Synthesis and Spectroscopic Properties of Non-Symmetrical Benzo-Annulated Porphyrazines and Their Metal Complexes

Sergej I. Vagin[b] and Michael Hanack*[a]

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New highly stable benzo-fused *m*-trifluoromethylphenyl porphyrazines and their complexes with Mg and In were synthesized by cross-condensation of phthalonitrile and bis(*m*-trifluoromethylphenyl)fumaronitrile. Their ^1H and ^{13}C NMR spectra were recorded and described. The Q- and B-bands in the UV/Vis spectra of the metal complexes show the characteristic splitting upon consecutive benzoannulation. The strong variation of spectral features upon benzo-fusing and metallation/demetallation, as well as the good solubility of the metal complexes in organic solvents, make these materials potentially valuable for optical applications including nonlinear optics.

Introduction

Phthalocyanines and their metal complexes have been investigated systematically during the last decades not only because of their use as dyes, but also as very promising compounds in the field of materials science.[1,2] Due to peculiarities in their molecular and electronic structure, metallophthalocyanines exhibit a wide range of interesting properties that determine their practical usage in different electronic and optical devices. In recent years some very interesting nonlinear optical properties of phthalocyanine-based materials have been discovered and studied intensively.[3,4] A particularly promising nonlinear optical application of the phthalocyanines is the intensity-dependent transmission of light which is called "optical limiting".

Among the many different metallophthalocyanines, indium complexes have been found to possess one of the largest positive nonlinear absorption coefficients, giving good results for the optical limiting effect.[5,6] The preparation and nonlinear optical properties of different substituted indium phthalo- (PcIn) and naphthalocyanines (NcIn) were described in detail in our previous papers.[6,7]

It is known that metallophthalocyanines are good materials for nonlinear optics mainly due to their extended π-electron system. Another important factor is the dipole moment of the molecule. For symmetrically substituted phthalocyanines, the introduction of a metal, which is located out of the phthalocyanine plane, in some cases gives rise to a substantial dipole moment. Especially high dipole moments arise in Pc complexes having one axial ligand, as observed, for example, for chloro- and arylindium phthalocyanines [R_nPcIn(X)] (X = Cl, Ar).[7d]

We found earlier that indium octaarylporphyrazines (Ar_8PzIn), having a conjugated π-system of 26 electrons and eight aryl groups which are in partial conjugation with the porphyrazine macrocycle, possess a quite high second-order hyperpolarizability,[8] especially in the case of octa(*m*-trifluoromethylphenyl) derivatives [{(*m*-CF_3Ph)$_8$}PzIn(X)] (X = Cl, *p*-CF_3Ph). Other advantages of these systems are their uniquely high solubility in organic solvents and their light stability in solutions due to the presence of the strongly electron withdrawing CF_3 groups.[9] However, these systems still have a C_{4v} axis of symmetry, and their average dipole moments are determined by the out-of-plane location of metal and axial ligand. A decrease in the symmetry of the porphyrazine macrocycle and expansion of its π-electron system should lead to higher nonlinear optical effects for these compounds.

We describe here the preparation and spectral properties of nonsymmetrically benzo-annulated (*meta*-trifluoromethylphenyl)porphyrazines and their magnesium and indium complexes (see Figure 1).

Results and Discussion

Synthesis

In recent years nonsymmetrical porphyrazines have received much attention mainly because of their unusual optical properties. Various methods have been used for the preparation of porphyrazine systems with unsymmetrically fused conjugated rings.[10–13] Many results on the preparation of unsymmetrical phthalocyanines have been reported as well.[14]

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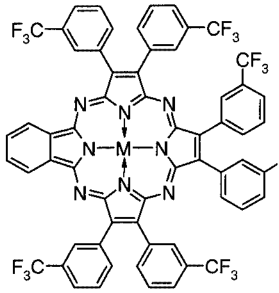
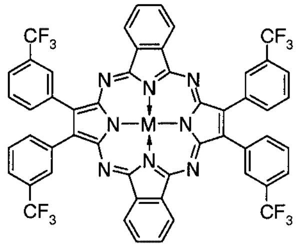
[a] Universität Tübingen, Institut für Organische Chemie,
Auf der Morgenstelle 18, 72076 Tübingen, Germany
[b] Ivanovo State University of Chemistry and Technology,
Organic Chemistry Department, 153460,
F. Engels str., 7, Ivanovo, Russia



AAABM, M = Mg, H_2 or In(Cl)



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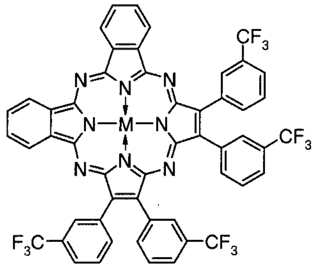

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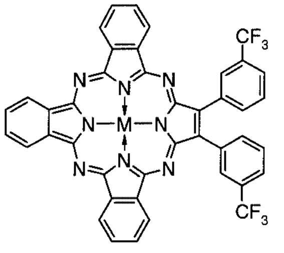
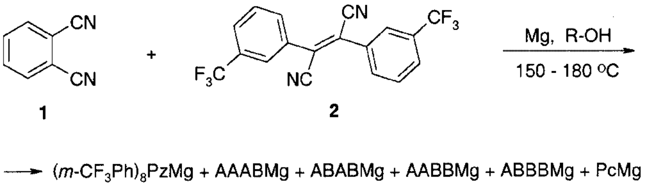


ABBBM, M = Mg, H_2 or In(Cl)

Figure 1

In this work, the template condensation with magnesium alkoxides in high-boiling alcohols was found to be suitable for the reaction of phthalonitrile (**1**) and bis(*m*-trifluoromethylphenyl)fumaronitrile (**2**) in order to obtain unsymmetrical porphyrazines (see Scheme 1). The reaction of **1** and **2** in a ratio of approximately 1:1 gave six products, namely [{(m-$CF_3Ph)_8$}PzMg] (or AAAAMg), PcMg (or BBBBMg), AAABMg, ABABMg, AABBMg and ABBBMg, in a statistical condensation, five of which (except for PcMg) can be easily separated by column chromatography. Magnesium as the central metal in porphyrazine macrocycles makes the separation especially effective, although time consuming. Nevertheless, the obtained magnesium complexes possess a high stability since they do not decompose even when remaining on the column for more then one week.



Scheme 1. Structure and assignment of the synthesized porphyrazines

The solubility of the unsymmetrical porphyrazines in chloroform decreases in the order AAABMg > ABABMg > AABBMg > ABBBMg, although in coordinating solvents such as THF all complexes are highly soluble.

Treatment of the magnesium complexes in appropriate acidic media yields the corresponding metal-free macrocycles. The removal of the coordinated magnesium leads to a drastic decrease of solubility of the compounds, even in THF. For this reason we were unable to characterize $AABBH_2$ by ^{13}C NMR spectroscopy, and $ABBBH_2$ by ^{1}H or ^{13}C NMR spectroscopy, or by FD-MS.

The introduction of indium into the macrocycle core was achieved by the reaction of the metal-free porphyrazines with $InCl_3$ in refluxing DMF. This method was used successfully in our previous work in order to obtain [{(m-$CF_3Ph)_8$}PzInCl].[9] The yields of the performed demetallation and metallation reactions are close to quantitative, and the products do not require additional purification.

The indium complexes are less soluble in THF then the corresponding magnesium compounds, but more soluble than the metal-free porphyrazines.

Spectroscopic Characterization

The IR spectra of the porphyrazines are rather specific in the region 500−1000 cm^{-1}, although the strongest vibration bands are found at almost the same position for different macrocycles in the region 1000−1400 cm^{-1}. These intense bands are due to the stretching, deformation and combinatorial vibrations of the CF_3 groups in the aryl rings of the macrocycles. In metal-free porphyrazines a very weak band at about 3290 cm^{-1} appears due to the stretching vibration of inner N−H bonds.

Field desorption (FD) mass spectrometry is very useful for the identification of the template condensation products (except for the *cis* and *trans* isomers AABBMg and ABABMg). The recorded spectra show only the peaks of the corresponding molecular ion M^+, neither the fragmentation of compounds nor admixtures were observed.

The ^{1}H NMR spectra contain additional information about the structure and behavior of the synthesized compounds. The spectrum of symmetrical [(m-$CF_3Ph)_8$PzMg] is rather simple and consists of four groups of peaks in the region of δ = 8.30−7.50 ppm in the following order: a doublet and a singlet for the *ortho* protons (*o*-H and *o*′-H), a doublet for the *para* protons and a triplet for the *meta* protons. In the case of the AAAB macrocycles, a characteristic multiplet, consisting of four equal sharp peaks, appears at around $\delta = 9$ ppm, which corresponds to two protons in the 1- and 4-positions of the annulated benzene ring (ABR). Due to the nonequivalence of the aryl substituents in this macrocycle, the signals of the aryl protons split and give rise to complex multiplets in the range $\delta = 7.50-8.30$ ppm, covering the resonances of the 2,3-protons of ABR. An additional singlet at ca. $\delta = 8.8$ ppm corresponds to two *ortho* protons (*o*′-H) of the aryls next to the ABR (see Figure 2). The large downfield shift of their resonance can be explained as a deshielding effect of the ABR part of the macrocycle due to the contribution of the special conformation of these two aryls so that the CF_3 groups are directed towards the ABR coplanar to the macrocycle, which becomes energetically favorable. The spectra of the ABAB species are simplified because of an equivalence of both aryls and annulated benzene rings. All the signals appear at a lower field than the AAAB species (see Figure 3). However, the positions and the shape of the proton resonances of the investigated compounds depend on the solvents and concentrations used for recording the spectra due to the strong tendency of the compounds to aggregate. This aggregation causes a broadening and a high-field shift of all the signals, although to different extents. The best solvent found to prevent aggregation is [D$_8$]THF. In the ^{1}H NMR spectra of the AABB and ABBB species, the signals of the ABR protons become more complicated, as expected from the symmetry of the molecules (see Figure 3).

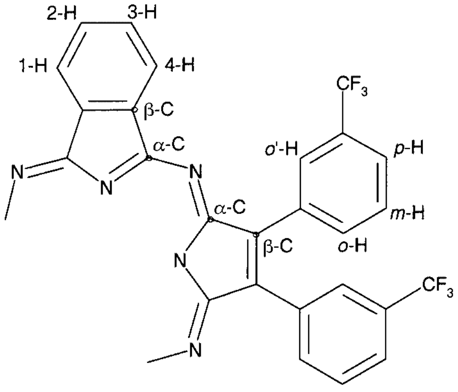


Figure 2. Numbered H and C atoms in the porphyrazin molecules

The ^{1}H NMR spectra of the Mg complexes {except for (m-$CF_3Ph)_8PzMg$]}, which were recrystallized from methanol-containing solutions, clearly indicate the presence of coordinated methanol in the ratio 1:1 to magnesium even after vacuum drying at 100 °C. In coordinating solvents such as [D$_6$]acetone or [D$_8$]THF, the proton resonances of free methanol were observed along with the signals of the macrocyclic magnesium complexes because of the complete exchange of coordinated methanol by solvent.

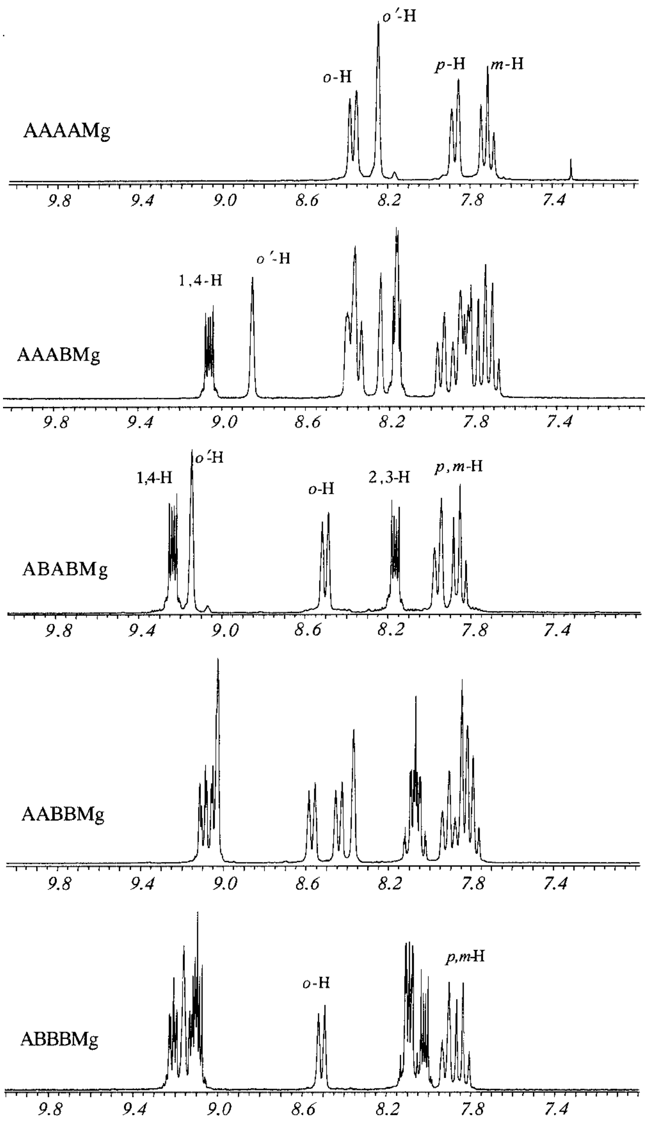


Figure 3. ^{1}H NMR spectra of magnesium complexes

For the metal-free porphyrazines, the subsequent annulation of benzene rings leads to high-field shifted singlet resonances of the inner N−H protons in the order (m-$CF_3Ph)_8PzH_2$ ($\delta = -1.76$ ppm) [9] > $AAABH_2$ ($\delta = -3.04$ ppm) > $AABBH_2$ ($\delta = -3.90$ ppm) > $ABABH_2$ ($\delta = -4.49$ ppm) due to the increasing π-electron ring-current effect. The substantial difference in N−H resonances between the $AABBH_2$ and $ABABH_2$ isomers could also be due to a more effective conjugation of the aryls with the porphyrazine macrocycle in $ABABH_2$.

The ^{13}C NMR spectra give indisputable evidence for the redistribution of the electron density in the nonsymmetrical porphyrazines, thus proving their structure. The signals of the α- and β-carbons are split to a lager extent than the other carbon signals (their positions and numbers are given in Table 1). The highest splitting of α-carbon resonances was observed for the metal-free compounds due to the influence of inner >N−H groups. The complete ^{13}C NMR spectroscopic data are presented in the Exp. Sect.

Table 1. Selected ^{13}C NMR signals of porphyrazines

Compound	Position and numbers of α-carbon singlet signals δ	No.	Position and numbers of β-carbon singlet signals δ	No.	Solvent
AAAAIn(Cl)[a]	156.6	1	143.0	1	$CDCl_3$
AAAAMg	157.4	1	142.2	1	[D_6]acetone
AAAAH_2 [a]	153.6	1 br.[b]	141.4	1	$CDCl_3$
AAABIn(Cl)	158.8, 157.9, 154.6, 153.9	4	143.1, 141.8, 140.8, 138.5	4	$CDCl_3$
AAABMg	158.7, 158.1, 155.4, 154.7	4	141.9, 140.7, 140.1, 140.0	4	[D_6]acetone
AAABH_2	158.6, 155.4, 148.7, 146.5	4 br.	140.8, 139.1, 138.6, 137.0	4	$CDCl_3$
AABBMg	161.0, 157.5, 156.2, 153.1	4	141.5, 141.2, 140.4, 139.1	4	[D_6]THF
ABABMg	156.9, 156.6	2	140.9, 140.6	2	[D_6]THF
ABABH_2	160.3, 136.0	2	143.3, 140.2	2	[D_6]THF
ABBBMg	158.9, 158.3, 153.7, 152.4	4	141.1, 140.5, 140.0, 138.0	4	[D_6]THF

[a] Taken from ref.[9] [b] br. = broad.

The UV/Vis spectra were recorded for all synthesized compounds, and some of them are shown in Figure 4. Diamagnetic metal complexes of porphyrazines and phthalocyanines with D_{4h} symmetry exhibit two intense absorption bands (Q and B) caused by $\pi\rightarrow\pi^*$ transitions. An absorption in the visible region due to the $a_{1u}\rightarrow e_g^*$ transition is ascribed to the Q-band. In the near UV region the B-band appears owing to the $a_{2u}\rightarrow e_g^*$ transition. The positions of these bands depends on the nature of the macrocycles, the Q-band undergoes a large red shift upon annulation of four benzene rings when passing from porphyrazines to phthalocyanines. For comparison, the Q-band maxima of PzMg, [{(m-CF_3Ph)$_8$Pz}Mg] and PcMg appear at around 585,[15] 630 and 670 nm, respectively.

According to the four-orbital approach,[16] for the porphyrazine systems with D_{4h} symmetry two degenerate perpendicularly oriented e_g^* orbitals should split upon the lowering of the symmetry due to benzene annulation. This should lead to a splitting of the Q- and B-bands into x and y components. In the case of dibenzo derivatives, the band splitting of the ABAB isomer was predicted to be substantially higher than that of the AABB isomer.[16] The splitting for the AABB form should be very small. These predictions agree very well with the experimental data. The characteristic splitting of the Q- and B-bands upon benzene annulation was observed for the AABBM and ABABM complexes. The Q-band of AABBIn(Cl) or AABBMg is only broadened, whereas for ABABM species the Q-band splitting is about 120 nm (see Figure 4). The systems with one or three annulated benzene rings also have characteristically distinctive UV/Vis spectra with split Q- and B-bands. Therefore, UV/Vis spectroscopy is a very convenient method for the determination of the structure of unsymmetrically annulated porphyrazines.

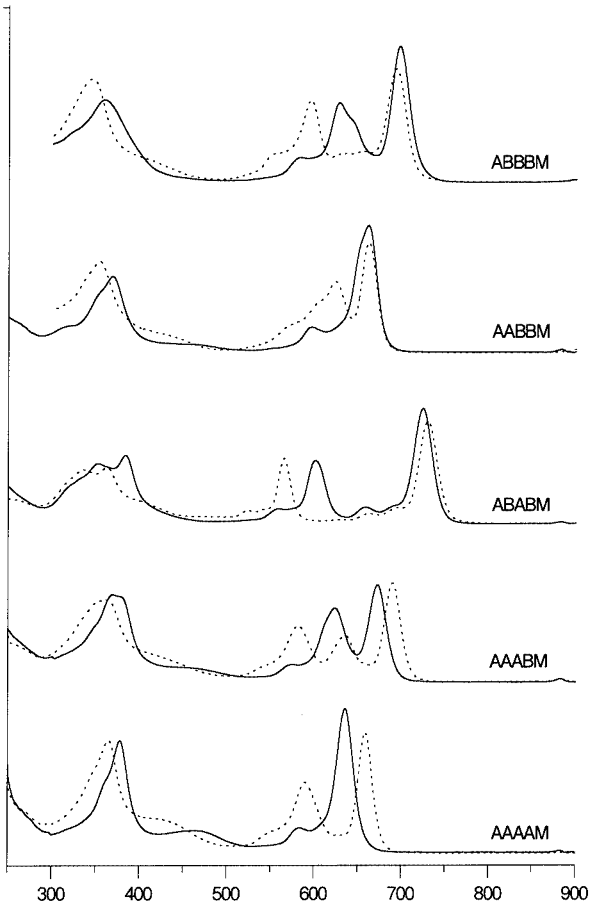


Figure 4. UV/Vis spectra of porphyrazines (M = H_2, dotted lines) and their indium complexes (M = InCl, solid lines) in CH_2Cl_2 (for ABBBM and AABBH_2 the presented spectra were recorded in THF); the spectra of AAAAM are taken from ref.[9]

Comparing our results with literature data describing the structure and spectral properties of dibenzotetraphenylporphyrazines,[13] we noticed a difference in the structure assignment made by the authors: the reported UV/Vis spectra do not correspond to those observed for our compounds despite the considerable structural similarity of both types of porphyrazines. The spectrum of the species assigned as AABBM[13] fits exactly with the spectra of the AAABM species in our work and the spectrum of the ABABM isomer[13] clearly shows that it is the isomer AABBM with a nonsplit Q-band.

Substitution of magnesium by indium leads to a slight red shift of all bands without changing the shape of the UV/Vis spectra of the complexes. In metal-free porphyrazines the splitting of the bands increases and the band shape changes (see Figure 4).

The variation of the absorption spectra upon demetallation and metal substitution in the synthesized compounds, as well as their high stability, makes these compounds interesting for different optical applications such as, for example, optical digital information carriers. The introduction of indium with an axial chlorine into the AABB, AAAB or ABBB macrocycles lowers the symmetry of the molecules to C_1, which makes these complexes potentially promising for nonlinear optic applications.

Experimental Section

Reagents and solvents for synthesis, chromatography and spectroscopic characterization of compounds were pure chemicals (Fluka, Aldrich). Bis(*m*-trifluoromethylphenyl)fumaronitrile was prepared according to the described procedure.[9]

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), MS: Varian Mat 711; elemental analyses: Carlo−Erba Elemental Analyser 1104, 1106.

All metal-exchange reactions were performed under TLC and UV/Vis control.

Due to the high content of fluorine in the prepared compounds, their elemental analyses gave satisfactory to good results only for carbon and nitrogen. The values of hydrogen content are low for all samples because of the formation of HF under the analysis conditions.

Synthesis of Compounds. Magnesium Complexes: Magnesium turnings (70 mg, 2.88 mmol) were refluxed in a mixture of 1-octanol (5 mL) and 1-pentanol (1 mL). After 3 h, phthalonitrile (0.3 g, 2.34 mmol) and bis(*m*-trifluoromethylphenyl)fumaronitrile (1 g, 2.73 mmol) were added, and the mixture was refluxed with stirring for 12 h in a 180 °C oil bath. After cooling, and in order to remove the excess high-boiling alcohols, the reaction mixture was poured into 200 mL of aqueous methanol and centrifuged. The obtained precipitate was repeatedly washed with aqueous methanol, dried under vacuum at 100 °C and chromatographed on silica gel under UV/Vis control. The first red fraction, consisting of the by-product, and the second green fraction of octa(*m*-trifluoromethylphenyl)porphyrazinatomagnesium(II) were eluted with dichloromethane. The following fractions were eluted by a gradual addition of acetone or THF, with an initial CH_2Cl_2/THF ratio of about 500:1 and a final ratio of about 10:1.

Octa(*m*-trifluoromethylphenyl)porphyrazinatomagnesium {(m-$CF_3Ph)_8$PzMg or AAAAMg} was collected as a second fraction. It was recrystallized from methanol solution upon dropwise addition of water and then dried under vacuum at 100 °C to yield 130 mg (0.086 mmol, 12.6% with respect to **2**) of a powder with violet reflection. UV/Vis (CH_2Cl_2): λ (lg ε) = 374 nm (5.16), 579 (4.48), 631 (5.24). FT-IR (KBr): $\tilde{\nu}$ = 1616 cm^{-1} vw, 1595 vw, 1474 vw, 1435 vw, 1369 w, 1331 vs, 1312 s, 1277 m, 1169 s, 1126 s, 1097 m, 1074 s, 1005 m, 912 m, 808 s, 768 w, 717 m, 698 s, 654 w. ^{1}H NMR ([D$_6$]acetone): δ = 7.65 (t, $^3J \approx$ 7.9 Hz, 8 H), 7.81 (d, $^3J \approx$ 8.1 Hz, 8 H), 8.18 (s, 8 H), 8.30 (d, $^3J \approx$ 7.7 Hz, 8 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 124.4 (q, $^1J \approx$ 271.4 Hz), 124.6 (q, $^3J \approx$ 3.7 Hz), 128.7 (q, $^3J \approx$ 4.1 Hz), 129.2 (s), 130.2 (q, $^2J \approx$ 31.9 Hz), 134.5 (s), 136.2 (s), 142.2 (s), 157.4 (s) ppm. MS (FD): *m/z* = 1488.0 [M$^+$]. $C_{72}H_{32}F_{24}MgN_8 \cdot H_2O$ (1489.3 + 18): calcd. C 57.37, H 2.27, N 7.43; found C 57.03, H 1.60, N 7.49.

2,3,7,8,12,13-Hexa(*m*-trifluoromethylphenyl)benzo[*q*]porphyrazinatomagnesium (AAABMg) was collected as a third, green fraction with red luminescence on the column under 365 nm irradiation. The solution was partially evaporated, mixed with methanol, and AAABMg was precipitated by dropwise addition of water. The obtained compound was dried at 100 °C under vacuum (0.1 bar), yielding 230 mg (0.178 mmol, 19.6% with respect to **2**) of a greenish-blue powder with violet reflection. UV/Vis (CH_2Cl_2): λ (lg ε) = 371 nm (5.02), 571 (4.35), 619 (4.94), 665 (5.04). FT-IR (KBr): $\tilde{\nu}$ = 1477 cm^{-1} w, 1433 w, 1369 w, 1329 vs, 1313 s, 1279 m, 1169 s, 1128 s, 1099 m, 1074 m, 995 m, 914 m, 808 m, 758 w, 735 w, 717 m, 700 m, 658 w, 534 w. ^{1}H NMR ([D$_6$]acetone): δ = 7.67−7.97 (m, 12 H), 8.15−8.18 (m + s, 4 H), 8.23 (s, 2 H), 8.33−8.40 (m, 6 H), 8.85 (s, 2 H), 9.04−9.07 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 123.0 (s), 124.2−124.6 (group of quadruplets, $^3J \approx$ 3.7 Hz), 124.4 (q, $^1J \approx$ 271.9 Hz), 124.8 (q, $^1J \approx$ 271.4 Hz), 128.5−128.7 (group of quadruplets, $^3J \approx$ 4.1 Hz), 129.1 (s), 129.2 (s), 129.7 (q, $^3J \approx$ 4.1 Hz), 130.1 (q, $^2J \approx$ 31.9 Hz), 130.2 (q, $^2J \approx$ 32.4 Hz), 130.3 (q, $^2J \approx$ 31.9 Hz), 130.8 (s), 134.8 (s), 135.0 (s), 135.9 (s), 136.2 (s), 140.0 (s), 140.1 (s), 140.7 (s), 141.9 (s), 154.7 (s), 155.5 (s), 158.1 (s), 158.7 (s) ppm. MS (FD): *m/z* = 1250.8 [M$^+$]. $C_{62}H_{28}F_{18}MgN_8 \cdot CH_3OH \cdot 1/2\ H_2O$ (1251.2 + 41): calcd. C 58.55, H 2.57, N 8.67; found C 58.63, H 1.46, N 8.70.

2,3,12,13-Tetra(*m*-trifluoromethylphenyl)dibenzo[*g*,*q*]porphyrazinatomagnesium (ABABMg) was collected as a fourth, blue fraction with blue luminescence, crystallized as described above for AAABMg and dried at 100 °C under vacuum. Yield 70 mg (0.067 mmol, 5.7% with respect to **1**) of a deep blue crystalline powder. UV/Vis (CH_2Cl_2 + 1% THF): λ (lg ε) = 353 nm (4.84), 378 (4.84), 553 (4.19), 593 (4.83), 648 (4.26), 711 (5.09). FT-IR (KBr): $\tilde{\nu}$ = 3082 cm^{-1} vw, 1610 vw, 1475 w, 1456 m, 1416 w, 1329 vs, 1304 s, 1277 m, 1202 w, 1167 s, 1134 vs, 1097 m, 1074 s, 974 s, 916 w, 899 w, 889 w, 812 m, 800 m, 758 m, 748 m, 716 m, 708 m, 698 m, 658 w. ^{1}H NMR ([D$_8$]THF): δ = 7.87 (t, $^3J \approx$ 7.7 Hz, 4 H), 7.97 (d, $^3J \approx$ 7.8 Hz, 4 H), 8.15−8.20 (m, 4 H), 8.51 (d, $^3J \approx$ 7.8 Hz, 4 H), 9.16 (s, 4 H), 9.23−9.27 (m, 4 H) ppm. ^{13}C NMR ([D$_8$]THF): δ = 123.7 (s), 125.2 (q, $^3J \approx$ 3.7 Hz), 125.9 (q, $^1J \approx$ 272 Hz), 129.9 (s), 130.8 (s), 131.1 (q, $^3J \approx$ 4.1 Hz), 131.6 (q, $^2J \approx$ 31.9 Hz), 136.4 (s), 136.7 (s), 140.6 (s), 140.9 (s), 156.6 (s), 156.9 (s) ppm. MS (FD): *m/z* = 1012.4 [M$^+$]. $C_{52}H_{24}F_{12}MgN_8 \cdot CH_3OH$ (1013.1 + 32): calcd. C 60.91, H 2.70, N 10.72; found C 60.88, H 1.66, N 10.82.

2,3,7,8-Tetra(*m*-trifluoromethylphenyl)dibenzo[*l*,*q*]porphyrazinatomagnesium (AABBMg) was eluted as a fifth, bluish-green fraction with red luminescence, crystallized as described above and dried at 100 °C under vacuum. Yield 170 mg (0.160 mmol, 13.7% by **1**) of thin violet needles. UV/Vis (CH_2Cl_2 + 1% THF): λ (lg ε) = 367 nm (4.98), 588 (4.55), 652 (5.23). FT-IR (KBr): $\tilde{\nu}$ = 3074 cm^{-1} vw, 1479 w, 1429 w, 1420 w, 1325 vs, 1310 s, 1277 m, 1215 w, 1178 m, 1153 s, 1126 s, 1096 m, 1076 m, 1007 m, 930 w, 918 w, 910 w, 802 m, 764 w, 756 w, 721 m, 712 w, 700 m. ^{1}H NMR ([D$_8$]THF): δ = 7.78−7.95 (m, 8 H), 8.04−8.14 (m, 4 H), 8.39 (s, 2 H), 8.46 (d, $^3J \approx$ 7.7 Hz, 2 H), 8.59 (d, $^3J \approx$ 7.4 Hz, 2 H), 9.04−9.13 (m + s, 6 H) ppm. ^{13}C NMR ([D$_8$]THF): δ = 123.8 (s), 124.0 (s), 124.9 (q, $^3J \approx$ 3.7 Hz), 125.1 (q, $^3J \approx$ 3.7 Hz), 125.5 (q, $^1J \approx$ 271.9 Hz), 125.9 (q, $^1J \approx$ 271.9 Hz), 129.8 (s), 129.9 (s + q, $^3J \approx$ 4 Hz), 130.9 (q, $^3J \approx$ 3.7 Hz), 131.0 (s), 131.3 (q, $^2J \approx$ 31.9 Hz), 131.4 (s), 131.5 (q, $^2J \approx$ 31.9 Hz), 136.4 (s), 136.5 (s), 136.6 (s), 137.1 (s), 139.1 (s), 140.4 (s), 141.2 (s), 141.5 (s), 153.1 (s), 156.2 (s), 157.5 (s), 161.0 (s) ppm. MS (FD): m/z = 1012.7 [M$^+$]. $C_{52}H_{24}F_{12}MgN_8\cdot CH_3OH\cdot H_2O$ (1013.1 + 50): calcd. C 59.88, H 2.84, N 10.54; found C 60.21, H 1.50, N 10.13.

2,3-Bis(*m*-trifluoromethylphenyl)tribenzo[*g*,*l*,*q*]porphyrazinatomagnesium (ABBBMg) was obtained as a sixth, blue fraction with blue luminescence. Precipitation from CH_2Cl_2 by addition of methanol, filtration and drying yielded 130 mg (0.158 mmol, 20.2% by **1**) of a fine, blue crystalline powder. UV/Vis (CH_2Cl_2 + 1% THF): λ (lg ε) = 354 nm (4.91), 578 (4.37), 621 (4.89), 635 (4.78), 689 (5.12). FT-IR (KBr): ṽ = 3628 cm^{-1} vw, 3082 vw, 1610 vw, 1514 w, 1493 w, 1460 m, 1423 w, 1327 vs, 1310 s, 1283 m, 1167 s, 1157 s, 1124 vs, 1076 s, 1003 s, 916 w, 893 w, 808 w, 800 w, 777 w, 756 s, 746 m, 725 s, 700 m, 675 w. ^{1}H NMR ([D$_8$]THF): δ = 7.82−7.95 (m, 4 H), 8.00−8.15 (m, 6 H), 8.52 (d, ^3J ≈ 7.5 Hz, 2 H), 9.07−9.15 (m, 4 H), 9.17 (s, 2 H), 9.20−9.23 (m, 2 H) ppm. ^{13}C NMR ([D$_8$]THF): δ = 123.4 (s), 123.8 (s), 124.5 (q, ^3J ≈ 3.7 Hz), 126.0 (q, ^1J ≈ 271.9 Hz), 129.7 (s), 130.0 (s), 130.6 (s), 130.8 (s), 131.1 (q, ^3J ≈ 4 Hz), 131.4 (q, ^2J ≈ 31.9 Hz), 136.7 (s + s); 137.3 (s), 138.0 (s), 140.0 (s), 140.5 (s), 141.1 (s), 152.4 (s), 153.7 (s), 158.3 (s), 158.9 (s) ppm. MS (FD): m/z = 774.8 [M$^+$]. $C_{42}H_{20}F_6MgN_8\cdot CH_3OH\cdot H_2O$ (775.0 + 50): calcd. C 62.60, H 3.18, N 13.58; found C 62.78, H 2.12, N 13.81.

2,3,7,8,12,13-Hexa(*m*-trifluoromethylphenyl)benzo[*q*]porphyrazine (AAABH$_2$): AAABMg (150 mg, 0.12 mmol) was dissolved in CH_3COOH (20 mL) and stirred at room temperature for 2 h. Water (30 mL) was added to the solution, the formed precipitate was centrifuged, washed thoroughly with water and dried under vacuum at 100 °C. Yield 120 mg (0.098 mmol, 81%) of a bluish-green powder. UV/Vis (CH_2Cl_2): λ (lg ε) = 363 nm (4.90), 582 (4.73), 635 (4.65), 690 (4.97). FT-IR (KBr): ṽ = 3296 cm^{-1} w, 3080 vw, 1612 vw, 1537 vw, 1487 w, 1433 w, 1329 vs, 1313 s, 1279 m, 1169 s, 1124 vs, 1097 m, 1076 s, 1030 w, 1003 vw, 966 w, 914 m, 876 w, 804 s, 760 w, 750 m, 731 w, 698 s, 683 w, 654 w. ^{1}H NMR ($CDCl_3$): δ = −3.04 (s, 2 H), 7.54−7.71 (m, 6 H), 7.78−7.92 (m, 6 H), 7.99 (s, 2 H), 8.05−8.24 (m, 10 H), 8.68 (s, 2 H), 8.89−8.92 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 123.3 (s), 123.9 (q, ^1J ≈ 272.8 Hz), 124.0 (q, ^1J ≈ 272.8 Hz), 124.2 (q, ^1J ≈ 272.4 Hz), 125.0 (q, ^3J ≈ 3 Hz), 125.5−125.7 (group of quadruplets, ^3J ≈ 3.7 Hz), 128.8−129.0 (group of quadruplets, ^3J ≈ 3.7 Hz), 128.9 (s), 129.0 (s), 129.1 (s), 129.9 (q, ^3J ≈ 3.7 Hz), 130.8 (q, ^2J ≈ 32.4 Hz), 131.1 (q, ^2J ≈ 32.8 Hz), 131.2 (q, ^2J ≈ 32.3 Hz), 131.7 (s), 132.5 (s), 133.3 (s), 135.5 (s), 135.7 (s), 135.8 (s), 137.0 (s), 138.6 (s), 139.1 (s), 140.8 (s), 146.5 (s), 148.7 (s), 155.4 (s), 158.6 (s), ppm. MS (FD): m/z = 1228.7 [M$^+$]. $C_{62}H_{30}F_{18}N_8$ (1229.0): calcd. C 60.60, H 2.46, N 9.12; found C 60.64, H 1.54, N 9.07.

2,3,12,13-Tetra(*m*-trifluoromethylphenyl)dibenzo[*g*,*q*]porphyrazine (ABABH$_2$): CF_3COOH (1 mL) was added to a solution of ABABMg (110 mg, 0.109 mmol) in 20 mL of THF and the reaction mixture was stirred for 5 h at 50 °C. After that, water (20 mL) was added to precipitate the metal-free compound. The product was filtered off, washed with aqueous methanol and dried under vacuum at 100 °C. Yield 95 mg (0.096 mmol, 88%) of a red-violet powder. UV/Vis (CH_2Cl_2): λ (lg ε) = 336 nm (4.83), 363 (4.84), 524 (4.25), 565 (4.90), 630 (3.85), 663 (4.15), 696 (4.32), 730 (5.09). FT-IR (KBr): ṽ = 3294 cm^{-1} vw, 3080 vw, 1539 w, 1483 w, 1425 w, 1329 s, 1315 s, 1281 w, 1259 w, 1169 s, 1128 s, 1099 w, 1076 m, 1024 w, 932 m, 872 m, 806 m, 746 m, 739 m, 714 w, 696 s, 652 w, 609 m. ^{1}H NMR ($CDCl_3$): δ = −4.49 (s, 2 H), 7.60 (t, ^3J ≈ 7.9 Hz, 4 H), 7.85−7.92 (m, 8 H), 7.99 (d, ^3J ≈ 8.1 Hz, 4 H), 8.47−8.51 (m, 4 H), 8.62 (s, 4 H) ppm. ^{13}C NMR ([D$_8$]THF): δ = 125.6 (q, ^1J ≈ 272.4 Hz), 126.1 (q, ^3J ≈ 4.2 Hz), 129.9 (s), 130.7 (q, ^3J ≈ 4.2 Hz), 131.4 (s), 131.6 (q, ^2J ≈ 32.4 Hz), 133.7 (s), 136.0 (s), 136.8 (s), 140.2 (s), 143.3 (s), 160.3 (s) ppm. MS (FD): m/z = 990.6 [M$^+$]. $C_{52}H_{26}F_{12}N_8$ (990.8): calcd. C 63.04, H 2.64, N 11.31; found C 62.88, H 1.30, N 11.28.

2,3,7,8-Tetra(*m*-trifluoromethylphenyl)dibenzo[*l*,*q*]porphyrazine (AABBH$_2$): The corresponding Mg complex (100 mg, 0.099 mmol) was dissolved in 30 mL of THF, then CF_3COOH (1 mL) was added. The obtained solution was stirred at 50 °C for 4 h. After cooling, water (10 mL) was added, and the formed precipitate was filtered off, washed thoroughly with aqueous methanol and dried under vacuum at 100 °C. Yield 92 mg (0.093 mmol, 94%) of dark blue powder. UV/Vis (CH_2Cl_2 + 1% THF): λ (lg ε) = 353 nm (4.93), 624 (4.84), 663 (5.03). FT-IR (KBr): ṽ = 3292 cm^{-1} vw, 3082 vw, 1614 vw, 1558 vw, 1541 vw, 1520 vw, 1487 w, 1429 w, 1329 vs, 1277 w, 1169 s, 1124 s, 1097 m, 1076 m, 1037 w, 989 w, 916 w, 905 w, 883 w, 804 m, 777 vw, 748 m, 727 m, 712 w, 700 m, 681 w. ^{1}H NMR ([D$_8$]THF): δ = −3.90 (s, 2 H), 7.31−7.37 (m, 2 H), 7.46−7.52 (m, 4 H), 7.57−7.76 (m, 6 H), 7.86−7.89 (m, 4 H), 7.96−8.00 (m, 6 H), 8.34 (s, 2 H) ppm. MS (FD): m/z = 990.4 [M$^+$]. $C_{52}H_{26}F_{12}N_8$ (990.8): calcd. C 63.04, H 2.64, N 11.31; found C 63.00, H 0.54, N 11.32.

2,3-Bis(*m*-trifluoromethylphenyl)tribenzo[*g*,*l*,*q*]porphyrazine (ABBBH$_2$): CF_3COOH (1 mL) was added to a solution of ABBBMg (100 mg, 0.13 mmol) in THF (40 mL), and the reaction mixture was stirred at 50 °C for 6 h, the formation of precipitate was observed. After cooling, the precipitation of the product was completed by addition of water (5−10 mL). The product was filtered off, washed thoroughly with methanol and dried under vacuum at 100 °C, yielding 90 mg (0.12 mmol, 92%) of a bluish-violet powder. UV/Vis (THF), λ (rel. intensity) = 345 (0.918), 595 (0.733), 634 (0.270), 655 (0.289), 693 (1.000). FT-IR (KBr): ṽ = 3290 cm^{-1} w, 3082 vw, 1549 w, 1524 w, 1475 m, 1443 w, 1418 w, 1327 vs, 1280 w, 1256 w, 1167 m, 1151 m, 1121 s, 1097 m, 1076 m, 1030 w, 980 m, 810 m, 773 w, 739 m, 731 s, 708 m, 698 m, 671 w. $C_{42}H_{22}N_8F_6$ (752.7): calcd. C 67.02, H 2.95, N 14.89; found C 66.81, H 1.52, N 14.61.

The indium complexes were prepared according to the following general procedure: The metal free porphyrazine and $InCl_3$ were heated in DMF at 155 °C. After the reaction was finished, the product was precipitated by dropwise addition of water, filtered off, washed thoroughly with aqueous methanol and dried under vacuum at 100 °C.

2,3,7,8,12,13-Hexa(*m*-trifluoromethylphenyl)benzo[*q*]porphyrazinatoindium(III) Chloride [(AAAB)InCl]: $InCl_3$ (100 mg, 0.45 mmol), AAABH$_2$ (100 mg, 0.081 mmol), DMF (15 mL), 2 h. Yield 95 mg (0.069 mmol, 85%) of a dark greenish powder. UV/Vis (CH_2Cl_2): λ (rel. intensity) = 370 (0.909), 575 (0.211), 624 (0.771), 673 (1.000). FT-IR (KBr): ṽ = 1468 cm^{-1} w, 1445 w, 1373 w, 1329 vs, 1277 m, 1182 s, 1169 s, 1130 s, 1097 m, 1076 s, 1020 w, 1003 m, 916 m, 812 m, 806 m, 754 vw, 717 w, 698 s, 687 vw, 658 w. ^{1}H NMR (dilute solution in $CDCl_3$): δ = 7.63−7.95 (m, 12 H), 8.17 (s, 2 H), 8.26−8.40 (m, 10 H), 8.95 (s, 2 H), 9.34−9.38 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 123.9 (q, ^1J ≈ 272.8 Hz), 124.3 (q, ^1J ≈ 272.8 Hz), 124.4 (s), 125.3−125.8 (group of quadruplets, ^3J ≈ 4 Hz), 129.4−129.2 (m); 130.3 (q, ^3J ≈ 4.2 Hz), 131.1 (q, ^2J ≈ 32.4 Hz), 131.2 (q, ^2J ≈ 32.4 Hz), 131.5 (q, ^2J ≈ 32.4 Hz), 132.6 (s), 132.9 (s), 133.1 (s + s); 135.3 (s), 135.5 (s), 135.6 (s), 138.5 (s), 140.8 (s), 141.8 (s), 143.1 (s), 153.9 (s), 154.6 (s), 157.9 (s), 158.8 (s) ppm. MS (FD): m/z = 1376.3 [M$^+$]. $C_{62}H_{28}ClF_{18}InN_8$ (1377.2): calcd. C 54.07, H 2.05, N 8.14; found C 53.79, H 0.86, N 8.10.

2,3,12,13-Tetra(*m*-trifluoromethylphenyl)dibenzo[*g*,*q*]porphyrazinatoindium(III) Chloride [(ABAB)InCl]: $InCl_3$ (70 mg, 0.32 mmol), AB-

ABH$_2$ (70 mg, 0.071 mmol), DMF (20 mL), 3 h. Yield 70 mg (0.061 mmol, 86%) of a dark, violet-blue powder. UV/Vis (CH$_2$Cl$_2$): λ (lg ε) = 352 nm (4.80), 384 (4.85), 559 (4.24), 601 (4.82), 659 (4.28), 724 (5.07). FT-IR (KBr): $\tilde{\nu}$ = 3082 cm^{-1} vw, 1456 m, 1371 w, 1331 vs, 1310 s, 1279 m, 1202 w, 1169 s, 1134 vs, 1097 m, 1074 s, 982 s, 1914 w, 887 w, 814 m, 804 m, 779 w, 754 m, 744 m, 717 m, 698 s, 658 w. ^{1}H NMR ([D$_8$]THF): δ = 7.91 (t, $^3J \approx$ 7.7 Hz, 4 H), 8.02 (d, $^3J \approx$ 8.1 Hz, 4 H), 8.34−8.37 (m, 4 H), 8.53 (d, $^3J \approx$ 7.7 Hz, 4 H), 9.07 (s, 4 H), 9.35−9.38 (m, 4 H) ppm. MS (FD): *m/z* = 1138.6 [M$^+$]. $C_{52}H_{24}ClF_{12}InN_8$ (1139.1): calcd. C 54.83, H 2.12, N 9.84; found C 54.61, H 0.64, N 9.91.

2,3,7,8-Tetra(*m*-trifluoromethylphenyl)-dibenzo[*l*,*q*]porphyrazinatoindium(III) Chloride [(AABB)InCl]: InCl$_3$ (70 mg, 0.32 mmol), AABBH$_2$ (70 mg, 0.071 mmol), DMF (20 mL), 8 h. Yield 70 mg (0.061 mmol, 86%) of a dark, greenish powder. UV/Vis (CH$_2$Cl$_2$ + 1% THF): λ (lg ε) = 369 nm (4.89), 596 (4.46), 661 (5.11). FT-IR (KBr): $\tilde{\nu}$ = 3082 cm^{-1} vw, 1474 w, 1327 vs, 1279 w, 1211 w, 1167 s, 1126 s, 1096 w, 1074 m, 1011 m, 899 br.w; 806 m, 779 vw, 756 w, 750 w, 725 m, 712 w, 698 m. ^{1}H NMR ([D$_8$]THF): δ = 7.75−7.98 (m, 8 H), 8.32−8.41 (m, 8 H), 8.50 (d, $^3J \approx$ 7.7 Hz, 2 H), 8.91 (s, 2 H), 9.25−9.29 (m, 2 H), 9.49−9.53 (m, 2 H) ppm. $C_{52}H_{24}ClF_{12}InN_8$ (1139.1): calcd. C 54.83, H 2.12, N 9.84; found C 54.97, H 1.03, N 9.81.

2,3-Bis(*m*-trifluoromethylphenyl)-tribenzo[*g*,*l*,*q*]porphyrazinatoindium(III) Chloride [(ABBB)InCl]: InCl$_3$ (70 mg, 0.32 mmol), ABBBH$_2$ (70 mg, 0.093 mmol), DMF (30 mL), 12 h. Additionally washed with pure methanol in order to remove the violet by-product. Yield 55 mg (0.061 mmol, 66%) of a blue powder. UV/Vis (CH$_2$Cl$_2$ + 5% THF): λ (lg ε) = 357 nm (4.76), 587 (4.25), 633 (4.74), 704 (4.95). FT-IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1} vw, 1512 w, 1460 m, 1329 vs, 1312 s, 1283 m, 1167 s, 1155 s, 1126 vs, 1096 m, 1074 s, 1009 s, 916 w, 897 w, 887 m, 812 m, 800 m, 777 m, 750 m, 741 m, 723 s, 698 m, 673 m. $C_{42}H_{20}ClF_6InN_8$ (900.9): calcd. C 55.99, H 2.24, N 12.44; found C 60.32, H 1.26, N 12.50.

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