Synthesis and Characterization of Soluble Octaaryl- and Octaaryloxy-Substituted Metal-Naphthalocyanines

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An easy route for the synthesis of vanadium, zinc, magnesium, etc. complexes of new soluble symmetrical octa(*m*-trifluoromethylphenyl) or octa(*m*-trifluoromethylphenoxy) substituted 2,3-naphthalocyanines {[(*m*-$CF_3Ph)_8NcM$] or [(*m*-$CF_3PhO)_8NcM$]} in good yields is described in detail. The structures of the synthesized compounds were verified by UV/Vis and ^1H and ^{13}C NMR spectroscopy, as well as by mass spectrometry. The good solubilities of the prepared compounds in toluene and coordinating solvents (e.g., THF), was explained in terms of the nonplanar arrangements of eight *m*-CF_3Ph substituents in relation to the Nc macrocycle, preventing aggregation of the molecules. The Q-bands in the UV/Vis spectra of the [(*m*-$CF_3Ph)_8NcM$] species are each bathochromically shifted by ca. 13 nm in relation to [(*m*-$CF_3PhO)_8NcM$] species, appearing at 817 nm for [(*m*-$CF_3Ph)_8NcVO$] in toluene. All NcMs prepared exhibit very high molar extinction coefficients for the Q-band {$\lg(\varepsilon) \approx 5.6$} in THF. Some of prepared Nc complexes appeared to be very unstable on exposure to daylight. In addition, a nickel-catalyzed Kumada cross-coupling synthesis of substituted *o*-terphenyls, intermediate compounds for the preparation of octaaryl-substituted Ncs, is described.

Introduction

Despite the interesting properties of phthalocyanines (Pcs) and their analogues for different applications in materials science, including as semiconductors, gas sensors, nonlinear optical limiters, liquid crystals, sensitizers for photodynamic therapy of cancer, and others,[1,2] naphthalocyanines (Ncs) have received less attention, which is partially due to the greater difficulties involved in their preparation. Another disadvantage of naphthalocyanines is their poor solubility in organic solvents. The solubility can be increased by introduction of peripheral substituents (mainly alkyl, alkylthio, or alkoxy) and/or axial ligands in their metal complexes. An additional effect that has to be reduced for better performance of Ncs and their metal complexes − in various nonlinear optical devices such as optical limiters,[3] for example − is their strong tendency to form aggregates in solution,[4,5] because of the strong van-der-Waals interactions between different rings due to the mostly planar structures of the molecules and their extended conjugated π-electron systems. Introduction of bulky substituents at the peripheries of Nc macrocycles should prevent these cofacial interactions of the Nc molecules and thus increase the solubility of the compounds. Good results in this respect were obtained in our previous work on indium naphthalocyanines, octa-substituted either with *tert*-butyl or with 2-ethylhexyloxy groups, or both, at the peripheral positions and bearing axial substituents (e.g., chloro, *p*-trifluoromethylphenyl, or pentafluorophenyl).[6] The highest solubility was observed for 3,(4)-tetra-*tert*-butyl-2,(5)-tetrakis(2-ethylhexyloxy)-substituted indium Nc. This unsymmetrical substitution pattern results in a mixture of four isomers and effectively hinders the aggregation of the Nc macrocycles even at high concentrations.[7a] The introduction of only four *tert*-butyl groups also results in the readily soluble tetra-*tert*-butylnaphthalocyanine and its metal complexes, including dimeric (tBuNcGa$)_2O$ species.[7b] Polyfluorination of the Nc macrocycle also results in the solubilization of Nc species, so soluble hexadecafluorinated (chloro)(naphthalocyanine)gallium and its μ-oxo-dimer were recently synthesized by our group.[7c] The preparation of tetraaryloxy-substituted naphthalocyanines as isomeric mixtures in which aryloxy substituents bear different bulky groups has also been reported.[8] These naphthalocyanines show good solubility in common organic solvents, due to the particular mutual arrangement of peripheral substituents and Nc-macrocycle, hindering self-association of the molecules.

In addition, we have recently found[9] that the introduction of eight *meta*-trifluoromethylphenyl (*m*-CF_3Ph) groups into the porphyrazine macrocycle produces greatly enhanced solubility in relation to octaphenylporphyrazine. The CF_3 substituents in the *meta* positions of the eight phenyl groups cause nonplanar arrangements of the *m*-CF_3Ph

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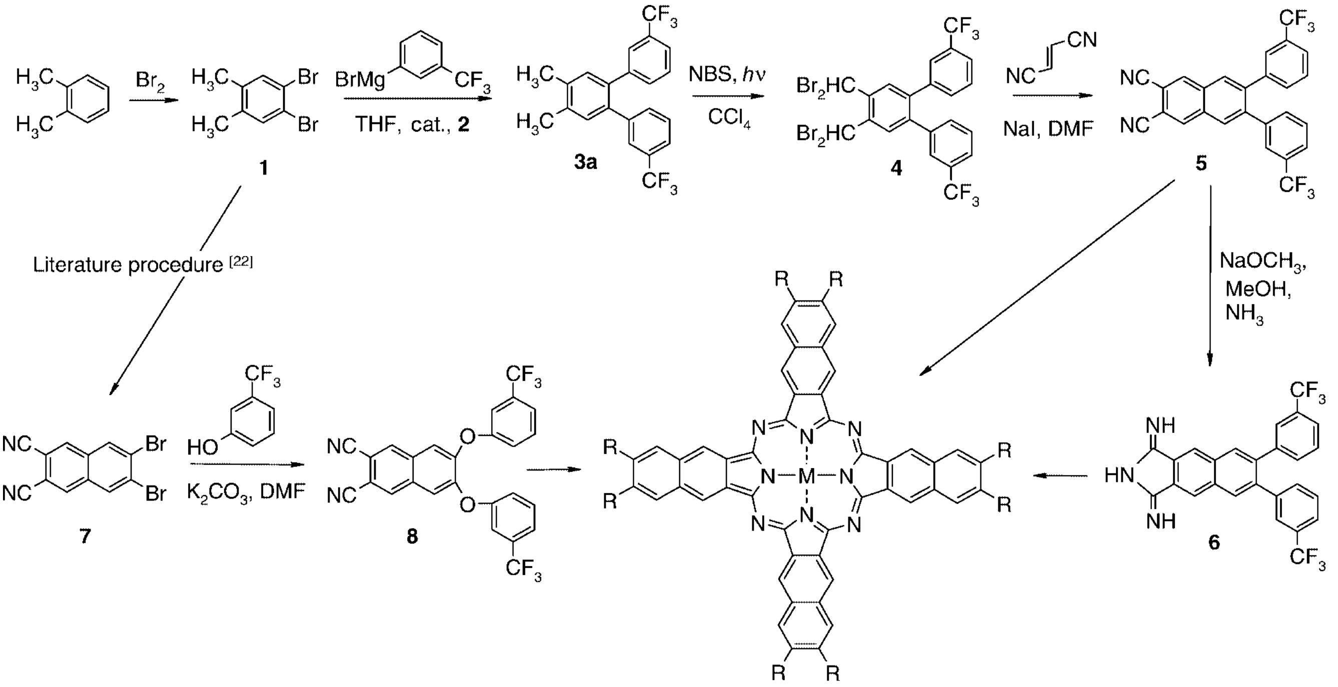
groups in relation to the porphyrazine ring, which prevents aggregation of the molecules in solution. We also found high solubilities for unsymmetrically benzo-annulated porphyrazines bearing six to four *m*-CF_3Ph groups,[10a] such as 2,3,7,8,12,13-hexakis(*m*-trifluoromethylphenyl)benzo[*q*]-porphyrazine, 2,3,7,8-tetrakis(*m*-trifluoromethylphenyl)-benzo-[*l*,*q*]porphyrazine and 2,3,12,13-tetrakis(*m*-trifluoromethylphenyl)benzo[*g*,*q*]porphyrazine and their magnesium and indium complexes. The large conjugated π-electron systems of these compounds, together with their low aggregation in solutions, met conditions for their behavior as optical limiters.[9][10b] It is known that naphthalocyanines, having more extended π-electron systems, display especially high optical limiting effects in solutions, if soluble.[3]

Here we have tried to utilize the solubilizing effect of *m*-CF_3-substituted aryls in order to prepare soluble naphthalocyanines with eight *meta*-trifluoromethylphenyl or *meta*-trifluoromethylphenoxy groups as peripheral substituents and to compare their properties in solutions qualitatively.

Results and Discussion

Synthesis of Precursors: The synthesis of the *meta*-trifluoromethylphenyl-substituted naphthalocyanine complexes **9a−13a** was carried out as shown in Scheme 1. Reactions between aryl-Grignard reagents and halogenated benzene derivatives are known to be catalyzed by nickel or palladium compounds (Kumada cross-coupling),[11−14] but this method had not previously been applied in the preparation of *ortho*-terphenyls (e.g., 4,5-diaryl-*o*-xylenes). The few convenient reported methods for the preparation of substituted *ortho*-terphenyls are the treatment of *ortho*-dihalogenated benzenes (e.g., 1,2-diiodobenzene or 3,4-dibromotoluene) with arylzinc compounds with catalysis by tetrakis(triphenylphosphane)palladium(0),[15] Suzuki cross-coupling reactions involving phenylboronic acids,[16a] and the Ullman coupling reaction.[16b] The first method gives fairly high yields, but requires working with butyllithium at −78 °C under inert atmosphere and gives several by-products that have to be separated by column chromatography. We have found that the reactions between 4,5-dibromo-*ortho*-xylene (**1**) and excesses of aryl-Grignard reagents derived from 3-bromobenzotrifluoride or 4-bromoveratrol, with catalysis by nickel(II) acetylacetonate in the presence of 1,3-bis(2,6-diisopropyl-phenyl)imidazolium chloride,[14] also provide the corresponding *ortho*-terphenyls {4,5-bis[(*m*-trifluoromethyl)phenyl]-*o*-xylene (**3a**) and 4,5-bis[3,4-dimethoxyphenyl]-*o*-xylene (**3b**)} in one step and represent a good alternative to the method involving organozinc compounds. The reaction is easy to carry out and proceeds with good yields (e.g., 62% for **3a**). The only by-product formed in noticeable amounts in this case was bis[3,3′-(trifluoromethyl)biphenyl], which could easily be separated by column chromatography. In the case of **3b**, 3,3′,4,4′-tetramethoxybiphenyl and veratrol were formed as



M =	Mg	V(O)	Zn	In(Cl)	Cu
R = $C_6H_4CF_3$	**9a**	**10a**	**11a**	**12a**	**13a**
R = $OC_6H_4CF_3$	**9b**	**10b**	**11b**	**12b**	**13b**

Scheme 1. Synthesis and numbering of the compounds

by-products but were easily separated from the desired product (see Exp. Sect.). The polar, dark-brown by-products, which stayed on top of the column, were formed in higher amounts only when the reaction mixture was overheated because of the strong exothermic effect of the reaction during the addition of the Grignard reagent.

Compound **3a** readily undergoes α,α′-tetrabromination in CCl_4 in the presence of four equivalents of NBS under UV irradiation conditions, to give **4**. Use of an excess of NBS under these conditions results in the formation of an α,α′-pentabrominated product, which can be isolated by column chromatography on silica gel. These products were also described in cases of radical bromination of similar compounds.[17,18] NBS-bromination of **3a** in CCl_4 at reflux in the presence of catalytic amounts of AIBN without irradiation was not effective enough, requiring a much longer reaction time and affording a mixture of di-, tri-, and tetrabrominated products even in the presence of excess NBS. The recorded ^1H and ^{13}C NMR spectra of **4** revealed strong through-space influence of the bromines of the dibromomethyl groups on the resonances of neighboring C and H atoms. Probably, several different conformations of **4** become considerably stabilized due to the hindered rotation of the $CHBr_2$ groups, and the signals of several C and H atoms at room temperature are significantly broadened (see Exp. Sect.).

Dinitrile **5** was obtained by the standard procedure, through a Diels−Alder reaction between fumaronitrile and the *ortho*-quinodimethene generated in situ from **4**.

The analogous diaryloxy-substituted dicyanonaphthalene **8** was obtained by aromatic nucleophilic substitution of the bromines in **7** by 3-hydroxybenzotrifluoride in the presence of K_2CO_3 in DMF at 130 °C. Although a similar reaction with 4,5-dihalo-phthalonitriles proceeds readily at 70−90 °C,[19] the influence of the cyano groups on substitution of the bromine in 6,7-dibromo-2,3-dicyanonaphthalene (**7**) is less strong, and substitution requires a higher temperature and a longer reaction time. Nevertheless, the yield of **8** is fairly satisfactory (49%). Compound **8** can be purified either by recrystallization or by column chromatography, depending on the purity of the starting material **7**. Use of less pure **7** results in the formation of polar dark-brown by-products, which usually stay at the top of the column during chromatography, but they may also substantially disturb the reaction, lowering the yield. Although the preparation of 6,7-diphenylthio- or 6,7-dialkylthio-2,3-dicyanonaphthalene by treatment of **7** with thiolate ions, catalyzed by Cu_2O, has already been described,[4] the above route for the preparation of 6,7-diaryloxy-substituted 2,3-dicyanonaphthalene (e.g., **8**) is presented here for the first time.

It is interesting to note that both dinitriles **5** and **8** exhibit slight splitting of their -C≡N stretching vibrations in their IR spectra recorded in KBr, whereas in the ^{13}C NMR spectra of **5** and **8** in solution both of their CN groups are equivalent and give only one ^{13}C resonance: at δ = 115.7 ppm for **5** and at δ = 115.6 ppm for **8**. This unusual effect can be explained in terms of the dinitriles' crystal packings or the presence of different crystalline forms for both compounds in the solid state.

Synthesis of Naphthalocyanine Compounds: The dinitriles **5** and **8** were used for the template cyclotetramerization to form the Ncs either directly (preparation of **9a**, **11a**−**13a**, **9b**−**13b**) or by transformation of **5** into the isoindole-1,3-diylidenediamine derivative **6** (preparation of **10a**) followed by cyclotetramerization. Satisfactory to good yields were obtained for the magnesium, zinc, and vanadyl Ncs. Naphthalocyanine complexes with Mg (**9a**, **9b**) were prepared by treatment of dinitriles **5** and **8**, respectively, with magnesium alkoxide in pentanol/octanol mixtures. Complexes **9a** and **9b** appeared to be unstable in solution and degraded noticeably on exposure to daylight. For this reason these compounds could not be purified by column chromatography and were prepared in their pure states by several fast recrystallizations, the amount of impurities formed during cyclotetramerization in high-boiling alcohols not being as high as in the cases of the reactions in quinoline or 1-chloronaphthalene. The complexes with V (**10a**, **10b**) and Zn (**11a**, **11b**), obtained by reactions in these last two solvents and possessing higher stabilities, were purified by column chromatography on silica gel. It was noticed that the metal-naphthalocyanines **10a**, **10b**, **11a**, and **11b** slowly decompose in solution in the crude state, but are more stable after purification. Solutions of purified **10a**, **10b**, **11a**, or **11b** in toluene or THF can be kept in a closed quartz cuvette for several days without noticeable degradation. In general, the prepared Ncs with aryloxy substituents show better stability in solution than the analogous octaaryl derivatives. For example, the degradation of **9a** in THF or toluene proceeds visually more rapidly than that of **9b** in daylight. However, both compounds were stable in complete darkness, which made it possible to measure their ^{13}C NMR spectra with long scan accumulations.

We have also found that condensation of dinitriles **5** or **8** with VCl_3 in 1-chloronaphthalene results in the formation of monochlorinated macrocycles. These were observed as peaks of 15−20% intensity in the FD-mass spectra of the reaction products, together with the 100% intensity M^+ or $[M + H]^+$ peaks of **10a** or **10b**. No chlorination of the macrocycles was observed when the isoindole-1,3-diylidenediamine derivative **6** was used for the reaction with VCl_3 (synthesis of **10a**) or when three equivalents KI to one equivalent VCl_3 were added (synthesis of **10b**). The formation of molecular iodine vapor was observed in the latter case, the addition of KI not affecting the yield of **10b**. It should be noted that the crude complexes of vanadium Ncs have to be treated with THF in order to become soluble in other solvents. The solubilization of the crude products was very slow if they had been dissolved directly in other solvents such as toluene. This observation is probably connected with the hydrolysis of the crude materials to give the vanadium(IV) oxides **10a** or **10b**, which proceeds much more rapidly in THF.

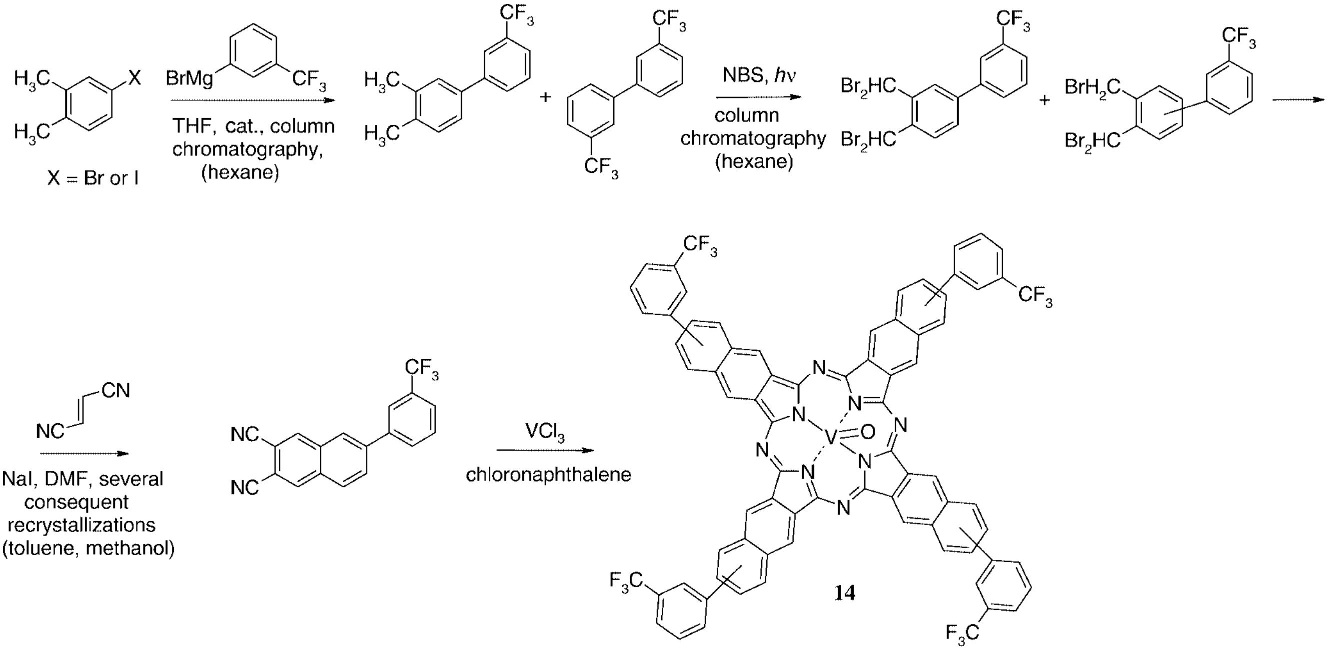
In order to obtain more information about the properties of the new substituted naphthalocyanines of series **a** {octa(*m*-trifluoromethylphenyl-substituted Ncs} and series

b {octa(m-trifluoromethylphenoxy-substituted Ncs}, we tried to prepare their complexes with indium and copper by a route similar to that used for the synthesis of vanadium compounds **10a** and **10b**. Treatment of dinitriles **5** and **8** with $InCl_3$ in chloronaphthalene yielded the corresponding (chloro)indium(III) complexes **12a** and **12b**, respectively, though these appeared to be very unstable in solution (e.g., in THF or toluene) and for this reason could not be isolated in their pure states. The copper(II) complexes **13a** and **13b** were also prepared by treatment of dinitriles **5** and **8** with anhydrous $CuCl_2$ in chloronaphthalene. Although they were stable in solution, they did not possess high solubility and were heavily aggregated even in THF, which is due to the square-planar coordination geometry of NcCu complexes and their low ability to coordinate axial ligands. These compounds were also not isolated in their pure states.

It is remarkable that the $(m\text{-}CF_3Ph)_8NcM$ complexes **9a−11a** cannot be crystallized by addition of methanol, since they are soluble in this solvent, although showing very strong aggregation. For this reason we had to use hexane to precipitate them from concentrated CH_2Cl_2, toluene, or THF solutions. In contrast, the $(m\text{-}CF_3PhO)_8NcM$ complexes **9b−11b** crystallize easily upon addition of methanol. The vanadium (**10a**, **10b**) and indium (**12a**, **12b**) compounds, in which the central metal with the axial ligand (oxygen or chlorine) is located out of the Nc plane, show good solubilities in coordinating solvents and moderate solubilities in some noncoordinating solvents. According to their UV/Vis spectra, they virtually do not aggregate in THF at concentrations of ca. 1×10^{-4} M, as well as in toluene at concentrations lower 5×10^{-5} M for **10a** and 1×10^{-5} M for **10b**, but are already displaying noticeable aggregation in $CHCl_3$ or CH_2Cl_2 at 1×10^{-6} M. Complexes of zinc(II) (**11a**, **11b**) and, especially, of magnesium(II) (**9a**, **9b**) are even more aggregated in noncoordinating solvents such as chloroform or toluene, although they are highly soluble in THF, showing very low aggregation even at high concentrations, as can be seen from their ^1H and ^{13}C NMR spectra.

To compare the solubility of **10a** with those of Ncs possessing only four peripheral *meta*-trifluoromethylphenyl substituents, we prepared the corresponding vanadyl tetra(m-trifluoromethylphenyl)naphthalocyanine (**14**, see Scheme 2) by a route similar to that used for **10a**, starting from 4-bromo- or 4-iodo-o-xylene. As expected, **14** shows a strong tendency to aggregate even in THF and is practically insoluble in toluene, in contrast to the octasubstituted derivative **10a**, and so was not further investigated. Its preparation was also complicated by the formation of two products, namely the desired 3,4-dimethyl-3′-trifluoromethyl biphenyl and the by-product 3,3′-bis(trifluoromethyl)biphenyl (see Scheme 2) during the first step, and by these not being separable by column chromatography. It was possible to remove this by-product only after partial NBS-bromination of the mixture. For these reasons we do not describe the detailed preparation of **14** in the Exp. Sect.

We conclude that the presence of eight *meta*-trifluoromethylphenyl substituents in the 3-, 4-, 12-, 13-, 21-, 22-, 30-, and 31-positions of 2,3-naphthalocyanine effectively prevents aggregation of the Nc metal complexes **9a−12a**, but only in the presence of an axial ligand or ligands (e.g. −Cl, =O, or THF) bound to the central metal atom (vanadium, indium, zinc, or magnesium). The square-planar copper complex **13a** is poorly soluble and strongly aggregated even in coordinating solvents, due to its weak ability to form penta- or hexacoordinate species. The presence of only four *meta*-trifluoromethylphenyl groups in positions 3(4), 12(13), 21(22), and 30(31) does not solubilize naphtha-



Scheme 2. Preparation of tetrakis(m-trifluoromethylphenyl)-substituted Nc complex of vanadium

Table 1. UV/Vis data for naphthalocyanine complexes

Compound	Q-band, λ [nm] (lgε)			B-band and others λ [nm] (lgε)	Solvent
	Q $_{0,0}$	Q $_{1,0}$	Q $_{2,0}$		
[(m-$CF_3Ph)_8$NcMg] (**9a**)	770 (5.63)	733 (4.78)	687 (4.82)	351 (5.15)	THF
[(m-$CF_3PhO)_8$NcMg] (**9b**)	757 (5.66)	721 (4.80)	677 (4.85)	357 (5.07)	THF
[(m-$CF_3Ph)_8$NcVO] (**10a**)	807 (5.59)	765 (4.77)	718 (4.81)	364 (5.16), 346 (5.16)	THF
[(m-$CF_3Ph)_8$NcVO] (**10a**)	817	773	725	446; 368; 325	Toluene
[(m-$CF_3PhO)_8$NcVO] (**10b**)	796 (5.57)	754 (4.77)	708 (4.80)	362 (5.07), 334 (5.06)	THF
[(m-$CF_3PhO)_8$NcVO] (**10b**)	805	763	715	440 sh., 369, 327	Toluene
[(m-$CF_3Ph)_8$NcZn] (**11a**)	771 (5.58)	733 (4.79)	688 (4.80)	344 (5.16)	THF
[(m-$CF_3Ph)_8$NcZn] (**11a**)	779	739	694	422, 350	Toluene
[(m-$CF_3PhO)_8$NcZn] (**11b**)	758 (5.59)	721 (4.81)	678 (4.83)	351 (5.13), 330 (5.16)	THF
[(m-$CF_3PhO)_8$NcZn] (**11b**)	767	729	684	351	Toluene
[(m-$CF_3Ph)_8$NcIn(Cl)] (**12a**)[a]	808	769 sh.	719	367, 346	THF
[(m-$CF_3Ph)_8$NcIn(Cl)] (**12a**)[a]	812	771	720	457, 370, 348	Toluene
[(m-$CF_3PhO)_8$NcIn(Cl)] (**12b**)[a]	796	757	709	366, 337	THF
[(m-$CF_3PhO)_8$NcIn(Cl)] (**12b**)[a]	800	760	711	448 sh., 373, 339	Toluene
[(m-$CF_3Ph)_8$NcCu] (**13a**)[a]	777, 733, 435 sh., 338				THF
[(m-$CF_3PhO)_8$NcCu] (**13b**)[a]	761, 715, 326				THF
[(m-$CF_3Ph)_4$NcVO] (**14**)[a]	796 sh., 736				THF
[$(PhS)_8$NcZn] [4]	779 (5.67)	741 (4.90)	694 (4.92)	353 (5.16)	THF

[a] Not isolated in pure state.

locyanines even in the case of the square-pyramidal complex [(m-$CF_3Ph)_4$NcVO] **14**. The key point determining the solubilities of the prepared substituted naphthalocyanines is the presence of *meta*-substituted aryls in *neighboring* positions at the periphery of the macrocycle, resulting in their nonplanar arrangement relative to the Nc plane.

The unusual instability of some Nc-metal complexes under irradiation, especially in solution, might result from the photocatalytic generation of singlet oxygen, destroying the Nc macrocycle. Complexes of Ncs with vanadium appeared to be more stable to light exposure than those with zinc or, especially, with magnesium and indium.

Spectroscopic Characterization of the Nc Complexes 9−14: The structures of the prepared Ncs were verified by mass spectrometry and UV/Vis and NMR spectroscopy, as well as by elemental analysis. The EA results are satisfactory to good for carbon and nitrogen, but less exact for hydrogen, due to the high fluorine contents in the molecules, which, as we have also observed in our previous work,[10a] disturb the determination of hydrogen.

The IR spectra do not contain much additional information on the structures of the prepared compounds **9a−11a** or **9b−11b**. The presence of CF_3 groups and aryls gives rise to intense and medium-strength vibrations, which dominate in the regions 1060−1340 cm^{-1} ($-CF_3$) and 600−930 cm^{-1} (aryls), as we have described earlier,[9,10a] the positions of which do not depend on the nature of the central metal. The Nc complexes of the series **a** and **b** have fairly similar spectral patterns. They differ mainly in the positions and intensities of several vibrations in the 1350−1600 cm^{-1} region (more intense vibrations were observed for **9b−11b**), and an additional band at ca. 1284 cm^{-1} appears in the spectra of compounds of series **b**.

The UV/Vis data for **9−14** are collected in Table 1, and the spectra of some selected compounds are shown in Figure 1. The spectra of In-, V-, Zn-, and Mg-Nc complexes in THF at low concentrations are typical of non-aggregated naphthalocyanines and consist of an intense sharp Q-band in the red or near-infrared region (750−820 nm) with two vibronic satellites on the blue side. The B-band in the UV region is very broad and in some cases has several maxima (see Figure 1). The measured molar extinction coefficients of **9a**,**b-11a**,**b** in THF are high, which also indicates no aggregation at least at low concentrations ($< 10^{-5}$ M). The lg(ε) values for the Q-bands of V, Zn, and Mg compounds in THF are in the range of 5.57−5.66, similar to that seen in [$(PhS)_8$NcZn][4] and higher than those found for alkylthio-, alkyl-, and alkoxynaphthalocyanine complexes.[4,20] A change in the solvent from THF to toluene shifts the absorption bands bathochromically, by up to 10 nm for the Q-band (see Table 1). The naphthalocyanines with m-trifluoromethylphenoxy (m-CF_3PhO) substituents (series **b**) show a blue-shifted Q-band relative to the octakis(m-trifluoromethylphenyl) derivatives (series **a**) and the phenylthio-, alkyl-, alkoxy-, and alkylthio-substituted metal-

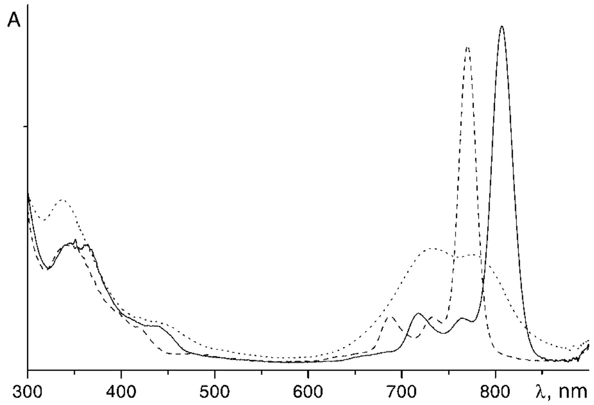
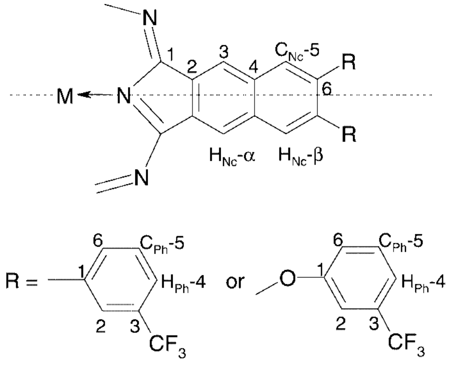


Figure 1. UV/Vis spectra of (m-$CF_3Ph)_8$NcVO (**10a**, solid line), (m-$CF_3Ph)_8$NcZn (**11a**, dashed line), and (m-$CF_3Ph)_8$NcCu (dotted line) in THF at concentrations lower than 1×10^{-5} M

naphthalocyanines with the same substitution pattern, as well as the unsubstituted NcMs.[4,20] The difference in the absorption maxima of the Q-band between $(m\text{-}CF_3Ph)_8NcM$ and $(m\text{-}CF_3PhO)_8NcM$ reaches 13 nm for Zn and Mg complexes, respectively, even though substituents at the most distant peripheral positions of Nc macrocycle possess the weakest abilities to shift the Q-band.[20] This is due to the weaker conjugation of the oxygen in the aryloxy substituents with the Nc macrocycle in $(m\text{-}CF_3PhO)_8NcM$ **9b**−**12b**, caused by competitive delocalization of oxygen electron pairs onto the trifluoromethylphenyl groups. This can affect even the electron-withdrawing properties for $m\text{-}CF_3PhO$ substituents in contrast to alkyloxy groups. In contrast, the $m\text{-}CF_3Ph$ groups are in partial conjugation with the macrocycle, donating π-electrons and shifting the Q-band slightly towards the red. However, the "shifting" effect of $m\text{-}CF_3Ph$ substituents in the Nc unit is much weaker than their effect in the porphyrazine unit.[9,10a]

The high solubilities of the Zn and Mg complexes **9a**, **9b**, **11a**, and **11b** in THF allowed well resolved ^1H and ^{13}C NMR spectra to be recorded for these compounds. The ^1H NMR spectra each show two singlets for the macrocyclic α and β protons (see Scheme 3), shifted downfield in relation to the protons of the corresponding dinitriles **5** and **8** due to the ring current effect, and the multiplets of aryl or aryloxy substituents (see Exp. Sect. and Figure 2). Signals of small amounts of co-crystallized or coordinated solvents such as methanol, THF, hexane, or toluene, which were replaced by [D$_8$]THF upon dissolving, were also observed. All 13 nonequivalent carbons signals were observed in the 110−160 ppm region in the ^{13}C NMR spectra of **9a**, **9b**, **11a**, and **11b** and were assigned (see Exp. Sect. and Figure 2). The assignment was carried out in the light of our previous results on aryl-substituted porphyrazines,[9,10a] with analysis of the numerous data obtained in this work for precursors and Nc complexes, and also by consideration of nuclear Overhauser effects and the influence of fluorine nuclei. The ^1H and ^{13}C spectra of $(m\text{-}CF_3PhO)_8NcMg$ **9b** are shown as an example in Figure 2, demonstrating the resolution of ^1H and ^{13}C signals and their assignment. The ^1H NMR spectrum of $[(m\text{-}CF_3Ph)_8NcVO]$ **10a** in [D$_8$]THF was also recorded. Because of the paramagnetism of V^{IV}, the signals of Nc-macrocycle protons were not observed in the $\delta = -6$ to $\delta = 18$ ppm region, the signals of the $m\text{-}CF_3Ph$ substituents appearing in their usual region as a broadened multiplet. Along with the paramagnetism of the central metal, the broadening of these signals is also caused by aggregation of the compound at concentrations close to saturation. The solubility of **10a** was not high enough for its ^{13}C NMR spectrum to be recorded.



Scheme 3. Numbering of H and C atoms of naphthalocyanines **9a**, **9b**, **11a**, and **11b** used for describing their NMR spectroscopic data

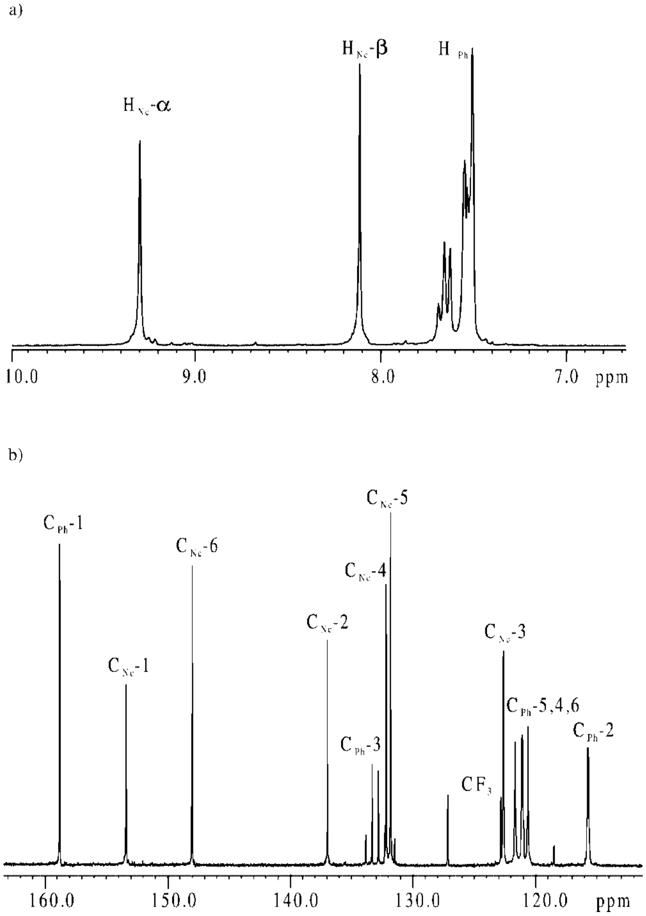


Figure 2. ^1H (a) and ^{13}C (b) NMR spectra of $(m\text{-}CF_3PhO)_8NcMg$ (**9b**) in [D$_8$]THF (the signal assignment is given in Scheme 3)

Experimental Section

General: 4,5-Dibromo-*o*-xylene (**1**),[21] 6,7-dibromo-2,3-dicyanonaphthalene (**7**),[22] and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**2**)[11] were synthesized according to the literature. 3-Bromobenzotrifluoride (98% pure), 4-bromo-*o*-xylene, 4-iodo-*o*-xylene, 4-bromoveratrol, and 3-hydroxybenzotrifluoride were purchased from Lancaster, Avocado, or Aldrich and were used without additional purification. THF for Grignard reactions was dried over sodium and distilled, and the other solvents were used without additional purification.

The following equipment was used for characterization: UV/Vis: Schimadzu 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: Finnigan TSQ 70 MAT (EI), Varian Mat 711 (FD), G2025A Hewlett Packard (MALDI-TOF). Elemental analyses: Carlo−Erba Elemental Analyzer 1104, 1106.

4,5-Bis[*m*-(trifluoromethyl)phenyl]-*o*-xylene (3a): A mixture of **1** (11 g, 41.7 mmol), **2** (0.7 g, 1.64 mmol), and nickel(II) acetylacetonate [Ni(Acac)$_2$] (0.2 g, 0.74 mmol, 95% pure, Aldrich) in dry THF (30 mL) was stirred for 20 min under inert atmosphere. A solution of the Grignard reagent prepared from 3-bromobenzotrifluoride (34 g, 151 mmol) and magnesium turnings (3.7 g, 152 mmol) in dry THF (150 mL) was then added dropwise to the obtained light-greenish suspension, over a period of 1 h, the reaction mixture immediately turning dark brown. To avoid a vigorous exothermic process, the reaction mixture had to be cooled in a ice/water bath during the addition. It was kept overnight at room temperature, and the formation of MgBr$_2$ precipitate was observed. The obtained mixture was quenched with ice/water/dilute HCl solution and extracted with diethyl ether (2 × 100 mL). The obtained organic solution was washed with brine and dried over anhydrous MgSO$_4$, and the solvent and other volatile compounds were rotary evaporated off to yield a brown, viscous oil, which was chromatographed with *n*-hexane on silica gel. The second UV-active large fraction was collected, the solvent was removed in a rotary evaporator, and the colorless, viscous residue was dissolved in 100 mL of hot methanol. After having been kept at −20 °C overnight, the methanol solution gave 10.2 g (62%) of **3a** as a pure white, crystalline substance. M.p. 68−70 °C. ^{1}H NMR (CDCl$_3$): δ = 2.40 (s, 6 H, C*H$_3$*), 7.20−7.50 (m, 10 H, H_{Ph} + H_{Xy}) ppm, where Ph = 3-CF$_3$-phenyl ring, Xy = xylene ring. ^{13}C NMR (CDCl$_3$, the atom numbering is according to nomenclature): δ = 19.4 (s, *C*H$_3$), 123.2 (q, $^3J \approx 3.9$ Hz, C_{Ph}-4), 124.0 (q, $^1J \approx 272$ Hz, *C*F$_3$), 126.7 (q, $^3J \approx 3.9$ Hz, C_{Ph}-2), 128.4 (s, C_{Ph}-5), 130.5 (q, $^2J \approx 32.4$ Hz, C_{Ph}-3), 131.7 (s, C_{Xy}-3,6), 133.1 (s, C_{Ph}-6), 136.7 (s, C_{Ph}-1), 137.0 (s, C_{Xy}-1,2), 141.7 (s, C_{Xy}-4,5) ppm. $C_{22}H_{16}F_6$ (394.36): calcd. C 67.01, H 4.09, F 28.90; found C 67.27, H 3.66.

4,5-Bis(3,4-dimethoxyphenyl)-*o*-xylene (3b): Compounds **1** (16 g, 60.6 mmol), **2** (1.1 g, 2.6 mmol), and [Ni(Acac)$_2$] (0.34 g, 1.3 mmol) in 30 mL of THF, and 4-bromoveratrol (46 g, 212 mmol) and Mg (5.15 g, 212 mmol) in 210 mL of THF were used for the same procedure as described for the preparation of **3a**. The reaction mixture was quenched with ice/water/NH$_4$Cl solution and extracted with diethyl ether. The organic phase was dried and the solvent was rotary evaporated. The residue was chromatographed on silica gel with CH$_2$Cl$_2$. The first fraction, probably containing veratrol, was removed. The second fraction, containing **3b** in admixture with 3,3′,4,4′-tetramethoxybiphenyl, was collected, the solvent was removed, and the solid was recrystallized from hexane. After drying, the obtained material was additionally recrystallized from methanol, giving a white powder. Yield 10 g (44%) after drying in vacuo. M.p. 138−139 °C. ^{1}H NMR (CDCl$_3$, Ph = 3,4-dimethoxyphenyl ring, numbering according to IUPAC nomenclature): δ = 2.33 (s, 6 H, C*H*$_3$), 3.59 (s, 6 H, OC*H*$_3$), 3.83 (s, 6 H, OC*H*$_3$), 6.59 (s, broadened, 2 H, H_{Ph}-2), 6.74−6.75 (m, 4 H, H_{Ph}-5,6), 7.20 (s, 2 H, H_{Xy}-3,6) ppm. ^{13}C NMR (CDCl$_3$, the atom-numbering is according to IUPAC nomenclature): δ = 19.3 (s, *C*H$_3$), 55.6, 55.8 (s + s, 3-O*C*H$_3$ and 4-O*C*H$_3$), 110.8 (s, C_{Ph}-2), 113.6 (s, C_{Ph}-5), 121.8 (s, C_{Ph}-6), 131.6 (s, C_{Xy}-3,6), 134.4 (s, C_{Ph}-1), 135.6 (s, C_{Xy}-1,2), 137.7 (s, C_{Xy}-4,5), 147.6, 148.2 (s + s, C_{Ph}-3 and C_{Ph}-4) ppm. MS (EI): *m*/*z* = 378.1 (100), [M$^+$]. $C_{24}H_{26}O_4$ (378.47): calcd. C 76.17, H 6.92; found C 75.79, H 7.55.

1,2-Bis(dibromomethyl)-4,5-bis[*m*-(trifluoromethyl)phenyl]benzene (4): A mixture of **3a** (1 g, 2.54 mmol) and *N*-bromosuccinimide (NBS, 1.8 g, 10.1 mmol) in tetrachloromethane (40 mL) was heated at reflux under UV irradiation (mercury lamp) for 10 h until all the NBS had been converted into succinimide, floating on the surface of the tetrachloromethane solution. After cooling, the reaction mixture was filtered, the solvent was removed from the filtrate, and the obtained viscous residue was recrystallized from methanol to yield 1.3 g (72%) of **4** as a white powder. M.p. 147−150 °C. ^{1}H NMR (CDCl$_3$): δ = 7.18−7.75 (m, 12 H, C*H*Br$_2$ + H_{Ph} + H_{Benz}) ppm. ^{13}C NMR (CDCl$_3$, the atom-numbering is according to nomenclature): δ = 35.5 (s, *C*HBr$_2$), 123.7 (q, $^1J \approx 273$ Hz, *C*F$_3$), 124.5 (q, $^3J \approx 3.7$ Hz, C_{Ph}-4), 126.5 (q, $^3J \approx 3.7$ Hz, C_{Ph}-2), 129.0 (s, C_{Ph}-5), 130.9 (q, $^2J \approx 32.8$ Hz, C_{Ph}-3), 131.4 (s, very broad, C_{Benz}-3,6), 132.8 (s, C_{Ph}-6), 137.6 (s, very broad, C_{Benz}-1,2), 139.4 (s, C_{Ph}-1), 141.2 (s, broadened, C_{Benz}-4,5) ppm. MS (FD): *m*/*z* = 709.5 (100), quint, [M$^+$]. $C_{22}H_{12}Br_4F_6$ (709.95): calcd. C 37.22, H 1.70, Br 45.02, F 16.06; found C 36.74, H 1.12, Br 41.08.

2,3-Dicyano-6,7-bis[*m*-(trifluoromethyl)phenyl]naphthalene (5): A mixture of **4** (4 g, 5.63 mmol), fumaronitrile (0.6 g, 7.7 mmol), and NaI (5.5 g, 36.7 mmol) in DMF (30 mL) was heated on the oil bath at 60−70 °C for 6 h and then left at room temperature for 10 h. A saturated NaHSO$_3$ solution was then added to the formed dark brown, half-solidified mass until the dark color of the solution had disappeared. The precipitated yellowish substance was filtered off, washed thoroughly with NaHSO$_3$ solution and then with water, and dried under vacuum at 80 °C. The obtained powder was dissolved in CH$_2$Cl$_2$ to give a saturated solution, which was slowly diluted with an excess of hexane. The formed off-white crystalline precipitate was filtered off and dried. Yield 1.8 g (67%) of **5**. M.p 215−217 °C. FT-IR (KBr): $\tilde{\nu}$ = 3072 cm^{-1} vw, 2235 m, 2229 m, 1630 vw, 1593 vw, 1558 vw, 1490 vw, 1481 vw, 1444 w, 1431 m, 1404 vw, 1388 vw, 1330 vs, 1287 vw, 1258 m, 1216 m, 1167 s, 1124 s, 1098 m, 1075 m, 1050 m, 1002 vw, 984 vw, 922 m, 905 m, 856 w, 814 m, 805 m, 739 w, 709 m, 691 w, 659 m, 554 vw, 534 w, 475 m. ^{1}H NMR (CDCl$_3$, the atom-numbering is according to IUPAC nomenclature): δ = 7.35−7.58 (m, 8 H, H_{Ph}), 8.08 (s, 2 H, H_{Naph}-5,8), 8.42 (s, 2 H, H_{Naph}-1,4) ppm. ^{13}C NMR (CDCl$_3$): δ = 111.0 (s, C_{Naph}-2,3), 115.7 (s, *C*N), 123.6 (q, $^1J \approx 273$ Hz, *C*F$_3$), 124.7 (q, ^{3}J≈ 3.8 Hz, C_{Ph}-4), 126.5 (q, ^{3}J≈ 3.8 Hz, C_{Ph}-2), 129.1 (s, C_{Ph}-5), 130.1 (s, C_{Naph}-1,4), 131.0 (q, $^2J \approx 32.4$ Hz, C_{Ph}-3), 132.6 (s, C_{Naph}-9,10), 132.9 (s, C_{Ph}-6), 135.7 (s, C_{Naph}-5,8), 139.6 (s, C_{Naph}-6,7), 142.5 (s, C_{Ph}-1) ppm. MS (EI): *m*/*z* = 466.0 (100) [M$^+$], 397.1 (50) [M − CF$_3$]$^+$], 328.1 (40), [M − 2CF$_3$]$^+$, and other fragments with the peaks of lower intensity. $C_{26}H_{12}F_6N_2$ (466.39): calcd. C 66.96, H 2.59, N 6.01, F 24.44; found C 67.24, H 2.18, N 6.11.

6,7-Bis[*m*-(trifluoromethyl)phenyl]benzo[*f*]isoindole-1,3-diylidenediamine (6): Compound **5** (1 g, 2.15 mmol) was suspended in a methanol (25 mL) solution of Na (55 mg, 2.4 mmol) for 20 h with bubbling of a stream of dry ammonia through the reaction mixture at room temperature. The reaction was monitored by TLC until complete disappearance of the starting material. The formed yellowish suspension was diluted with water (ca. 10 mL) and filtered, and the obtained precipitate was washed thoroughly with water and dried at 70 °C under vacuum. Yield 1 g (96%) of white-yellowish poor soluble powder. FT-IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} vw, 3216 w, broad, 3038 m, broad, 1701 w, 1641 m, 1597 w, 1538 m, 1475 m, 1453 m, 1392 w, 1336 vs, 1301 m, 1274 w, 1256 m, 1168 s, 1120 s, 1098 m, 1076 m, 1047 w, 911 m, 863 w, 807 m, 709 m, 660 w, 610 w, 480 w. $C_{26}H_{15}F_6N_3$ (483.42): calcd. C 64.60, H 3.13, N 8.69, F 23.58; found C 64.41, H 2.78, N 8.07.

2,3-Dicyano-6,7-bis[*m*-(trifluoromethyl)phenyloxy]naphthalene (8): Compound **7** (2.5 g, 7.4 mmol), 3-hydroxybenzotrifluoride (8 g, 49.4 mmol), and anhydrous K$_2$CO$_3$ (10 g, 72.5 mmol) in DMF (50 mL) were heated at 130 °C for 15 h. After cooling, the reaction mixture was slowly diluted with water (200−300 mL) and the formed precipitate was filtered off, thoroughly washed with water, and dried at 80 °C under vacuum. This crude product was purified further either by column chromatography (silica gel, CH_2Cl_2), or by crystallization as follows: the crude material was dissolved in boiling toluene, and hexane or heptane was added dropwise after the solution had been allowed to cool down slightly, in order to initiate the crystallization process. After the formation of the first crystals, the addition was stopped and the solution was left to cool to room temperature. The formed precipitate was filtered off and dried at 80 °C under vacuum. Yield (after purification by column chromatography) 1.8 g (49%) of white-yellowish powder. M.p. 203−205 °C. FT-IR (KBr): $\tilde{\nu}$ = 3074 cm^{-1} vw, 2238 m, 2233 m, 1630 w, 1597 m, 1492 s, 1464 s, 1450 s, 1420 w, 1395 m, 1324 vs, 1285 s, 1263 s, 1233 m, 1213 s, 1187 vs, 1122 vs, 1094 m, 1064 m, 1003 vw, 925 s, 917 m, 903 m, 880 m, 801 m, 744 w, 698 m, 656 w, 532 w, 473 w. ^1H NMR ($CDCl_3$, the atom-numbering is according to IUPAC nomenclature, Ph = 3-CF_3-phenoxy group): δ = 7.21−7.28 (m, 4 H, H_{Ph}), 7.40 (s, 2 H, H_{Naph}-5,8), 7.46−7.57 (m, 4 H, H_{Ph}), 8.15 (s, 2 H, H_{Naph}-1,4) ppm. ^{13}C NMR ($CDCl_3$): δ = 110.0 (s, C_{Naph}-2,3), 115.6 (s, *C*N), 116.1 (q, $^3J \approx$ 3.8 Hz, C_{Ph}-2), 116.4 (s, C_{Ph}-6), 121.8 (q, $^3J \approx$ 3.8 Hz, C_{Ph}-4), 122.4 (s, C_{Ph}-5), 123.4 (q, $^1J \approx$ 272 Hz, CF_3), 130.7 (s, C_{Naph}-9,10), 130.9 (s, C_{Naph}-5,8), 132.9 (q, $^2J \approx$ 32.8 Hz, C_{Ph}-3), 134.4 (s, C_{Naph}-1,4), 150.8 (s, C_{Naph}-6,7), 155.5 (s, C_{Ph}-1) ppm. MS (EI): *m*/*z* = 498.0 (100) $[M^+]$, 336.0 (30) $[M - OC_7H_4F_3 - H]^+$, 317.0 (50) $[M - OC_7H_4F_3 - HF]^+$, 268.1 (30) $[M - OC_7H_4F_3 - CF_3]^+$ and other fragments with the peaks of lower intensity. $C_{26}H_{12}F_6N_2O_2$ (498.39): calcd. C 62.66, H 2.43, N 5.62, F 22.87; found C 62.65, H 2.08, N 5.60.

{3,4,12,13,21,22,30,31-Octakis[*m*-(trifluoromethyl)phenyl]-2,3-naphthalocyaninato}magnesium (9a): Mg turnings (40 mg, 1.65 mmol) were dissolved in a pentanol/octanol mixture (1:1, 7 mL) at 160 °C, and compound **5** (0.7 g, 1.50 mmol) was added. The reaction mixture was stirred at 160 °C for 2.5 h, cooled down, and transferred into methanol (50 mL). Water was added dropwise to the obtained mixture in order to complete the precipitation of product, followed by centrifugation. The solid material was again washed several times with methanol and water and was dried in vacuo at 60 °C. After drying, the compound was dissolved in a CH_2Cl_2/THF mixture (1:1) and rapidly filtered into hexane, the formed precipitate being centrifuged and dried. Yield 0.28 g (40%) of green powder. UV/Vis (THF): λ (lgε) = 770 (5.63), 733 (4.78), 687 (4.82), 351 (5.15) nm. FT-IR (KBr): $\tilde{\nu}$ = 1613 cm^{-1} vw, 1592 vw, 1490 vw, 1474 vw, 1441 vw, 1422 w, 1372 m, 1332 vs, 1257 m, 1238 w, 1167 s, 1128 s, 1095 s, 1077 s, 1046 w, 1034 m, 1002 vw, 981 vw, 906 m, 879 w, 848 vw, 804 m, 745 w, 736 vw, 702 s, 659 w, 564 vw, 476 w. ^1H NMR ($[D_8]$THF, for numbering see Scheme 3): δ = 7.50−7.80 (m, 32 H, H_{Ph}), 8.53 (s, 8 H, H_{Nc}-β), 9.40 (s, 8 H, H_{Nc}-α) ppm. ^{13}C NMR ($[D_8]$THF): δ = 122.5 (s, C_{Nc}-3), 124.6 (q, low resolved, C_{Ph}-4), 125.3 (q, $^1J \approx$ 272 Hz, CF_3), 128.0 (q, low resolved, C_{Ph}-2), 130.0 (s, C_{Ph}-5), 131.4 (q, $^2J \approx$ 32.4 Hz, C_{Ph}-3), 132.5 (s, C_{Ph}-6), 134.0 (s, C_{Nc}-4), 134.6 (s, C_{Nc}-5), 137.7 (s, C_{Nc}-2), 138.6 (s, C_{Nc}-6), 142.9 (s, C_{Ph}-1), 153.9 (s, C_{Nc}-1) ppm. $C_{104}H_{48}F_{24}MgN_8 \times 2H_2O$ (1889.9 +36.0): calcd. C 64.86, H 2.72, N 5.82, F 23.68; found C 64.19, H 2.68, N 5.25.

{3,4,12,13,21,22,30,31-Octakis[*m*-(trifluoromethyl)phenoxy]-2,3-naphthalocyaninato}magnesium (9b): Mg turnings (10 mg, 0.41 mmol) were dissolved in a pentanol/octanol mixture (1:1, 3 ml) at 160 °C and compound **8** (380 mg, 0.76 mmol) was added. The reaction mixture was heated at reflux for 1 h and cooled. The formed dense mass was washed thoroughly with methanol, dried, dissolved in THF, and rapidly filtered into methanol. The obtained precipitate was centrifuged and dried in vacuo at 60 °C. Yield 240 mg (62%) of dark green powder. UV/Vis (THF): λ (lgε) = 757 (5.66), 721 (4.80), 677 (4.85), 357 (5.07) nm. FT-IR (KBr): $\tilde{\nu}$ = 3675 cm^{-1} vw, 3072 vw, 1615 w, 1594 m, 1491 m, 1449 s, 1356 m, 1328 vs, 1284 m, 1253 s, 1219 m, 1172 m, 1125 s, 1091 m, 1081 m, 1064 m, 1034 m, 1001 vw, 925 m, 908 m, 881 w, 793 w, 764 vw, 745 w, 724 vw, 696 m, 655 w, 626 vw, 538 vw, 475 w, 452 vw. ^1H NMR ($[D_8]$THF): δ = 7.48−7.68 (m, 32 H, H_{Ph}), 8.07 (s, 8 H, H_{Nc}-β), 9.22 (s, 8 H, H_{Nc}-α) ppm. ^{13}C NMR ($[D_8]$THF): δ = 115.7 (q, $^3J \approx$ 3.7 Hz, C_{Ph}-2), 120.6 (s, C_{Ph}-6), 121.1 (q, $^3J \approx$ 4.1 Hz, C_{Ph}-4), 121.6 (s, C_{Ph}-5), 122.6 (s, C_{Nc}-3), 125.0 (q, $^1J \approx$ 272 Hz, CF_3), 131.8 (s, C_{Nc}-5), 132.2 (s, C_{Nc}-4), 133.0 (q, $^2J \approx$ 32.4 Hz, C_{Ph}-3), 136.9 (s, C_{Nc}-2), 148.0 (s, C_{Nc}-6), 153.4 (s, C_{Nc}-1), 158.8 (s, C_{Ph}-1) ppm. MS (MALDI-TOF): *m*/*z* = 2018.9 (100) $[M + H]^+$. $C_{104}H_{48}F_{24}MgN_8O_8 \times H_2O$ (2017.9 +18.0): calcd. C 61.36, H 2.48, N 5.50, F 22.60; found C 61.42, H 2.31, N 5.65.

{3,4,12,13,21,22,30,31-Octakis[*m*-(trifluoromethyl)phenyl]-2,3-naphthalocyaninato}oxovanadium (10a): A small flask containing **6** (0.5 g, 1.04 mmol), VCl_3 (85 mg, 0.54 mmol), and 1-chloronaphthalene (1 mL) was placed in an oil bath (200 °C) and heated for 1 h. After cooling, the reaction mixture was thoroughly washed with hexane and dissolved in THF. The solvent was rapidly removed by rotary evaporation, and the solid material was chromatographed on silica gel with toluene/$CHCl_3$ (1:1). The first colored fraction was collected, concentrated on a rotary evaporator, and precipitated with hexane. The product was centrifuged and dried under vacuum at 70 °C. Yield 0.34 g (68%) of light green, fine powder. UV/Vis (THF): λ (lgε) = 807 (5.59), 765 (4.77), 718 (4.81), 364 (5.16), 346 (5.16) nm. FT-IR (KBr): $\tilde{\nu}$ = 1613 cm^{-1} vw, 1591 vw, 1470 vw, 1425 w, 1376 m, 1332 vs, 1256 m, 1237 w, 1168 s, 1128 s, 1090 s, 1077 s, 1044 m, 1007 w, 981 vw, 906 m, 885 w, 850 vw, 805 m, 773 vw, 750 w, 737 w, 702 s, 659 w, 565 vw, 476 w. ^1H NMR ($[D_8]$THF): δ = 7.50−7.75 (m, broadened, H_{Ph}) ppm. MS (FD): *m*/*z* = 1933.5 (100) $[M + H]^+$]. $C_{104}H_{48}F_{24}N_8OV$ (1932.5): calcd. C 64.64, H 2.50, N 5.80, F 23.59; found C 64.90, H 3.02, N 5.99.

{3,4,12,13,21,22,30,31-Octakis[*m*-(trifluoromethyl)phenoxy]-2,3-naphthalocyaninato}oxovanadium (10b): 1-Chloronaphthalene (0.2 mL) was added by syringe at 195 °C to a mixture of **8** (200 mg, 0.40 mmol), VCl_3 (20 mg, 0.13 mmol), and NaI (60 mg, 0.40 mmol), and the reaction mixture was heated at this temperature for 30 min. The evolution of I_2 was observed during the reaction. After cooling, the mixture was thoroughly washed with hexane to remove chloronaphthalene and iodine, and the purification was carried out as in the case of **10a**, including the treatment with THF. Yield 75 mg (37%) of green powder. UV/Vis (THF): λ (lgε) = 796 (5.57), 754 (4.77), 708)4.80), 362 (5.07) 334 (5.06) nm. FT-IR (KBr): $\tilde{\nu}$ = 1616 cm^{-1} vw, 1594 m, 1490 s, 1449 s, 1359 s, 1328 vs, 1284 s, 1254 s, 1220 m, 1171 s, 1125 s, 1088 s, 1064 m, 1044 vw, 1003 w, 926 m, 909 m, 884 m, 793 w, 750 w, 696 m, 654 vw, 477 vw. MS (FD): *m*/*z* = 2060.9 (100) $[M^+]$. $C_{104}H_{48}F_{24}N_8O_9V$ (2060.5): calcd. C 60.62, H 2.35, N 5.44, F 22.13; found C 60.72, H 2.57, N 5.57.

{3,4,12,13,21,22,30,31-Octakis[*m*-(trifluoromethyl)phenyl]-2,3-naphthalocyaninato}zinc (11a): Quinoline (0.1 mL) was added by syringe at 210 °C to a mixture of **5** (100 mg, 0.21 mmol) and $ZnCl_2$ (20 mg, 0.15 mmol), and the temperature was maintained for 30 min. After cooling, the reaction mixture was thoroughly washed with hexane, dissolved in CH_2Cl_2, and precipitated with hexane, and the obtained solid was chromatographed on silica gel with toluene/THF (3:1). The first colored fraction was collected, concentrated, precipitated with hexane, centrifuged, and dried in vacuo at 70 °C. Yield 28 mg (27%) of **11a**. UV/Vis (THF): λ (lgε) = 771 (5.58), 733 (4.79), 688 (4.80), 344 (5.16) nm. FT-IR (KBr): $\tilde{\nu}$ = 1612 cm^{-1} vw, 1592 vw, 1490 vw, 1471 vw, 1422 w, 1373 m, 1332 vs, 1256 m, 1237 w, 1167 s, 1127 s, 1095 s, 1075 s, 1046 w, 1035 m, 1001 vw, 981 vw, 905 m, 877 w, 804 m, 739 w, 701 s, 659 w, 561 vw, 475 w. ^{1}H NMR ([D$_8$]THF): δ = 7.54−7.75 (m, 32 H, H_{Ph}), 8.50 (s, 8 H, H_{Nc}-β), 9.30 (s, 8 H, H_{Nc}-α) ppm. ^{13}C NMR ([D$_8$]THF): δ = 122.4 (s, C_{Nc}-3), 124.7 (q, low resolved, C_{Ph}-4), 125.3 (q, $^{1}J \approx 272$ Hz, CF$_3$), 127.9 (q, low resolved, C_{Ph}-2), 130.0 (s, C_{Ph}-5), 131.5 (q, $^{2}J \approx 32.0$ Hz, C_{Ph}-3), 132.6 (s, C_{Ph}-6), 134.0 (s, C_{Nc}-4), 134.6 (s, C_{Nc}-5), 136.9 (s, C_{Nc}-2), 138.7 (s, C_{Nc}-6), 142.8 (s, C_{Ph}-1), 153.6 (s, C_{Nc}-1) ppm. $C_{104}H_{48}F_{24}N_8Zn \times 0.5$ toluene (1930.9 +46.07): calcd. C 65.31, H 2.65, N 5.67, F 23.61; found C 65.25, H 2.99, N 5.22.

{3,4,12,13,21,22,30,31-Octakis[*m*-(trifluoromethyl)phenoxy]-2,3-naphthalocyaninato}zinc (11b): The reaction between **8** (200 mg, 0.40 mmol), ZnCl$_2$ (40 mg, 0.29 mmol), and quinoline (0.2 mL) was carried out as in the case of **11a** (210 °C, 15 min). After cooling, the product was thoroughly washed with methanol, chromatographed as in case of **11a**, concentrated, and precipitated by addition of methanol. Yield 103 mg (50%) after drying in vacuo at 70 °C. UV/Vis (THF): λ (lgε) = 758 (5.59), 721 (4.81), 678 (4.83), 351 (5.13), 330 (5.16) nm. FT-IR (KBr): $\tilde{\nu}$ = 1616 cm^{-1} vw, 1595 m, 1490 m, 1449 s, 1358 m, 1329 vs, 1284 m, 1254 s, 1221 w, 1170 m, 1124 s, 1091 m, 1063 m, 1037 w, 925 m, 909 m, 879 w, 794 w, 739 w, 696 m, 656 vw, 476 vw. ^{1}H NMR ([D$_8$]THF): δ = 7.55−7.72 (m, 32 H, H_{Ph}), 8.02 (s, 8 H, H_{Nc}-β), 9.13 (s, 8 H, H_{Nc}-α) ppm. ^{13}C NMR ([D$_8$]THF): δ = 115.9 (q, $^{3}J \approx 4.1$ Hz, C_{Ph}-2), 120.2 (s, C_{Ph}-6), 121.2 (q, $^{3}J \approx 4.1$ Hz, C_{Ph}-4), 121.5 (s, C_{Ph}-5), 122.8 (s, C_{Nc}-3), 125.0 (q, $^{1}J \approx 272$ Hz, CF$_3$), 131.87 (s, C_{Nc}-5), 131.94 (s, C_{Nc}-4), 133.1 (q, $^{2}J \approx 32.4$ Hz, C_{Ph}-3), 135.9 (s, C_{Nc}-2), 148.1 (s, C_{Nc}-6), 152.8 (s, C_{Nc}-1), 158.7 (s, C_{Ph}-1) ppm. $C_{104}H_{48}N_8O_8F_{24}Zn$ (2058.9): calcd. C 60.67, H 2.35, N 5.44, F 22.15; found C 60.77, H 1.95, N 5.43.

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