Synthesis and Some Properties of Aryl- and Aryloxy-Substituted Phthalocyanines and Their Metal Complexes: A Comparison with Porphyrazine and Naphthalocyanine Analogues

Sergej Vagin[a,b] and Michael Hanack*[a]

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The preparation of new octakis[*m*-(trifluoromethyl)phenyl]- and octakis[*m*-(trifluoromethyl)phenoxy]phthalocyanines (**6a** and **6b**) and their complexes with magnesium (**5a**, **5b**) and indium (**7a**, **7b**) is described. Their spectroscopic properties and solubilities are discussed in relation to those of metal-free and metallated octakis[*m*-(trifluoromethyl)phenyl]porphyrazine, as well as those of metal *m*-(trifluoromethyl)-phenyl- and *m*-(trifluoromethyl)phenoxy-substituted 2,3-naphthalocyanines. A drastic decrease in the solubilities of the metal-free phthalocyanines in CH_2Cl_2 was observed on comparing them with *m*-CF_3-phenyl-substituted porphyrazine. However, their solubilities in THF were high enough for NMR spectra to be recorded. Insertion of (chloro)indium into the cavities of these phthalocyanines noticeably enhances the solubilization of the macrocycles, including in CH_2Cl_2.

Introduction

Porphyrazines (Pz) and their analogues, particularly phthalocyanines (Pc) and naphthalocyanines (Nc) and their metal complexes, having been the subjects of intense exploration over several decades due to their peculiar colour characteristics, are also very promising compounds for various applications in materials science.[1]

In recent years they have received attention as active materials in nonlinear optics,[2] in particular as materials displaying pronounced optical limiting effects under high-intensity light irradiation.[3−5]

In solutions of metal phthalo- or naphthalocyanines, it has been shown that solubility and aggregation effects play significant roles in manifestation of optical limiting properties: higher solubility and lower aggregation tendency favours the reverse saturable absorption mechanism.[4,5] In this respect, in a series of our work we have concentrated our attention on the preparation of various soluble porphyrazine derivatives for optical limiting applications. For titanium(IV) and indium(III) pthalocyanines we had previously shown that high solubilities and low tendencies to aggregation in solvents of medium polarity (e.g., chloroform) can be achieved through appropriate peripheral (tetra-*tert*-butyl) and axial (bulky axial ligand) substitution.[4−7] In the case of [tBu$_4$PcTi(X)], where X represents differently substituted catechols, a change in the nature of the axial substituent remarkably alters its optical limiting performance at 532 nm.[6] The highly soluble indium(III) and gallium(III) naphthalocyanines, with four to eight bulky substituents at the periphery of the macrocycle, were also shown to be promising materials for optical limiting in solutions,[4,8,9] as were the less soluble hexadecafluorinated gallium naphthalocyanines.[10]

In addition, we have recently reported on the synthesis and some solution properties of several porphyrazines and their metal complexes with peripheral *m*-(trifluoromethyl)-phenyl (*m*-CF_3Ph) substituents. In particular, [(*m*-CF_3Ph)$_8$PzIn(Cl)] has an extremely enhanced solubility and high photostability in relation to indium(chloro)octaphenylporphyrazine.[11] Furthermore, we have shown that the series of indium(chloro)porphyrazines with *m*-CF_3Ph substituents and annulated benzene rings (hexakis[*m*-(trifluoromethyl)phenyl]benzo[*q*]porphyrazine, tetrakis[*m*-(trifluoromethyl)-phenyl]dibenzo[*l*,*q*]- and [*g*,*q*]porphyrazine and bis[*m*-(trifluoromethyl)phenyl]tribenzo[*g*,*l*,*q*]-porphyrazine, respectively) display good to moderate solubility in THF with optical limiting being drastically enhanced with subsequent benzo-annulation.[12,13] It is also known that extension of the porphyrazine conjugated π-system favours increases in optical non-linearities on passing from tetraazaporphyrin to phthalocyanine and naphthalocyanine metal complexes.[2,14] From these findings, we have recently successfully utilized the solubilizing effect of *m*-(trifluoromethyl)phenyl groups at the peripheries of macrocycles to prepare soluble metal naphthalocyanines.[15]

In order to complete our investigations into the solubilizing effects of *m*-CF_3Ph groups at the peripheries of porphy-

[a] Universität Tübingen, Institut für Organische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-mail: hanack@uni-tuebingen.de
[b] Ivanovo State University of Chemistry and Technology, Organic Chemistry Department, 153460 Ivanovo, F. Engels 7, Russia

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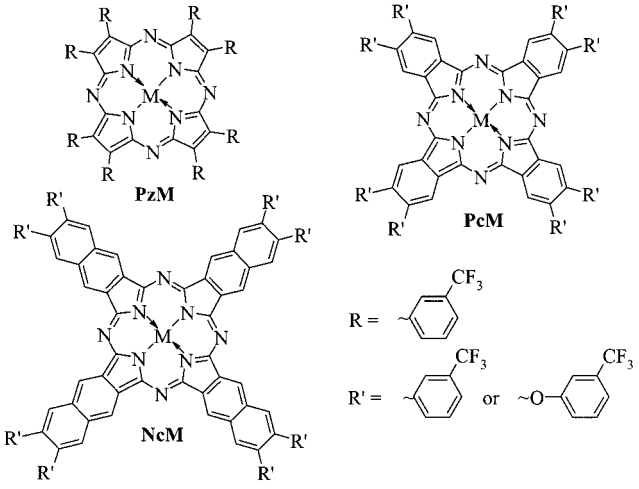
razine macrocycles, we report here on the synthesis and properties of novel octakis[*m*-(trifluoromethyl)phenyl]- (series **a**) and octakis[*m*-(trifluoromethyl)phenoxy]-substituted (series **b**) phthalocyanines and their complexes with magnesium (**5a**, **5b**) and indium (**7a**, **7b**), and summarize their properties in solutions in comparison with octakis(*m*-trifluoromethylphenyl)-substituted tetraazaporphyrin and octakis(*m*-trifluoromethylphenyl/-phenoxy)-substituted metal naphthalocyanine analogues (see Scheme 1).



Numeration of prepared phthalocyanines:

M =	H_2	Mg	In(Cl)
R' = *m*-$CF_3C_6H_5$	**6a**	**5a**	**7a**
R' = *m*-$CF_3C_6H_4O$	**6b**	**5b**	**7b**

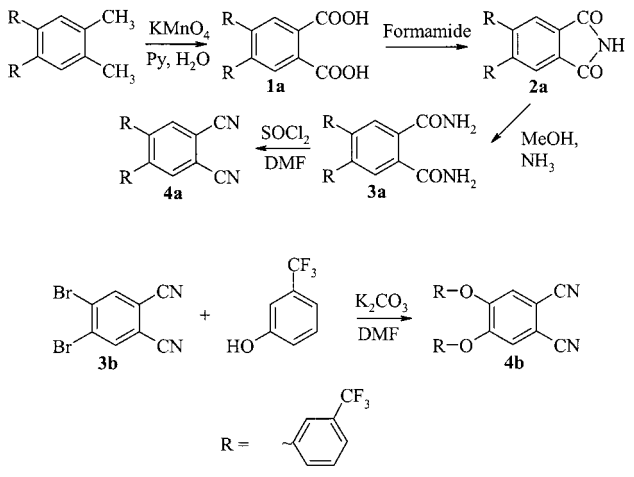
Scheme 1

Despite all the diversity of reported substituted phthalocyanines, only a little information on the preparation of phthalocyanines with eight aryl substituents in peripheral 2,3-positions is available.[16,17] A recent communication described an elegant route to aryl-disubstituted phthalonitriles through reactions between commercially available 4,5-dichlorophthalonitrile and arylboronic acids, and the prepared phthalonitriles underwent cyclotetramerization to give the corresponding phthalocyanines.[18a] Among them, octakis(*o*-trifluoromethylphenyl)- and octakis(*o*-tolyl)-substituted Pcs were prepared. However, no yields or spectroscopic data were reported for these phthalocyanines or their nickel complexes, except for absorption maxima in the visible range. Moreover, the authors only mention that these compounds are soluble in chloroform, which unfortunately does not allow their solubility characteristics to be compared quantitatively with those of other compounds. In general, the presence of bulky aryl groups at the periphery of the phthalocyanine macrocycle increases solubility and suppress aggregation. Thus, Kimura et. al. have reported that tetrakis[penta(*p*-*tert*-butylphenyl)phenyl]phthalocyaninato cobalt does not aggregate in ethanol over a wide range of concentrations.[18b]

We show here that the presence of eight *m*-CF_3-phenyl or *m*-CF_3-phenoxy groups at the periphery of the Pc macrocycle, in combination with suitable central metals, is also effective for the solubilization of phthalocyanines.

Results and Discussion

Synthesis: In our recent work on naphthalocyanines we had shown that bis[*m*-(trifluoromethyl)phenyl]-*o*-xylene can be prepared in sufficient amount by treatment of 4,5-dibromoxylene with the corresponding aryl-Grignard reagent, and can be considered as a starting material both for naphthalocyanines and phthalocyanines. Indeed, radical bromination of methyl groups and subsequent condensation with fumaronitrile gave the corresponding substituted naphthalenedinitrile, which could be used successfully for a cyclotetramerization to form metal naphthalocyanines.[15] On the other hand, oxidation of methyl groups should afford a phthalic acid derivative **1a**, which could be converted into a substituted phthalonitrile by a classical route (see Scheme 2). Here, we have therefore carried out the oxidation of methyl groups in bis[*m*-(trifluoromethyl)-phenyl]-*o*-xylene with $KMnO_4$ in aqueous pyridine in good yield. The formed phthalic acid derivative should be convertible into the anhydride, followed by transformation into the imide.[19] Here we applied the procedure disclosed in a Japanese patent,[22] which allows the acid to be converted into the imide in one step, by direct treatment of the substituted phthalic acid with formamide at high temperature (see Exp. Sect.). According to the obtained analytical data for product **2a**, it is formed quantitatively and contains almost no co-crystallized formamide, and so does not require additional crystallization before its further conversion into the diamide **3a**. Interestingly, this conversion could not be achieved through the usual procedure: treatment with saturated aqueous ammonia did not give the desired diamide



Scheme 2. Synthesis of dinitriles **4a** and **4b**

3a, only starting material **2a** was recovered, probably, due to its hydrophobicity. Only treatment of **2a** with a saturated methanolic solution of ammonia gave the corresponding diamide **3a**, but still containing some quantities of **2a**. It seems that the diamide **3a** is not stable enough for crystallization, so it was always handled at room temperature or below and was used for conversion into the dinitrile **4a** without additional purification. This was carried out by treatment with excessive thionyl chloride in DMF at 0 °C, followed by chromatographic purification and crystallization of the resulting substituted phthalonitrile **4a**.

The synthesis of 4,5-dibromophthalonitrile (**3b**) was carried out starting from 4,5-dibromo-*o*-xylene (oxidation to acid under the same conditions as used for the preparation of **1a**). A direct conversion of 4,5-dibromophthalic acid into imide was again achieved by treatment with formamide, analogously to the synthesis of **2a**, giving a crystalline product (4,5-dibromophthalimide·0.5 formamide) in 90−95% yield. This was treated with saturated aqueous ammonia, followed by treatment with $SOCl_2$ to form **3b** as described for the analogous dichloro and mononitro derivatives.[20,21]

4,5-Bis[*m*-(trifluoromethyl)phenoxy]phthalonitrile (**4b**) (Scheme 2), an oxygenated analogue of **4a**, was prepared by treatment of 4,5-dibromophthalonitrile (**3b**) with 3-trifluoromethylphenol as described in the Exp. Sect., similarly to literature procedures.[21,23]

Magnesium phthalocyanines **5a** and **5b**, and indium phthalocyanine **7a** (see Scheme 1) were prepared by template cyclotetramerization of the corresponding dinitriles **4a** and **4b**, respectively. Under the conditions described in the Exp. Sect., **7a** is formed as a crystalline product − a solvate with chloronaphthalene (1:1 by integration of its ^1H NMR spectrum), which gives pure indium(chloro)phthalocyanine **7a** after precipitation from THF solution into methanol. Metal-free phthalocyanines **6a** and **6b** were prepared by treatment of magnesium complexes **5a** and **5b**, respectively, in acidic media. Indium phthalocyanine **7b** was obtained through a direct metallation of **6b** with $InCl_3$, as often carried out in our previous work.[11,12]

Properties of Prepared Phthalocyanines in Solutions: As we had shown earlier,[11] the introduction of CF_3 groups at the *meta*-positions of phenyl groups in [(*m*-$CF_3Ph)_8PzH_2$] resulted in very good solubility of this macrocycle in most organic solvents, including methanol. Its solubility in dichloromethane was found to be ca. 200 mg/mL, and the solubility of its metal complexes was also very high. We were therefore also expecting a high solubility for (*m*-$CF_3Ph)_8PcH_2$ (**6a**). Surprisingly, though, both this compound and its oxygenated analogue (*m*-$CF_3PhO)_8PcH_2$ (**6b**) show poor solubility in CH_2Cl_2, while being moderately soluble in THF. The UV/Vis spectra of **6b** in CH_2Cl_2 (saturated solution) and in a mixture of $CHCl_3$ +1% THF are compared in Figure 1, in which the aggregation of compound **6b** in CH_2Cl_2 can clearly be seen. Additionally, aggregation of **6a** in CH_2Cl_2 was found to be a kinetic process, as demonstrated in Figure 2. Thus, being less aggregated upon dissolution in CH_2Cl_2 (with excess of solid), after some time it forms a colloidal solution exhibiting opalescence, which coagulates after several days. This can be seen in a decrease in the intensities of the Q_x and Q_y bands, which originate from non-aggregated macrocycle, and the growth of a broad absorption band on the red side of the Q_x band within a few hours, attributable to aggregated species and microparticles. Indeed, a red shift and broadening of the Q-bands of phthalocyanines in the solid state are often observed due to Davydov splitting.[24a] Additionally, the formation of J-aggregates of (tBu)$_4$PcSb in non-aqueous solvents resulting in a red shift of the Q-band was reported recently.[24b]

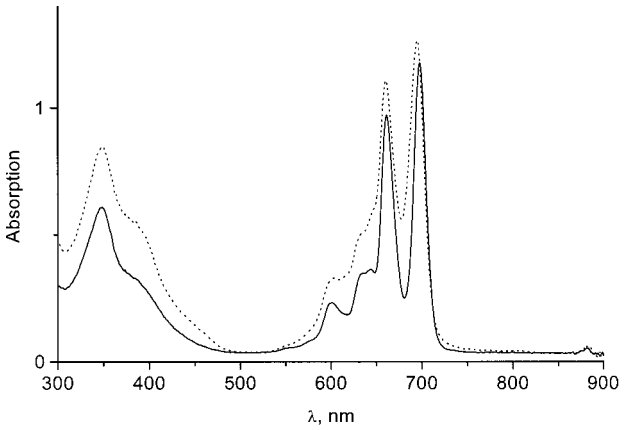


Figure 1. UV/Vis spectra of (*m*-$CF_3PhO)_8PcH_2$ (**6b**) in $CHCl_3$ + 1% THF (6.2×10^{-6} M, solid line) and in CH_2Cl_2 (saturated solution, 1 cm thick cuvette, dotted line)

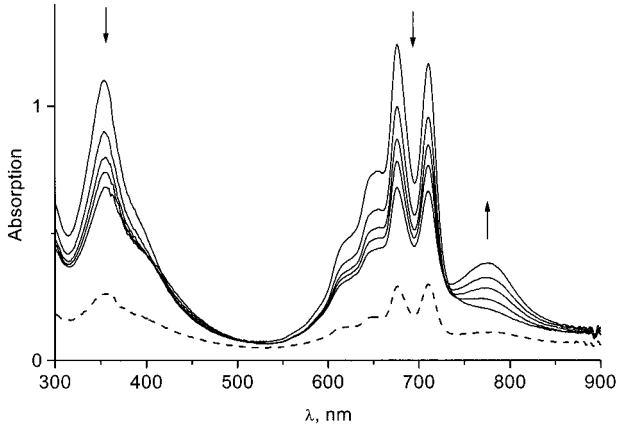


Figure 2. Changes in the UV/Vis spectrum (1-mm thick cuvette) of (*m*-$CF_3Ph)_8PcH_2$ in CH_2Cl_2 with time; in the order of the B-band decrease: immediately after dissolution, after 30 min, 1.5 h, 3 h and 8 h; dashed line shows the spectrum after several days, when coagulation has occurred

Such behaviour can be explained in terms of crystalline lattice features of compound **6a**: it can form several modifications (depending on their preparation method, e.g. fast precipitation from H_2SO_4), which differ in their solubility. Dissolution of the modification with a lower crystal lattice energy is fast and is followed by association of molecules to form a more stable modification, resulting in precipitation

of the compound after dissolution. The transformation of modifications can occur in the solid state as well, but much more slowly. In contrast, a true solution of **6a** in a chloroform/THF mixture does not show any evidence of colloid formation (or decomposition) with time: the solvation effect of this system is high enough to prevent the formation of microparticles.

As expected from the results on *m*-CF_3Ph- and *m*-CF_3PhO- substituted metal naphthalocyanines (Scheme 1),[15] the solubility of **6a** in THF appeared to be better than that of **6b**. Thus, because of the insufficient solubility of **6b** we were unable to record its ^{13}C NMR spectrum in [D_8]THF, whereas the solubility of **6a** was enough for the ^{13}C NMR spectrum to be obtained with all carbon signals being resolved. Surprisingly, the magnesium complex **5a** appeared to be poorly soluble in most organic solvents including THF, except in hot pyridine, in contrast to **5b**, which is highly soluble in THF and $CHCl_3$. On the other hand, indium(chloro) complexes **7a** and **7b** are highly soluble in THF and have good solubility in CH_2Cl_2. Thus, **7a** does not aggregate in CH_2Cl_2 at ca. 3×10^{-6} M or at 9×10^{-5} M concentrations, and shows only slight J-aggregation at a concentration of 3.5×10^{-4} M (see Figure 3). Similarly, **7b** is not aggregated in dichloromethane at concentrations of 3×10^{-6} M and 9×10^{-5} M, and is only slightly aggregated at concentrations higher than 3×10^{-4} M.

Both indium phthalocyanines **7a** and **7b** slowly decompose in solution, which is even more evident for diluted solutions. Thus, ca. 50% decomposition of a 3×10^{-6} M solution of **7a** or **7b** occurs within approximately one day. In the case of indium naphthalocyanine analogues, their decomposition was considerably faster, so we could not isolate them in pure state.[15] As was also found for other soluble indium phthalocyanines, such as tetra(alkenyloxy)phthalocyaninato(chloro)indium complexes, they also exhibit a tendency to decompose in solution, but are highly stable when incorporated into solid polymer films,[25] which permits their utilization for different applications in this state. This might also apply to the described indium compounds **7a** and **7b**.

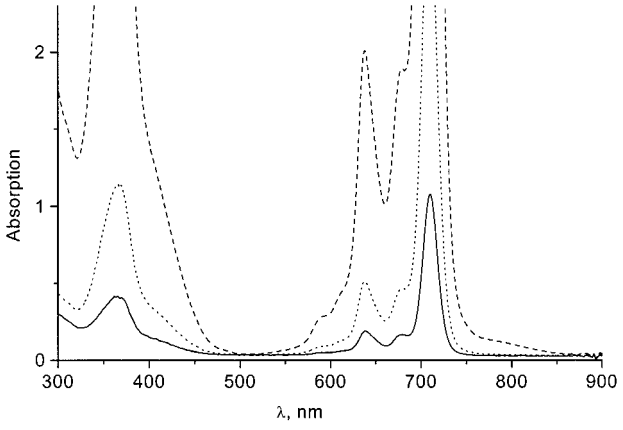


Figure 3. UV/Vis spectra of [(*m*-CF_3Ph)$_8$PcIn(Cl)] in CH_2Cl_2 at different concentrations: 2.86×10^{-6} M (solid line), 8.6×10^{-5} M (dotted line) and 3.5×10^{-4} M (dashed line)

UV/Vis data for compounds **5a**−**7a** and **5b**−**7b** are given in the Exp. Sect. As in the case of naphthalocyanines, introduction of oxygen between aryl substituents and the macrocycle results in a noticeable blue shift of the Q-bands, as well as in a decrease of molar extinction coefficients, for the same reason as explained for Ncs.[15] Additionally, it produces a red shift of the shoulder on the red side of the B-band in the indium complex **7b**, thus resulting in a narrowing of the transparent window between 430 and 620 nm as compared to **7a** in solution at equal concentration, which becomes even more obvious at higher concentrations.

Comparison of the literature data on Q_y and Q_x maxima of (*o*-CF_3Ph)$_8$PcH$_2$ (678 and 712 nm respectively) and (*p*-CF_3Ph)$_8$PcH$_2$ (690 and 723 nm)[18a] with (*m*-CF_3Ph)$_8$PcH$_2$ **6a** (688, 720 nm) in chloronaphthalene shows that the conjugation effect of *m*-CF_3Ph substituents on the Pc macrocycle is close to that of *p*-CF_3Ph, indicating lower steric hindrance for rotation of *m*-CF_3Ph around the C−C bond between the substituent and the Pc core in comparison with *o*-CF_3Ph. On the other hand, *m*-CF_3Ph substituents in the periphery of phthalocyanine have a larger radius of rotation than *p*-CF_3Ph, and so prevent the aggregation of the macrocycles more efficiently.

^{1}H NMR spectra of metal-free phthalocyanines **6a** and **6b** in [D_8]THF are shown for comparison in Figure 4. They were recorded at concentrations of **6a** and **6b** close to saturation. The concentration of **6a** in these measurements was approximately five times higher than that of **6b**, as estimated by comparative integration of their signals and the signals of non-deuterated solvent. The relative broadening of NH and α-H signals in the spectrum of **6a** indicates a noticeable aggregation of this compound, in contrast to **6b**. In ^{13}C NMR spectrum of **6a** the signals of inner carbon atoms (C-1 and C-2) were also substantially broadened, probably for the same reason. Unlike those of **6a**, the C-1 and C-2 signals of porphyrazine (*m*-CF_3Ph)$_8$PzH$_2$ in $CDCl_3$ show only slight broadening, and the inner NH protons ap-

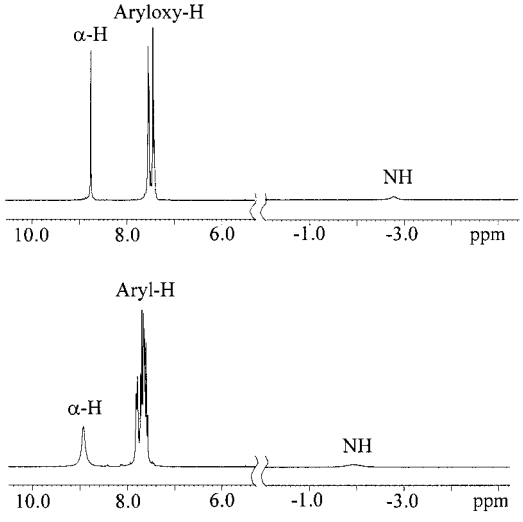


Figure 4. ^{1}H NMR spectra of **6b** (upper) and **6a** (lower) in [D_8]THF

pear at δ = −1.76 ppm as a relatively sharp signal, indicating no aggregation.[11,26]

^{13}C NMR spectra, showing good resolution, and signal assignments for indium phthalocyanines **7a** and **7b** are given for comparison in Figure 5. In contrast to **6a**, the inner carbon atoms in **7a** give sharp signals. Their positions depend on the natures of the peripheral substituents, being shifted to upper field upon oxygenation (see Figure 5), as well as on the nature of central metal. They exhibit low-field shifts when, for example, **6a** and **7a** are compared (150.3 and 136.3 ppm for **6a** and 154.7 and 137.8 ppm for **7a** respectively). In contrast, their positions in magnesium phthalocyanine **5b** and the naphthalocyanine (*m*-$CF_3PhO)_8$NcMg analogue[15] are almost the same (δ = 152.7, 137.0 and 153.4 and 136.9 ppm respectively), indicating no strong electron redistribution in the centre of the phthalocyanine macrocycle upon symmetrical benzo-annulation. In contrast, on going from indium phthalocyanine **7a** to indium porphyrazine [(*m*-$CF_3Ph)_8$PzIn(Cl)], the electron redistribution is more obvious and results in an increasing electron density in the centre of the porphyrazine macrocycle with benzo-annulation. Thus, the positions of C-1 and C-2 for [(*m*-$CF_3Ph)_8$PzIn(Cl)] were found at δ = 156.6 and 143.0 ppm, respectively.[11] However, the position of carbon resonance C-9 (quadruplet with splitting constant $^2J \approx 32-33$ Hz) was found to be almost independent of the nature of central metal, macrocycle or solvent in the series of *m*-CF_3Ph (δ = 131.2−131.5 ppm) and *m*-CF_3PhO (δ = 132.6−133.1) substituted compounds, as would be expected.

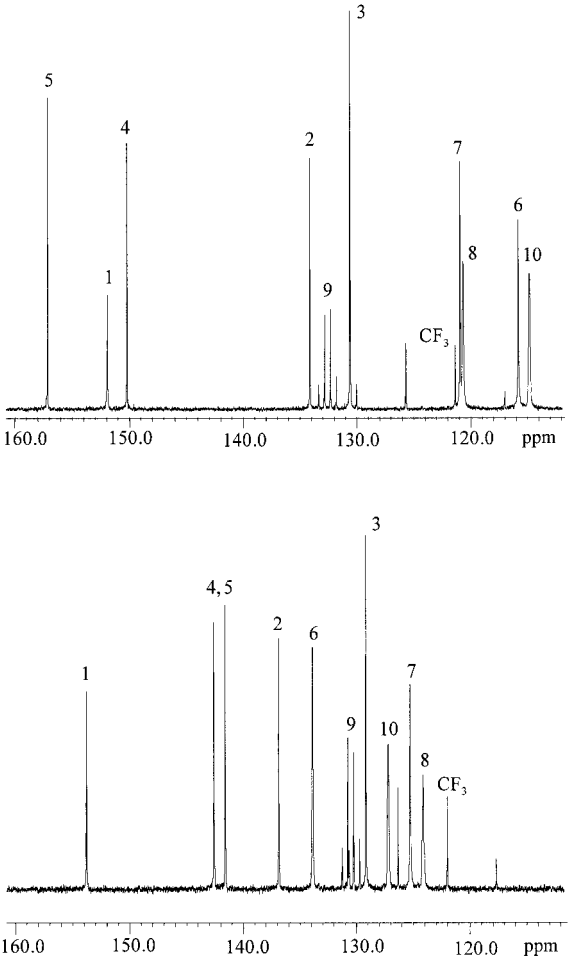
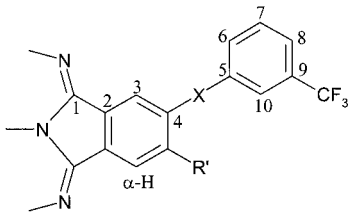


Figure 5. ^{13}C NMR spectra of indium phthalocyanines **7b** in $CDCl_3$ (upper) and **7a** in [D_8]THF (lower); the signal assignment (see Scheme 3) is based on results of previous work[11,15]



Scheme 3. Numbering of the atoms in phthalocyanines used for NMR assignment

Conclusions

We have demonstrated that the introduction of eight *m*-CF_3Ph groups at the peripheries of porphyrazine, phthalocyanine and naphthalocyanine macrocycles results in enhanced solubility of these compounds, so their spectral properties in solution can be investigated. However, in contrast to the very high solubilities of (*m*-$CF_3Ph)_8PzH_2$ and its metal complexes in most organic solvents, the solubilizing effect of *m*-CF_3Ph or *m*-CF_3PhO substituents on phthalocyanine and naphthalocyanine is not so pronounced: the nature of the central metal and solvent start to play important roles. The best solvent, in which the Pc and Nc derivatives have good solubility in most cases, was found to be tetrahydrofuran.

Experimental Section

4,5-Bis[*m*-(trifluoromethyl)phenyl]-*o*-xylene was prepared as described before.[15] 4,5-Dibromophthalonitrile was synthesised from *o*-xylene similarly to other phthalonitrile derivatives.[19−22] 3-trifluoromethylphenol (99% pure) and solvents were purchased chemicals and were used without additional purification.

The following equipment was used for characterization: UV/Vis: Shimadzu UV-365. FT-IR: Bruker Tensor 27; ^1H and ^{13}C NMR: Bruker AC 250 (^1H: 250.131 MHz. ^{13}C: 62.902 MHz). MS: Varian Mat 711 (FD, FAB); Elemental analyses: Euro EA 3000.

4,5-Bis[*m*-(trifluoromethyl)phenyl]phthalic Acid (1a): $KMnO_4$ (20 g, 127 mmol) was added slowly (***exothermic reaction!***) to a boiling solution of 4,5-bis[*m*-(trifluoromethyl)phenyl]-*o*-xylene (7.7 g, 19.5 mmol) in a pyridine (60 mL)/water (25 mL) mixture, and the reaction mixture was boiled without external heating. After all the $KMnO_4$ had been added, the mixture was heated at reflux for 1 h and cooled, and the excess $KMnO_4$ was removed with a small portion of ethanol. The formed MnO_2 was filtered off and washed with hot water, and the filtrate was acidified with concentrated HCl (until pH ≈ 1−2) and left overnight. The formed precipitate was filtered off, thoroughly washed with water and dried. Yield 7.7 g (87%) of white powder. M.p. 206 °C (dec.). ^1H NMR ([D_6]DMSO):

δ = 7.32 (s, 2 H, broadened), 7.47−7.57 (m, 6 H), 7.76 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 124.2 (q, $^1J \approx 272.4$ Hz), 124.5 (q, $^3J \approx 3.2$ Hz), 126.7 (q, $^3J \approx 3.7$ Hz), 129.5 (q, $^2J \approx 31.9$ Hz), 129.9 (s), 130.8 (s), 133.3 (s), 133.9 (s), 140.2 (s), 141.2 (s), 168.6 (s) ppm. $C_{22}H_{12}F_6O_4$ (454.33): calcd. C 58.16, H 2.66; found C 58.23, H 2.73.

4,5-Bis[*m*-(trifluoromethyl)phenyl]phthalimide (2a): Compound **1a** (7.7 g, 17 mmol) was heated in formamide (20 mL) at 180−190 °C for 1.5−2 h and then cooled to 140−150 °C. At this temperature a solidification process takes place, and the temperature was maintained until the complete solidification of reaction mixture to give a white solid cake. After cooling to room temperature, the solid was manually crushed, washed thoroughly with water and dried (80 °C, vacuum) to give the title compound in quantitative yield. M.p. 210.5−212.5 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 7.31 (s, 2 H, broadened), 7.48−7.60 (m, 6 H), 7.82 (s, 2 H), 11.41 (s, 1 H, broadened) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 124.2 (q, $^1J \approx 272.4$ Hz), 124.8 (q, $^3J \approx 3.7$ Hz), 125.1 (s), 126.8 (q, $^3J \approx 3.7$ Hz), 129.4 (q, $^2J \approx 31.9$ Hz), 130.0 (s), 132.8 (s), 134.0 (s), 140.2 (s), 144.9 (s), 168.9 (s) ppm. MS (FAB): *m*/*z* = 436.1 (100), [MH$^+$]; 418.0 (45), [M − F]$^+$. $C_{22}H_{11}F_6NO_2$ (435.33): calcd. C 60.70, H 2.55, N 3.22; found C 60.67, H 2.49, N 2.84.

4,5-Bis[*m*-(trifluoromethyl)phenyl]phthalamide (3a) and -phthalonitrile (4a): Methanol (100 mL) was saturated with dry ammonia at 0 °C and all the prepared phthalimide **2a** was transferred into this solution. The formed suspension was stirred in an ice-bath until complete dissolution of imide under a weak ammonia stream, which was continued for 20−30 min. The course of the reaction was also monitored by TLC (acetone). After that, ammonia and methanol were removed under vacuum at room temperature or below, and the residue was dried at room temperature in vacuo. As was found from its ^{1}H and ^{13} C NMR spectra, the obtained residue consists mainly of phthalamide **3a** with minor admixture of starting material and was used for further conversion into dinitrile without additional purification. The obtained material was dissolved in cold DMF (preliminary dried with molecular sieves, 50 mL) and cooled to −3 to −5 °C, followed by slow addition of freshly distilled $SOCl_2$ (20 mL) such that the temperature of the reaction mixture did not rise above 0 °C. After completion of the addition, the reaction mixture was kept at 0 °C for 1−2 h and then at room temperature overnight. The formed suspension was poured onto ice (approx. 300 g) and stirred for 1 h, followed by filtration and copious washing of the formed precipitate with water. After drying in vacuo (80 °C) it was subjected to column chromatography (silica gel, chloroform, first large colourless fraction was taken) followed by crystallization from heptane to yield colourless crystals (3.5 g, 50% by acid). M.p. 169.5−171 °C. ^{1}H NMR ($CDCl_3$): δ = 7.27−7.30 (d + s, 4 H, broadened), 7.45 (t, $^3J \approx 8.1$ Hz, 2 H, broadened), 7.59 (d, $^3J \approx 7.6$ Hz, 2 H, broadened), 7.90 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 114.8 (s), 115.6 (s), 123.4 (q, $^1J \approx 272.8$ Hz), 125.6 (q, $^3J \approx 3.7$ Hz), 126.2 (q, $^3J \approx 3.7$ Hz), 129.5 (s), 131.4 (q, $^2J \approx 33.3$ Hz), 132.5 (s, broadened), 135.3 (s), 137.7 (s), 144.4 (s) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (ν_{Ar-H}) w, 2238 ($\nu_{C\equiv N}$) m, 1598 w, 1539 vw, 1491 vw, 1477 w, 1442 w, 1373 m, 1332 (ν_{C-F}) vs, 1278 s, 1222 m, 1173 (ν_{C-F}) s, 1122 (ν_{C-F}) vs, 1099 m, 1078 s, 1053 m, 1002 w, 945 vw, 936 w, 924 w, 912 m, 901 w, 831 w, 811 m, 803 m, 755 vw, 719 m, 710 m, 703 m, 691 m, 654 m, 592 w, 544 w, 522 w. $C_{22}H_{10}F_6N_2$ (416.33): calcd. C 63.47, H 2.42, N 6.73; found C 63.54, H 2.39, N 6.43.

4,5-Bis[*m*-(trifluoromethyl)phenoxy]phthalonitrile (4b): 4,5-Dibromophthalonitrile (3 g, 10.5 mmol), 3-trifluoromethylphenol (12 g, 74 mmol) and K_2CO_3 (15 g, 109 mmol) in dry DMF (35 mL) were heated at 100 °C for 1.5 h. After cooling, the reaction mixture was transferred into water (300 mL) and stirred for 1 h. The formed precipitate was filtered off, washed with water, dried at 80 °C in vacuo and crystallized from toluene/heptane. Yield after drying: 3.2 g (68%) white crystals. M.p. 101.0−101.5 °C. ^{1}H NMR ($CDCl_3$): δ = 7.17−7.24 (m, 4 H), 7.31 (s, 2 H), 7.48−7.59 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 112.0 (s), 114.4 (s), 116.1 (q, $^3J \approx 3.7$ Hz), 122.3 (s), 122.4 (q, $^3J \approx 3.9$ Hz), 123.2 (q, $^1J \approx 272.8$ Hz), 123.8 (s), 131.2 (s), 133.1 (q, $^2J \approx 33.3$ Hz), 150.9 (s), 154.6 (s) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1} (ν_{Ar-H}) w, 3041 (ν_{Ar-H}) w, 2239 ($\nu_{C\equiv N}$) m, 1598 m, 1585 m, 1554 m, 1495 s, 1449 s, 1398 m, 1324 (ν_{C-F}) vs, 1302 vs, 1283 m, 1209 m, 1187 (ν_{C-F}) vs, 1127 (ν_{C-F}) vs, 1094 m, 1063 m, 1002 w, 925 s, 918 s, 899 m, 882 m, 872 m, 825 w, 798 s, 743 m, 697 s, 653 m, 534 m. $C_{22}H_{10}F_6N_2O_2$ (448.33): calcd. C 58.94, H 2.25, N 6.25; found C 59.03, H 2.05, N 5.90.

Octakis[*m*-(trifluoromethyl)phenyl]phthalocyaninatomagnesium (5a): Magnesium turnings (40 mg, 1.65 mmol) were dissolved in an octanol/pentanol mixture (1:1, 6 mL) at 170 °C and **4a** (850 mg, 2.04 mmol) was added. The reaction mixture was stirred at 170 °C for 1 h, resulting in solidification. After cooling, it was washed thoroughly with hexane and methanol, dissolved in boiling pyridine and filtered hot. After cooling, the precipitation of the product was completed by addition of methanol. Filtration and drying in vacuo (80 °C) yielded a dark bluish-green solid (660 mg, 76%). UV/Vis (pyridine): $\lambda_{max.}$ (rel. intensity) = 695 (1.000), 626 (0.173), 367 (0.387) nm. FT-IR (KBr): $\tilde{\nu}$ = 3675 cm^{-1} (ν_{O-H}) w, 1614 w, 1479 m, 1438 m, 1414 m, 1336 (ν_{C-F}) vs, 1276 w, 1255 m, 1218 w, 1169 (ν_{C-F}) s, 1125 (ν_{C-F}) s, 1098 s, 1086 s, 1076 s, 1064 m, 1044 m, 953 w, 896 m, 824 w, 805 m, 769 m, 752 m, 714 s, 705 m, 659 m. $C_{88}H_{40}F_{24}MgN_8 \cdot H_2O$ (1689.63 + 18.0): calcd. C 61.90, H 2.48, N 6.56; found C 61.66, H 2.16, N 6.32.

Octakis(*m*-(trifluoromethyl)phenyl)phthalocyanine (6a): Compound **5a** (400 mg, 0.24 mmol) was dissolved in 100% H_2SO_4 and filtered (G3) into water. The formed precipitate was centrifuged and washed with water and methanol. Drying in vacuo (60 °C) yielded a dark greenish-blue powder (290 mg, 73%). UV/Vis ($CHCl_3$ +1% THF): $\lambda_{max.}$(log ε) = 713 (5.32), 677 (5.25), 648 (4.75), 614 (4.58), 355 (5.06) nm. ^{1}H NMR ([D$_8$]THF): δ = −1.93 ppm(s, 2 H, broad), 7.57−7.82 (m, 32 H), 8.93 (s, 8 H, broadened) ppm. ^{13}C NMR ([D$_8$]THF): δ = 125.1 (s + q, non resolved), 125.1 (q, $^1J \approx 272.4$ Hz), 128.3 (q, $^3J \approx 3.2$ Hz), 130.2 (s), 131.4 (q, $^2J \approx 32.4$ Hz), 134.8 (s), 136.3 (s, broadened), 142.6 (s), 142.8 (s), 150.3 (s, broad) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3296 (ν_{N-H}) cm^{-1} w, 1615 w, 1503 w, 1492 w, 1428 m, 1332 (ν_{C-F}) vs, 1270 m, 1237 w, 1216 w, 1168 (ν_{C-F}) s, 1126 (ν_{C-F}) s, 1111 s, 1097 m, 1076 s, 1042 m, 1015 m, 948 w, 899 m, 822 w, 805 m, 754 m, 708 s, 675 vw, 658 m, 625 vw, 588 w. $C_{88}H_{42}F_{24}N_8$ (1667.33): calcd. C 63.39, H 2.54, N 6.72; found C 63.41, H 2.48, N 6.82.

Octakis(*m*-(trifluoromethyl)phenyl)phthalocyaninato(chloro)indium-(III) (7a): Dinitrile **4a** (300 mg, 0.72 mmol) and $InCl_3$ (60 mg, 0.27 mmol) were placed in a preheated oil bath (215 °C) followed by addition of chloronaphthalene (0.3 mL). The reaction mixture was kept at this temperature for 1−1.5 h (the formation of crystalline product was observed) and then cooled. The obtained mass was washed thoroughly with hexane and methanol, dissolved in THF and filtered into methanol. The precipitation was completed by addition of a small amount of water. The formed precipitate was centrifuged and dried in vacuo (60 °C), yielding a dark green powder (150 mg, 46%). UV/Vis ($CHCl_3$ +1% THF): $\lambda_{max.}$ (log ε) = 710 (5.56), 679 (4.68), 639 (4.75) nm. ^{1}H NMR ([D$_8$]THF): δ = 7.53−7.78 (m, 32 H), 9.41 (s, broadened) ppm. ^{13}C NMR

([D$_8$]THF): δ = 125.1 (q, $^1J \approx 271.9$ Hz), 125.1 (q, $^3J \approx 3.7$ Hz), 126.2 (s), 128.2 (q, $^3J \approx 3.7$ Hz), 130.1 (s), 131.5 (q, $^2J \approx 32.4$ Hz), 134.9 (s), 137.8 (s), 142.6 (s), 143.6 (s), 154.7 (s) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1} w, 1480 m, 1417 m, 1334 (ν_{C-F}) vs, 1254 m, 1217 w, 1169 (ν_{C-F}) s, 1128 (ν_{C-F}) s, 1101 s, 1076 s, 1042 w, 954 m, 900 m, 822 m, 804 m, 765 m, 746 m, 712 s, 658 m. $C_{88}H_{40}ClF_{24}InN_8$ (1815.59): calcd. C 58.22, H 2.22, N 6.17; found C 58.52, H 2.15, N 6.20.

Octakis(*m*-(trifluoromethyl)phenoxy)(phthalocyaninato)magnesium (5b): Magnesium turnings (54 mg, 2.22 mmol) were dissolved in an octanol/pentanol mixture (1:1, 10 mL) at 170 °C, followed by addition of the dinitrile **4b** (1 g, 2.23 mmol), and the temperature was maintained for 1.5 h. After cooling, the reaction mixture was transferred into hexane, centrifuged, washed thoroughly with hexane and chromatographed on silica gel (chloroform). The coloured fraction was collected, the solvent was partially evaporated, and hexane was added to the residue. The formed precipitate was filtered off, washed with a hexane/chloroform mixture (ca. 4:1) and dried in vacuo to give a blue powder (470 mg, 46%). UV/Vis ($CHCl_3$): $\lambda_{max.}$ (log ε) = 678 (5.47), 650 (4.61), 612 (4.65), 359 (5.07) nm. ^{1}H NMR ([D$_8$]THF): δ = 7.43−7.59 (m, 32 H), 8.87 (s, 8 H) ppm. ^{13}C NMR ([D$_8$]THF): δ = 114.8 (q, $^3J \approx 4.2$ Hz), 117.2 (s), 120.7 (q, $^3J \approx 3.7$ Hz), 121.7 (s), 124.9 (q, $^1J \approx 272.4$ Hz), 131.6 (s), 132.9 (q, $^2J \approx 32.8$ Hz), 137.0 (s), 149.5 (s), 152.7 (s), 159.3 (s) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1} (ν_{Ar-H}) vw, 1594 m, 1490 s, 1450 s, 1400 s, 1328 (ν_{C-F}) vs, 1283 s, 1212 m, 1171 (ν_{C-F}) s, 1126 (ν_{C-F}) s, 1092 s, 1064 s, 1029 s, 1002 w, 921 s, 823 w, 793 m, 751 m, 696 m, 656 w, 515 vw. $C_{88}H_{40}F_{24}MgN_8O_8$ (1817.62): calcd. C 58.15, H 2.22, N 6.16; found C 58.26, H 2.24, N 6.36.

Octakis[*m*-(trifluoromethyl)phenoxy]phthalocyanine (6b): Compound **5b** (600 mg) was suspended in a mixture of CH_3COOH (50 mL) and CF_3COOH (5 mL) at 100 °C for 3−4 h. The course of the reaction was monitored by UV/Vis and TLC. After complete conversion of starting material into metal-free Pc, the reaction mixture was cooled and a small amount of water was added to precipitate the product completely. The precipitate was centrifuged and washed thoroughly with methanol. Drying in vacuo (60 °C) gave a greenish-blue powder (500 mg, 84%). UV/Vis ($CHCl_3$ +1% THF): $\lambda_{max.}$ (log ε) = 698 (5.26), 662 (5.18), 644 (4.72), 601 (4.50), 349 (4.96) nm. ^{1}H NMR ([D$_8$]THF): δ = −2.77 (s, 2 H, broad), 7.40−7.57 (m, 32 H), 8.76 (s, 8 H) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3290 cm^{-1} (ν_{N-H}) w, 3074 (ν_{Ar-H}) vw, 1594 m, 1492 m, 1449 s, 1401 m, 1329 (ν_{C-F}) vs, 1287 s, 1171 (ν_{C-F}) s, 1126 (ν_{C-F}) s, 1087 m, 1064 m, 1016 m, 919 s, 793 m, 751 m, 697 m, 657 w. $C_{88}H_{42}F_{24}N_8O_8$ (1795.33): calcd. C 58.87, H 2.36, N 6.24; found C 59.09, H 2.29, N 6.28.

Octakis[*m*-(trifluoromethyl)phenoxy]phthalocyaninato(chloro)-indium(III) (7b): Compound **6b** (100 mg) and $InCl_3$ (70 mg) in DMF (25 mL), with a few drops of 3-picoline, were heated at 150 °C for 1.5−2 h with periodical UV/Vis monitoring. After disappearance of starting material, the reaction mixture was cooled, poured into water, centrifuged and washed with methanol (with addition of a little water when necessary). After drying, a dark green material (100 mg, 92%) was obtained. UV/Vis ($CHCl_3$): $\lambda_{max.}$ (log ε) = 696 (5.45), 667 (4.64), 627 (4.65), 365 (4.99) nm. ^{1}H NMR ($CDCl_3$): δ = 7.27−7.49 (m, 32 H), 8.83 (s, 8 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 114.8 (q, $^3J \approx 4.2$ Hz), 115.8 (s), 120.7 (q, $^3J \approx 3.7$ Hz), 120.9 (s), 123.5 (q, $^1J \approx 272.4$ Hz), 130.6 (s), 132.6 (q, $^2J \approx 32.8$ Hz), 134.1 (s), 150.2 (s), 151.9 (s), 157.1 (s) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3074 cm^{-1} (ν_{Ar-H}) vw, 1594 m, 1491 s, 1450 s, 1402 s, 1326 (ν_{C-F}) vs, 1283 s, 1210 s, 1172 (ν_{C-F}) s, 1127 (ν_{C-F}) s, 1091 s, 1064 s, 1031 s, 1002 vw, 921 s, 820 vw, 794 m, 744 m, 696 s, 656 w, 515 vw. MS (FD): *m*/*z* = 1942.8 (100), [M$^+$]. $C_{88}H_{40}ClF_{24}InN_8O_8{\cdot}H_2O$ (1943.58 + 18.0): calcd. C 53.88, H 2.16, N 5.71; found C 53.35, H 2.04, N 5.64.

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