). Anal. Calcd for $C_{70}H_{43}N_8F_2In$, M = 1149.0 g/mol: C, 73.18; H, 3.77; N, 9.75. Found: C, 73.30; H, 3.55; N, 9.59.

Results and Discussion

Synthesis. The cyclotetramerization of diaryl derivatives of fumaronitrile in the presence of metal salts is a good method for the preparation of (octaaryltetraazaporphyrinato)-metal complexes. In particular, (octaphenyltetraazaporphyrinato)indium(III) chloride (**5a**) is formed in 37% yield by refluxing diphenylfumaronitrile with anhydrous $InCl_3$ in freshly distilled 1-chloronaphthalene.[11]

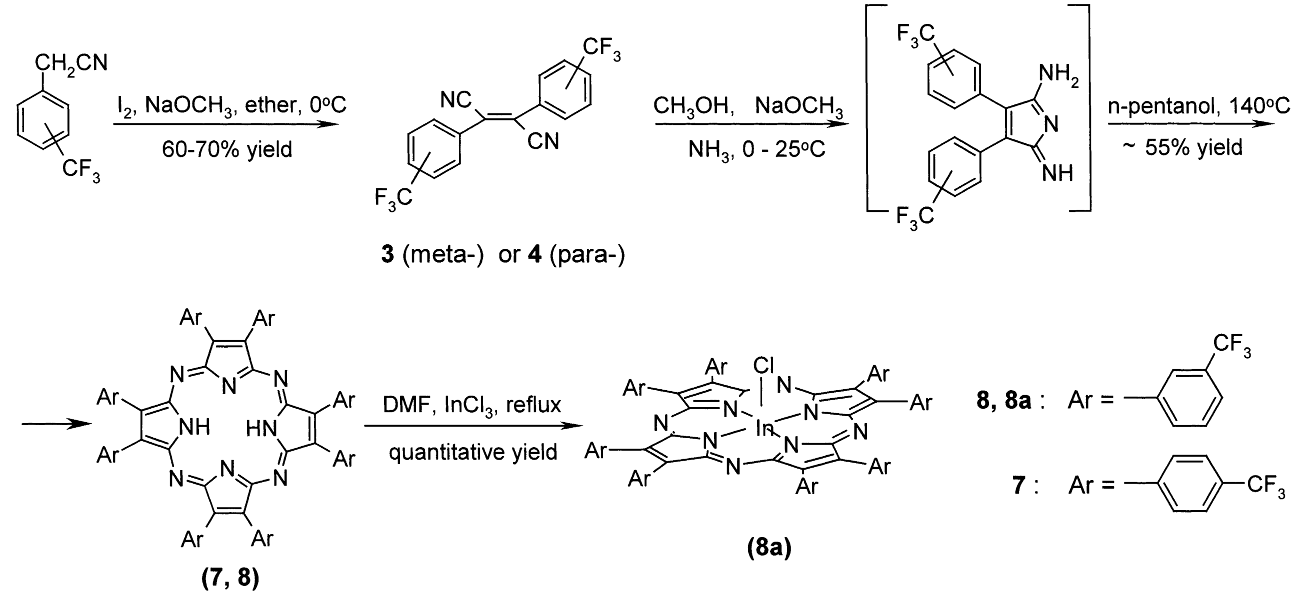
The similar route (see Scheme 1) was chosen here for the preparation of (octaphenyl-, (octakis(*p*-*tert*-butylphenyl)- and (octakis(*p*-(trifluoromethyl)phenyl)tetraazaporphyrinato)-indium(III) chlorides (**5a, 6a,** and **7a**, respectively). $[(Ph)_8TAP]In(Cl)$ (**5a)** was synthesized by heating diphenylfumaronitrile (**1**) with a slight excess of $InCl_3$ in freshly distilled quinoline in the presence of catalytic amounts of DBU. The poor solubility of the product in common organic solvents, caused by a strong aggregation of the macrocyclic molecules, suggested a continuous extraction of impurities in a Soxhlet apparatus.

The more soluble [(*p*-*t*-BuPh)$_8$TAP]In(Cl) (**6a)**, containing eight *tert*-butyl groups in the periphery of the macrocycle, was prepared by heating bis(*tert*-butylphenyl)fumaronitrile (**2**) and $InCl_3$ in 1-chloronaphthalene in the presence of DBU. The product precipitated from the reaction mixture after cooling as a crystalline powder and was purified by extraction of impurities with methanol, followed by recrystallization from CH_2Cl_2/CH_3OH solution, in 40% overall yield.

To prepare [(*p*-CF_3Ph)$_8$TAP]In(Cl) (**7a)**, quinoline was found to be a convenient solvent. However, the yield of the product appeared to be lower, compared to **5a** or **6a**, and the purification of **7a** requires column chromatography.

To use the similar route for the preparation of [(*m*-CF_3Ph)$_8$TAP]In(Cl) (**8a)** is more complicated due to the high

Scheme 2. Preparation of [(p-$CF_3Ph)_8$TAP]H_2 (**7**), [(m-$CF_3Ph)_8$TAP]H_2 (**8**). and [(m-$CF_3Ph)_8$TAP]In(Cl) (**8a**)



solubility of this compound in organic solvents. Furthermore, the usage of high-boiling solvents, such as quinoline or, especially, 1-chloronaphthalene, for the reaction of bis(m-(trifluoromethyl)phenyl)fumaronitrile (**3**) with $InCl_3$ leads to the formation of different byproducts, namely adducts with a molecular mass higher than the desired indium chloride complex, as well as the products of decomposition of the solvents. The preparation of **8a** was carried out according to the route presented in Scheme 2. The reaction of dinitrile **3** with ammonia in methanol in the presence of sodium methoxide gave most likely the diimino derivative, which easily underwent cyclotetramerization upon refluxing in 1-pentanol. The octakis(m-(trifluoromethyl)phenyl)tetraazaporphyrin (**8**), formed in this reaction, was reacted with $InCl_3$ in DMF to yield **8a**. However, this approach was not suitable for the preparation of **7a** since the corresponding octakis-(p-(trifluoromethyl)phenyl)tetraazaporphyrin (**7**) cannot be dissolved even in boiling DMF. For this reason compound **7** was not characterized by NMR and MS, but EA, solid-state UV−vis, and FT-IR were obtained to prove its formation. The heterogeneous reaction of **7** with $InCl_3$ in refluxing DMF led only to a decomposition of **7**, and no formation of **7a** was observed.

Substitution of the axial chlorine in **5a**−**8a** by aryl groups to form complexes with In−C bonds was carried out according to the procedure which we have published for indium phthalo- and naphthalocyanines:[16] reaction of the appropriate Grignard reagents with the corresponding indium chloride complexes in THF. The yields obtained are close to 50% and are similar to those found for the In−phthalocyanines.[16] Substitution of chlorine by the p-(trifluoromethyl)phenyl group (p-TMP) leads to a higher solubility of [$(Ph)_8$TAP]In(p-TMP) (**5b**) ($\approx 3 \times 10^{-3}$ M or 3.5 mg/mL, saturated solution in CH_2Cl_2) compared to **5a** ($< 10^{-3}$ M, CH_2Cl_2). Compounds **6a** and **6b** are highly soluble in solvents with medium polarity such as chloroform and dichloromethane ($> 8 \times 10^{-2}$ M or 120 mg/mL, CH_2Cl_2), as expected from their structure. The introduction of the trifluoromethyl group into a *meta*-position of the peripheral phenyl substituents leads to a remarkably high solubility of **8** ($\approx$200 mg/mL, CH_2Cl_2) and **8a**,**b** in most organic solvents including methanol due to the steric hindrance of the m-CF_3-Ph groups, which are not coplanar with the tetraazaporphyrin macrocycle, preventing aggregation of the molecules. In contrast, a trifluoromethyl group in the *para*-position of phenyl substituents leads to good solubility only in THF; the solubility of **7a** in dichloromethane is ca. 1.2×10^{-3} M (2 mg/mL). The values of solubility were estimated only at room temperature and are approximate, especially for highly soluble compounds.

Characterization. *Mass spectra* were obtained for all soluble complexes using field desorption technique. Only M^+ peaks were detected for all investigated compounds; no fragmentation signals were observed. For **7a** an additional FAB-mass spectrum was recorded and an intense peak of fragment $M^+ - Cl$ was detected. No peak of M^+ was found in this spectrum, indicating the splitting of the axial ligand under the conditions of FAB technique. Moreover, in the FAB-mass spectrum of **5b**, no M^+ peak nor its heavy fragments peaks were found due to complete decomposition under these conditions. The poor solubility of **5a**−**c** did not allow us to record their FD-mass spectra.

The UV−vis data obtained for **5a**−**8a**, **5b**−**8b**, and **5c** are given in the Experimental Section. The spectra of all compounds (see Figure 2) show two intense bands at 636−653 (Q-band) and 379−402 (B-band) nm caused by $\pi \rightarrow \pi^*$ transitions typical for diamagnetic (tetraazaporphyrinato)-metal complexes. The Q-band, observed in the visible region, is due to the $a_{1u} \rightarrow e_g^*$ transition, and the B-band in the near-ultraviolet region is caused by an $a_{2u} \rightarrow e_g^*$ transition.[17] The bands of lower intensity, found in the spectral window

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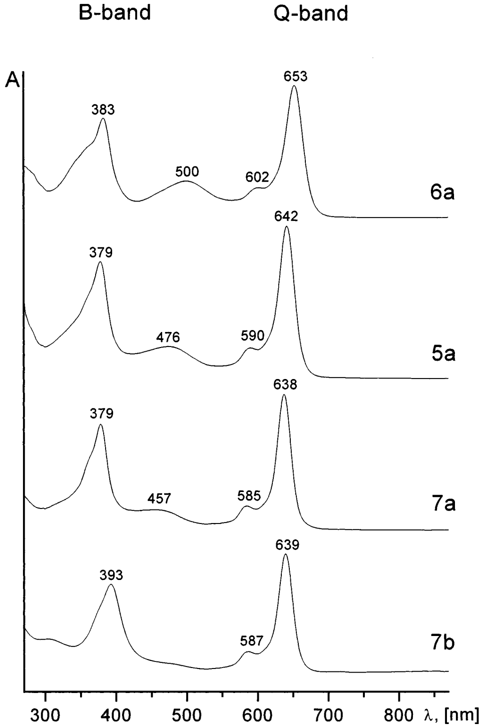

Figure 2. UV−vis spectra of compounds **5a**, **6a**, and **7a**,**b** in dichloromethane.

between the Q- and B-bands, are vibronic satellites on the blue side of the Q-band and charge transfer (CT) bands which usually occur on the red side of the B-band in metal octaphenyltetraazaporphyrins. Unlike the complexes of Fe, Ru, or other metals with an open d-configuration,[18a] the CT band in the gap between Q- and B-bands observed for the complexes of $(Ar)_8TAP$'s with metals with closed d^0 or d^{10} configuration, e.g. In(III) or Mg(II), cannot be associated with the transitions involving metal d-orbitals and is probably an $n \rightarrow \pi^*$ charge transfer localized on the macrocycle.

The $\log(\epsilon)$ values of the Q-bands of **5a**−**8a**, **5b**−**8b,** and **5c** are in the range of 5.07−5.17 depending on the nature of the peripheral substituents and axial ligands; they are slightly higher than those found for axially coordinated (octaphenyltetraazaporphyrinato)ruthenium(II) [18b] and -iron(II) [19] complexes.

Introduction of electron-donating *t*-Bu groups at the *para*-position of the peripheral phenyl rings leads to a red shift of the Q- and B-bands (11 and 4 nm, respectively) in **6a** and to a slight decrease of their intensity. That is likely due to a destabilization of occupied a_{1u} and a_{2u} orbitals, as compared with nonsubstituted (octaphenyltetraazaporphyrinato)indium chloride. The presence of electron-withdrawing CF_3 groups in *meta*- or *para*-positions in **7a** and **8a** results in an opposite effect, however, less pronounced (see Figure 2). A red shift and increasing intensity were observed for the CT band when changing the electron-withdrawing to -donating substituents in the order **7a** ≈ **8a** < **5a** < **6a**.

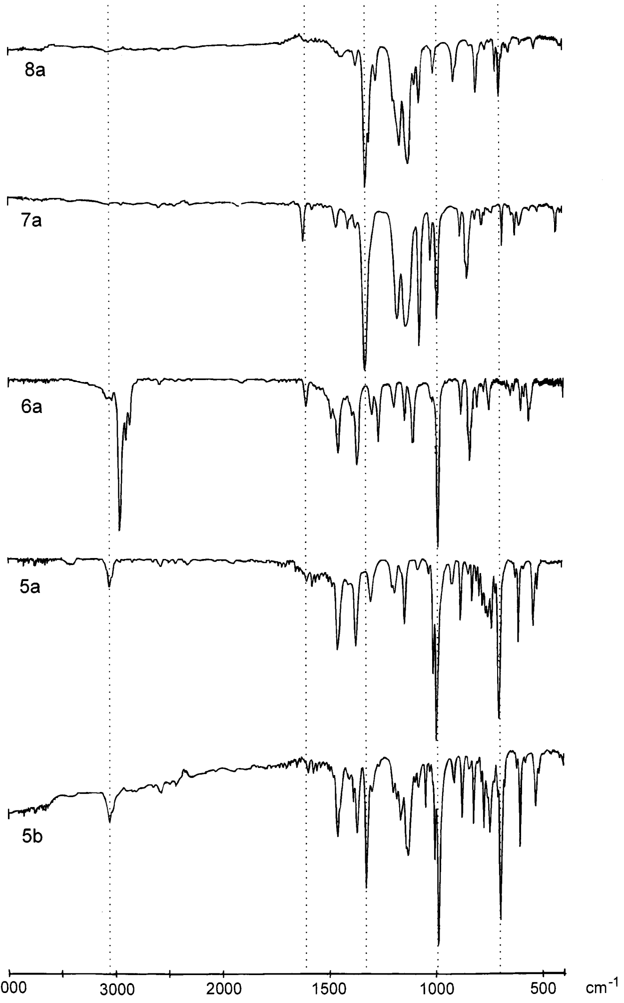

Figure 3. FT-IR spectra of compounds **5a,b**, **6a**, **7a**, and **8a** in KBr.

Substitution of axial chlorine by aryl results in a strong bathochromic shift of the B-band (19 nm for **6b** and 14 nm for **7b**) but has no noticeable influence on the position of the Q-band. This fact indicates that the a_{2u} orbital, which has a significant electron density on coordinating N-atoms of the macrocycle, is very sensitive to the nature of the axial ligand and is destabilized by axial aryls because of their electron-donating effect on indium. In contrast, the a_{1u} orbital has nodes on the internal N-atoms and may be considered as not influenced by axial ligands. This approach was also successfully used for describing qualitatively the spectra of bis-axially coordinated complexes of (octaphenyltetraazaporphyrinato)ruthenium(II).[18] Similar dependence of spectral pattern on axial substitution was observed for indium phthalo- and naphthalocyanines.[8a,16]

The IR spectra are rather specific for each of the prepared (octaaryltetraazaporphyrinato)indium chlorides **5a**−**8a**; the substitution of axial chlorine by the *p*-TMP group results in additional bands (see Figure 3). The most intense bands in the spectra of **5a**−**c** are observed in a region of 500−1600 cm^{-1} and are caused by combined vibrations of peripheral phenyl rings and the macrocyclic skeleton. They are similar

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(17) (a) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138. (b) Gouterman, M.; Wagniere, G.; Snyder, L. C. *J. Mol. Spectrosc.* **1963**, *11*, 108.

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to those observed for (octaphenyltetraazaporphyrinato)-indium(III) complexes with other axial ligands such as F, SCN, and OCN[11] and for complexes of octaphenyltetraazaporphyrin with other metals.[20] The stretching vibration of the macrocycle skeleton, in which the inner N-atoms are involved, appeared to be the most sensitive to the nature of central metal and was observed at 1456 cm^{-1} for **5a** in contrast to 1495 and 1472 cm^{-1} for bis(*tert*-butyl isocyanide)-(octaphenyltetraazaporphyrinato)iron(II) and -ruthenium(II) complexes, respectively.[20] Another intense vibration, sensitive to the metal nature, is found at 1140 cm^{-1}, which is probably a deformation vibration of the macrocycle skeleton. The IR spectra of **6a**,**b** and **7a**,**b** in the range of 600−900 cm^{-1} are different compared to **5a−c** due to the *para*-substitution in the peripheral phenyl rings. It results also in an increasing intensity of C═C valence vibration of phenyl rings at 1610 cm^{-1} for **6a,b** and 1618 cm^{-1} for **7** and **7a**,**b**. In addition, the spectra of **6a,b** show intense bands at 2964, 2905, and 2868 cm^{-1} due to the stretching vibrations of the *tert*-butyl groups. The very intense asymmetrical and symmetrical stretching vibrations of CF_3 groups in peripheral aromatic rings, along with the mixed ν_{C-F} and deformation aryl ring modes, are dominating in the spectra of **7**, **7a,b** and **8**, **8a,b**. They were observed at approximately 1330, 1170, 1130, and 1070 cm^{-1}; their positions slightly depend on the location of CF_3 groups in the aryl substituents.

The characteristic vibrations of axial *p*-TMP group were observed at 1325 (strong band), 1165, 1129, and 1048 (medium bands) cm^{-1}, and their frequencies are practically independent of the nature of the macrocycle. Similar vibrations at 1163, 1127, and 1047 were observed for $(t\text{-Bu})_4$PcIn-(*p*-TMP).[16] However, the vibration band of coordinated *p*-TMP at 1325 cm^{-1} was not revealed in this case because it was masked by the strong band of the phthalocyanine marocycle at 1330 cm^{-1}.

Due to the strong π-electron ring current of the macrocycle, the protons of axial *p*-TMP group in the ^{1}H NMR spectra of **5b−8b** are shielded and their resonances are significantly shifted to high field comparing to (trifluoromethyl)phenyl bromide. In contrast, the signals of peripheral aryl protons appear at lower field than in the corresponding dinitriles **1−4**, in the range of 7.5−8.4 ppm. Especially strong shifts, caused by the ring current effect, are observed for *ortho*-protons (both of axial ligand and peripheral aryls), which are the closest to the macrocycle center (see Figure 4 and Table 1). The small low-field shift of proton resonances of axial ligand, observed for **7b** or **8b** compared to **6b,** is the result of decreased shielding by π-electron ring current of the macrocycle due to the electron-withdrawing influence of peripheral substituents.

The ^{13}C NMR data of **5b**, **6a**,**b**, **7a**,**b**, and **8a,b** are given in Table 2. Although all carbon atoms of the macrocycles were observed, the intensity of signals of *p*-TMP carbons is very low and only ═CH− groups could be found (atoms C-α and C-β).

Due to the presence of fluorine atoms in most of the studied compounds, quadruplet splitting of some of ^{13}C signals was observed. The spin coupling constant are approximately 271 Hz (^1J), 33 Hz (^2J), and 3.7 Hz (^3J).

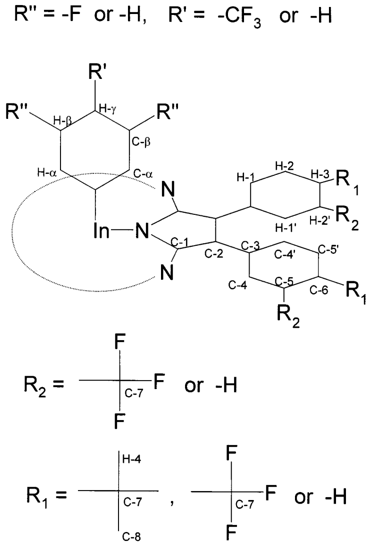

Figure 4. Designation of protons and carbon atoms used in Tables 1 and 2.

The assignment of ^{13}C resonances, made for compounds **5−7**, is obvious and was carried out according to the nuclear Overhauser effect as well as splitting of signals (for **7a,b** due to the presence of fluorine atoms). However, in the case of **8a,b** the correct assignment of atoms C-4, C-4′, C-5′, and C-6 required the additional exploration of one of the samples by the HC-Cosy technique. The two-dimensional spectra, recorded for **8b**, is presented in Figure 5. It clearly indicates that the signals of C-4, C-4′, C-5′, and C-6 atoms appear at 129.4, 135.6, 129.2, and 125.6 ppm, respectively.

The positions of C-1 and C-2 signals of the macrocycle and C-α and C-β signals of the coordinated *p*-TMP group are almost independent of the nature of substituents in the peripheral aryls, showing no strong electron redistribution. However, the positions of the peripheral aryl ^{13}C resonances are rather effected by substituents, as should be expected.

Substitution of axial chlorine by *p*-TMP results in a slight deshielding of C-1 and shielding of C-2 atoms, which was also observed for analogous complexes of phthalocyanines.[21]

EA data for the prepared compounds are in general in satisfactory agreement with the calculated values. However, the low conformity of data with the theoretical values for several porphyrazine samples, e.g. **8a**, can result from the influence of the heavy metal and/or fluorine present in these compounds. Similar difficulties in combustion analysis were also observed in case of phthalo- and naphthalocyanines.[16]

The preliminary investigation of light stability of some of the prepared compounds was carried out in chloroform solution in a quartz cuvette, directly exposed to sunlight. Under these conditions, compound **5b** moderately decomposes to form **5a**, followed by decomposition of the macrocycle. Under the same conditions, no decomposition was observed for compound **8a**, which indicates the stabilizing effect of electron-withdrawing substituents.

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Table 1. Assignment of Proton Resonances (See Figure 4) of (Octaaryltetraazaporphyrinato) indium Complexes in $CDCl_3$ (250 MHz)

	posn and multiplicity[a] of proton signals, ppm								
	macrocycle						ax ligand		
compd	H-1	H-1′	H-2	H-2′	H-3	H-4	H-α	H-β	H-γ
5b	8.30, m	8.30, m	7.56, m	7.56, m	7.56, m		4.22, d	6.33, d	
5c	8.30, m	8.30, m	7.56, m	7.56, m	7.56, m		3.61, m		5.76, m
6a	8.32, d	8.32, d	7.61, d	7.61, d		1.51, s			
6b	8.33, d	8.33, d	7.60, d	7.60, d		1.51, s	4.15, d	6.28, d	
7a	8.30, d	8.30, d	7.85, d	7.85, d					
7b	8.29, d	8.29, d	7.83, d	7.83, d			4.24, d	6.39, d	
8a	8.35, d	8.27, s	7.72, t		7.87, d				
8b	8.35, d	8.27, s	7.69, t		7.85, d		4.25, d	6.42, d	

[a] The spin coupling constants are given in the Experimental Section. Key: s, singlet; d, doublet; t, triplet; m, multiplet.

Table 2. Assignment of ^{13}C Resonances (See Figure 4) of (Octaaryltetraazaporphyrinato) indium Complexes in $CDCl_3$ or THF-d_8 (62.9 MHz)

	posn and multiplicity[a] of ^{13}C signals, ppm											
	macrocycle										ax ligand	
compd	C-1	C-2	C-3	C-4	C-4′	C-5	C-5′	C-6	C-7	C-8	C-α	C-β
5b	157.5, s	142.4, s	133.4, s	133.0, s	133.0, s	128.4, s	128.4, s	128.2, s			134.5, s	122.7, nr
6a	156.8, s	142.6, s	130.5, s	132.7, s	132.7, s	125.3, s	125.3, s	151.3, s	34.9, s	31.6, s		
6b	157.5, s	142.2, s	130.7, s	132.7, s	132.7, s	125.3, s	125.3, s	151.0, s	34.9, s	31.6, s	134.6, s	122.6, q
7a[b]	158.1, s	143.4, s	137.3, s	134.3, s	134.3, s	126.4, nr	126.4, nr	131.6, q	125.5, q			
7b[b]	158.6, s	143.1, s	137.5, s	134.3, s	134.3, s	126.3, nr	126.3, nr	131.4, q	125.5, q		135.3, s	123.6, q
8a	156.6, s	143.0, s	132.6, s	129.4, q	135.5, s	131.3, q	129.3, s	125.9, q	123.9, q			
8b	157.3, s	142.6, s	133.0, s	129.4, q	135.6, s	131.2, q	129.2, s	125.6, q	123.9, q		134.4, s	123.2, q

[a] The spin coupling constants are given in the Experimental Section. Key: s, singlet; q, quadruplet; nr, nonresolved multiplicity. [b] In THF-d_8.

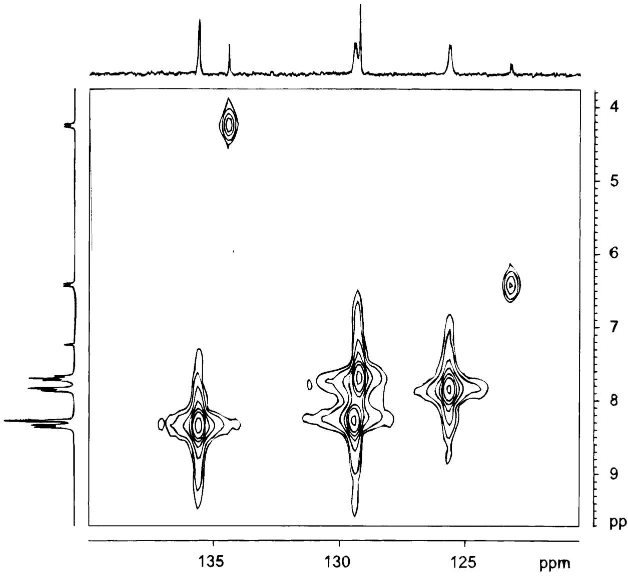

Figure 5. HC-Cosy spectra of **8b** in $CDCl_3$.

Optical Limiting Measurements. Conjugated macrocycles such as phthalocyanines and porphyrins usually give rise to the optical limiting effect by means of a mechanism based mostly upon the reverse saturable absorption (excited-state absorption ESA).[22] This could be verified in phthalocyanines by determining the absorption spectrum of optically pumped phthalocyanines[2c] which have an excited-state absorption cross section much higher than the ground-state absorption cross section at the wavelength of irradiation.[2b] In these systems such an effect has been described by considering the absorbing macrocycle as a four-level system whose excited state gives rise to reverse saturable absorption.[2b,c,22]

Previous studies on the nonlinear optical properties of porphyrins have been carried out mostly on *meso*-substituted[23] porphyrins whereas β-substituted systems have received attention only recently.[24] The reason for that has to be found in the early discovery of the reverse saturable absorption shown by solutions of *meso*-substituted porphyrins in high boiling point solvents, e.g. toluene, under pulsed irradiation with a Nd:YAG laser at 532 nm,[23d] which has stimulated further research on the nonlinear optical properties of these compounds. To our knowledge, studies on the nonlinear optical properties of tetraazaporphyrins and their derivatives with the structures analogous to those presented here have not been reported in the literature so far.

The synthesized $[(Ar)_8TAP]In(X)$'s have shown nonlinear optical behavior for the change of their transmittance in solution at different levels of irradiation.[25] $[(Ar)_8TAP]In(X)$'s solutions behave like reverse saturable absorbers (RSA)[22,26] which become more opaque with the augmentation of the irradiation.[23d] The effect of reverse saturable absorption

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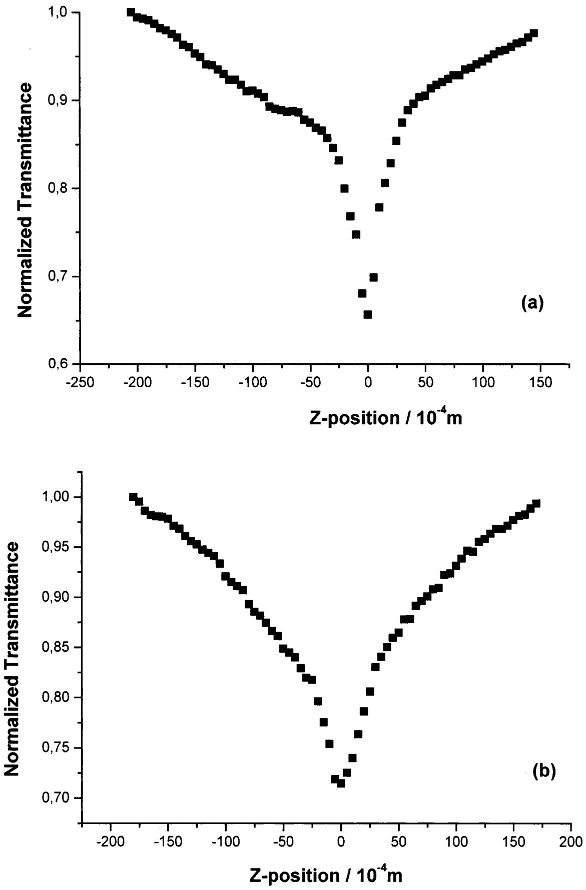

Figure 6. *Z*-scan profiles of **8a** (a) and **8b** (b).

consists of the reversible decrease of the system transmittance with the increase of the incident light intensity.[22] The solutions of dyes showing such a phenomenon are generally described as systems whose photogenerated excited states are strongly light-absorbing.[4d,27] Despite the nonlinearity of the resulting optical effect, the fundamental processes at the basis of the reverse saturable absorption are essentially two consecutive linear absorptions.[4d,22] Nonlinear transmission of $[(Ar)_8TAP]In(X)$ solutions is in the range 60−80% of the linear transmission value. The extent of the transmission decrease depends on the chemical nature of the absorbing $[(Ar)_8TAP]In(X)$. The lowest nonlinear transmission is presented by the groups of species **7** and **8** which are characterized by the presence of CF_3 group in the *para*- or *meta*-position of the phenyl substituent. In these cases the minimum transmittance ranges in the interval 65−70% of the linear value. The typical *Z*-scan profiles for the octakis-((trifluoromethyl)phenyl)-substituted TAP's are presented in Figure 6. In particular, the open-aperture *Z*-scan patterns for **8a**,**b** are shown.

The linear transmission of **8a**,**b** is 75% at 532 nm under the experimental conditions of OL data acquisition. The absorption cross sections σ_0 for **8a**,**b** in the ground state are respectively 1.99 and 1.78 × 10^{-17} cm^2. In these materials the diminution of transmittance is gradual and NLO behavior is observed already at fluence (F) values lower than 2 J cm^{-2} (this corresponds to $|Z| > 170 \times 10^{-4}$ m in the *Z*-scan profile). The presence of two regimes of nonlinearity in the profiles of Figures 6 can be observed. The change of transmittance slope in the *Z*-scan profiles occurs approximately at $Z \approx \pm 50 \times 10^{-4}$ m ($F \approx 10$ J cm^{-2}) and $Z \approx \pm 25 \times 10^{-4}$ m ($F \approx 15$ J cm^{-2}) respectively for **8a**,**b** (Figure 6). This is probably due to the onset of an additional fluence-activated mechanism of absorption when high irradiation occurs.[22] The minimum transmittance of **8a**,**b** in correspondence of the focus ($Z = 0$) is 65−70% of their linear value. If a mechanism of excited-state absorption (ESA)[2,22,23d,27b,28] takes place in the occurrence of RSA behavior for (trifluoromethyl)phenyl-substituted TAP's, then the observation of two possible regimes of nonlinearity could be associated with the involvement of various excited states with different absorption cross sections, whose absorption occurs at different levels of dye solution irradiation.[28b,29] For a RSA based on an ESA mechanism involving a five-level system (Figure 7) the relationship between light-intensity variation through the optical medium and the optical medium properties is[28b]

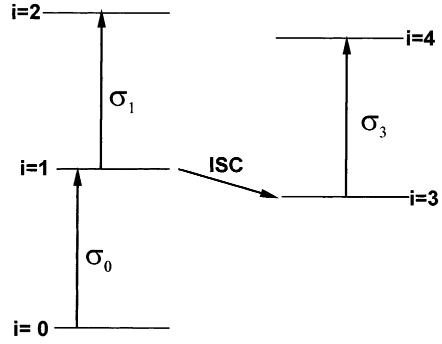

Figure 7. Electronic energy level diagram for a five-level system. The electronic states associated with energy levels $i = 0$, 1, and 2 are singlet states. The electronic states associated with energy levels $i = 3$ and 4 are triplet states.The symbol σ_i represents the absorption cross section for the electronic transition between the *i*th level (lower energy) and the $i + 1$th level (upper energy). ISC represents the process of intersystem crossing from singlet to triplet states. For sake of clarity the various relaxation processes of fluorescence and phosphorescence are omitted.

$$-(\mathrm{d}I_{\mathrm{in}}/\mathrm{d}z) = \sigma_0(N_{\mathrm{T}} - N_1 - N_3)I_{\mathrm{in}} + \sigma_1 N_1 I_{\mathrm{in}} + \sigma_3 N_3 I_{\mathrm{in}} \quad (2)$$

in which N_{T} represents the total number of dye molecules/volume unit, N_{i} defines the population of the *i*th level (see Figure 7) expressed with the same units of N_{T}, and σ_{i} is the absorption cross section of the optical transition originated from the *i*th level. Equation 2 is valid under the assumption that N_2 and N_4 are approximately zero; i.e., the populations of the excited states at the upper energy levels are negligible (Figure 7).[28b] Equation 2 shows that the variation of light intensity through a solution of a dye described as a five-level system is a function of four variable parameters, i.e., N_1, N_3,σ_1, and σ_3, σ_0 being known from the absorption

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characteristics of the dye in the linear regime and N_T being a fixed value in a sample. In the case of species **7** and **8** it is believed that the two different regimes of nonlinearity (Figure 6) are mostly due to different steady-state values of N_1 and N_3 at the various levels of irradiation, σ_1 and σ_3 being exclusively system-dependent and not intensity-dependent parameters.[28b,29] The sole recording of the Z-scan profile is not sufficient for the univocal determination of all variable parameters N_1,N_3,σ_1, and σ_3. If we assume that all the dye molecules are present in the same absorbing state in correspondence of the critical points of the Z-scan profiles (approximation of the saturation of the second-photon absorption from one type of excited state),[28b] in correspondence with the focus and the slope change point, it is reasonable to define an average absorption cross section σ_{av} in these two points as

$$\sigma_{av} = (N_0\sigma_0 + N_1\sigma_1 + N_3\sigma_3)/N_T \tag{3}$$

In correspondence with the slope change in the Z-scan profiles of Figure 6, it is expected that the main contribution of the second-photon absorption arises from the singlet excited state $i = 1$ possessing probably the maximum value of population N_1 at that level of irradiation. In this case $\sigma_{av}N_T$ is constituted mostly by the terms $N_0\sigma_0 + N_1\sigma_1$ and the process of intersystem crossing (ISC) populating the level 3 (Figure 7) is supposed to be not very active at low levels of irradiation. On the other hand, at the maximum levels of irradiation the contribution in $\sigma_{av}N_T$ should be mostly due to $N_0\sigma_0 + N_3\sigma_3$ because of the intervention of ISC which populates the level 3 and decreases the population at $i = 1$. In correspondence of the slope changes it is found $\sigma_{av} = 3.00$ and 3.41×10^{-17} cm^2 respectively for **8a**,**b** when $|Z| = 30 \times 10^{-4}$ m (Figure 6a) and 25×10^{-4} m (Figure 6b), whereas the values of σ_{av} at the focus ($Z = 0$) are respectively 4.89×10^{-17} and 4.29×10^{-17} cm^2 for **8a**,**b**. The present hypothesis of the intervention of different kinds of excited states for the process of second photon absorption involving the triplet excited state as most absorbing state in the regime of maximum irradiation is partially substantiated by the fact that triplet excited states have generally larger absorption cross sections with respect to singlet excited states in conjugated macromolcules.[2b,c, 23e,30]

Another type of Z-scan profile (Figure 8) is presented by the series **5** of the described compounds (Figure 1).

The optical behavior of the compounds belonging to the series **5** is characterized by constant transmission (70% at 532 nm in the linear regime) up to approximately $Z \approx \pm 20 \times 10^{-4}$ m, followed by an abrupt decrease of transmission when the sample approaches the focus. At the focus ($Z = 0$ cm) the incident intensity I_{in} is approximately 2 GW cm^{-2} and the system presents the minimum transmittance which is not less than the 80% of the value presented in the linear regime. This would correspond to an actual resulting transmission of about 55% at the maximum level of irradiation. The series **5** is photochemically stable when the incident radiation intensity is not higher than 2 GW cm^{-2} at 532 nm. For the series **5** the ground-state absorption cross sections σ_0 at 532 nm ranges in the interval (1.0−1.5) × 10^{-16} cm^2, thus resulting relatively higher with respect to compounds **7** and **8**. The solutions of **5** showing the Z-scan profiles of Figure 8 have a linear absorption coefficient α equal to 1.55 cm^{-1}. In correspondence to the focus, i.e., at the maxium level of irradiation, the average absorption cross sections σ_{av} are in the range (4.8−5.2) × 10^{-16} cm^2 for the species **5**.

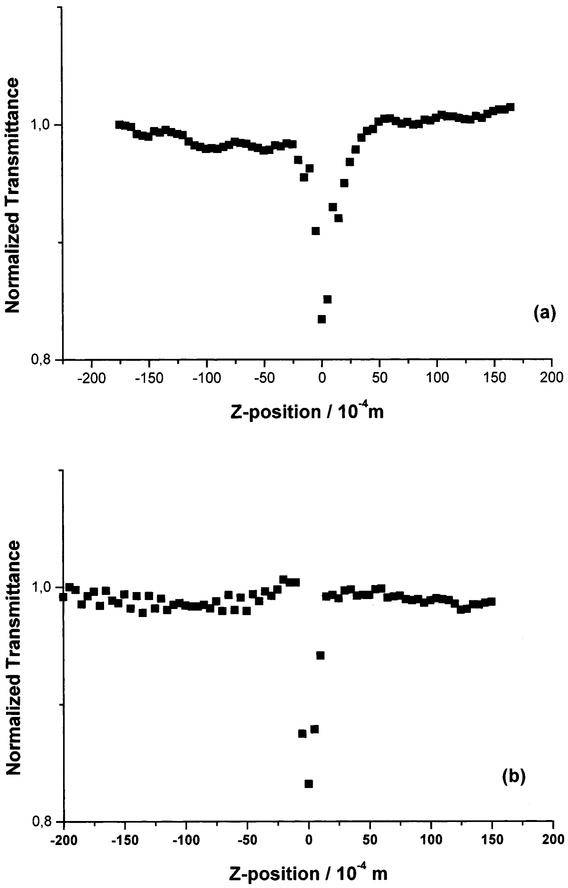

Figure 8. Z-scan profiles of **5b** (a) and **5c** (b).

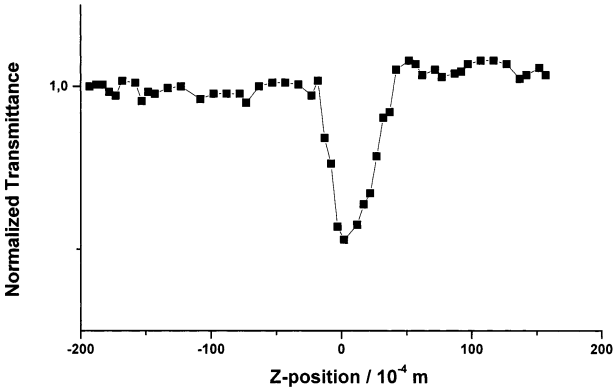

Figure 9. Z-scan profile of **6b** taken as an example of OL effect produced by compounds of series **6**.

In Figure 9, the Z-scan profile of the sole species **6b** is presented as an example for the OL effect produced by the group of compounds **6**.

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In the linear regime of transmission **6b** has a value of σ_0 equal to 2.48×10^{-18} cm^2 whereas at the beam focus ($Z = 0$) with $I_{\mathrm{in}} = 1.3$ GW cm^{-2} σ_{av} reachs the value 3.20×10^{-18} cm^2. At the beam focus the minimum transmittance of **6b** is approximately 90% of the linear transmittance value (=70%).

From the compared analysis of the OL data presented in Figures 6, 8, and 9, it is evident that $[(\mathrm{Ar})_8\mathrm{TAP}]\mathrm{In(X)}$ complexes bearing the same type of substituents on the peripheral phenyl rings have similar values of the minimum transmittance at the maximum levels of irradation. This would confirm unambiguously the determining role of the nature of the peripheral substituents Ar in this class of octaaryl-substituted (TAP)In(X) complexes. In terms of OL performance, the group of compounds **7** and **8**, i.e. those possessing the electron-withdrawing group $\mathrm{CF_3}$ in Ar, present the most convincing results in terms of low transmittance at high levels of irradiation and a NLO behavior starting at relatively low values of incident radiation fluence. The absence of any group with strong electronic character in Ar substituents (series **5**) gives rise to an OL response characterized by a high threshold value for the occurrence of the limiting effect and relatively small decreases of transmittance. The OL effect presented by the series **6** of $[(\mathrm{Ar})_8\mathrm{TAP}]$-In(X) whose structure contains an electron-releasing group $[-\mathrm{C(CH_3)_3}]$ in the substituent Ar is characterized by the lower variations of transmission with the increasing incident intensity. Such a behavior would indicate the relatively scarce polarizability of the conjugated π-electrons in these systems under the action of the high-intensity radiation electric field.[31]

Conclusions

The synthesis of new octaaryl-substituted (tetraazaporphyrinato)indium(III) complexes with nonlinear optical properties is reported. (Octaaryltetraazaporphyrinato)indium(III) chlorides with phenyl, *p-tert*-butylphenyl, *p*-(trifluoromethyl)phenyl, and *m*-(trifluoromethyl)phenyl as aryl substituents have been prepared, and their structures have been characterized. Axial substitution at the central indium atom within this series of compounds could be achieved via Grignard reactions producing novel systems with *p*-(trifluoromethyl)phenyl and 3,5-difluorophenyl as new axial ligands. The optical limiting effect of the synthesized aryl-substituted (tetraazaporphyrinato)indium(III) complexes has been studied with the *Z*-scan technique. It was found that the tetraazaporphyrins substituted with trifluoromethylphenyl groups showed the better limiting performance and presented the highest photochemical stability. Consequently, it was possible to correlate the nonlinear optical behavior of these structurally modulated compounds with the electronic nature of the substituents at the periphery of the macroring and the axial ligands.

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