Synthesis of Hexadecaalkoxy-Substituted Nickel and Iron Phthalocyanines

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Transition metal phthalocyanines **3a–g**, **4e,f** and **5e,g** substituted with sixteen alkoxy groups and various chain lengths were synthesized from the corresponding tetraalkoxyphthalodinitriles and characterized by spectroscopic methods. In the UV/vis spectra of the hexadecaalkoxy-substituted phthalocyanines a bathochromic shift of the Q band up to ca. 80 nm relative to the unsubstituted phthalocyanines was observed. All described phthalocyanines **3a–g**, **4e,f** and **5e,g** exhibit excellent solubility in organic solvents.

Over the last few years, soluble peripherally substituted metal phthalocyanines R_xPcM, their bisaxially coordinated complexes R_xPcML_2 and bridged systems $[R_xPcM(L)]_n$ have been investigated intensively with respect to their electrical conductivities, non-linear optical, liquid crystalline and other physical properties.[1] The good solubility of these systems is due to the introduction of bulky or long chain alkyl or alkoxy groups into the periphery of the macrocycle.[2]

In contrast to this, peripherally unsubstituted metal phthalocyanines PcM are practically insoluble in organic solvents thereby minimizing their applications. The best investigated soluble substituted phthalocyanines are the tetra- and octasubstituted derivatives, tetrasubstituted phthalocyanines exhibiting usually a higher solubility.[2] This is due to a higher disorder of these systems in the solid state caused by the formation of four constitutional isomers during synthesis.[2] The higher dipole moment of the tetrasubstituted phthalocyanines resulting from the unsymmetrical arrangement of the substituents in the periphery of the macrocycle also leads to a higher solubility of these systems. Some of the tetrasubstituted phthalocyanines were separated successfully by HPLC and MPLC methods into the constitutional isomers.[3]

Compared to tetra- and octasubstituted metal phthalocyanines,[1,2] fully substituted, i.e. hexadecasubstituted metal phthalocyanines $R_{16}PcM$ are relatively less studied[4,5,6] and only a few well-characterized species are known. To the best of our knowledge, nonfluorinated hexadecasubstituted alkoxy derivatives $(RO)_{16}PcM$ are unknown in the literature.

Hexadecaalkoxy-substituted transition metal phthalocyanines $(RO)_{16}PcM$ with M being for example Fe or Ru as the central metal ions are interesting starting materials for bridged phthalocyaninato transition metal complexes, ("shish-kebab"-polymers) which have been investigated by us in detail concerning their conductivities, non-linear optical and other properties.[1,2,7] High solubilities in organic solvents and different electronic properties, in comparison with the hitherto investigated tetra- and octaalkoxy-substituted systems, are expected for hexadecaalkoxy-substituted bridged transition metal phthalocyanines.

We report here a general synthesis of tetraalkoxyphthalodinitriles **2a–g** and their conversion to hexadecaalkoxy-substituted nickel phthalocyanines with linear **(3a–c)**, branched **(3d)** and fluorinated **(3e)** alkoxy chains as well as with substituted phenoxy groups **(3g)** (Figure 1). The synthesis of some hexadecaalkoxy-substituted iron phthalocyanines **4e–g** and their bisaxially coordinated species **5e,g** are also reported. The spectroscopic properties of the prepared compounds are described.

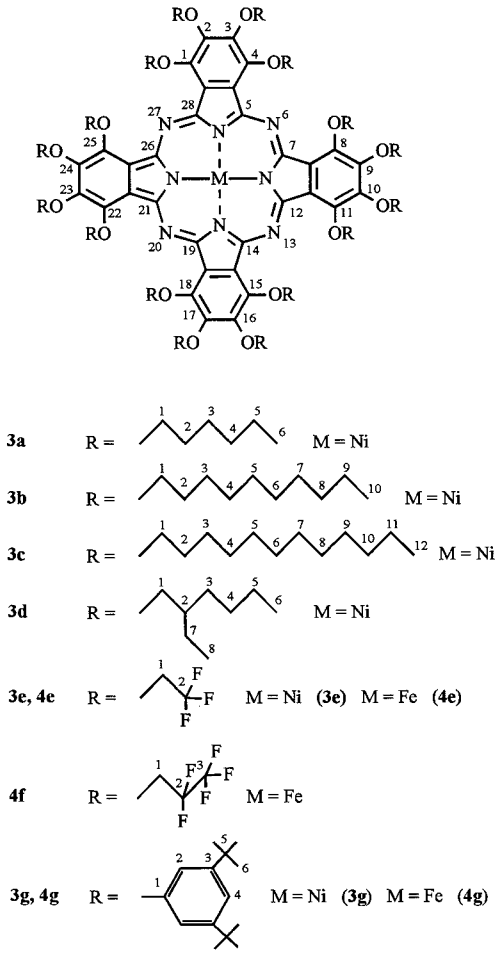
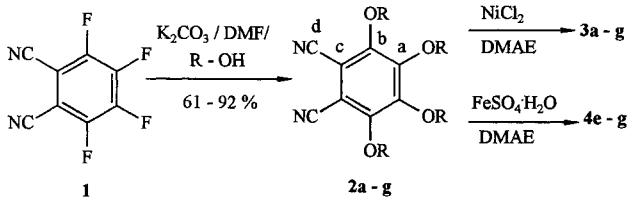


Figure 1. Structures of Hexadeca(alkoxy)phthalocyanines

The synthetic route to the hexadecaalkoxy-substituted phthalocyanines is shown in Scheme 1. The literature procedure[6] was modified to prepare the tetraalkoxy-substituted phthalodinitriles **2a–g**. The corresponding alcohols were reacted with tetrafluorophthalodinitrile **(1)** in dimethylformamide in the presence of potassium carbonate. The fluorinated alcohols, e.g. 2,2,2-trifluoroethanol, reacted rapidly with **1** at room temperature to give the completely substituted phthalodinitriles **2e–f** in high yields whereas the nonfluorinated alcohols, e.g. hexan-1-ol or 3,5-di-*tert*-butylphenol, reacted only at elevated temperatures to afford **2a–d** and **2g**, respectively.



Scheme 1

Hexadecaalkoxy-substituted nickel phthalocyanines **3a–g** were prepared by reaction of the corresponding phthalodinitriles **2a–g** with $NiCl_2$ in *N,N*-dimethylaminoethanol (DMAE). The yields given in the experimental part are not optimized. The nonfluorinated derivatives **3a–d** and **3g** show high solubilities in nonpolar organic solvents, e.g. chloroform, toluene or hexane. The solubility of these highly substituted phthalocyanines is larger than the solubility of the less substituted analogues, e.g. $PcNi(OC_6H_{13})_8$.[8] The fluorinated derivative $PcNi(OCH_2CF_3)_{16}$ **(3e)** shows a high solubility only in more polar organic solvents, e.g. acetone. All phthalocyanines **3a–g** are stable in solution.

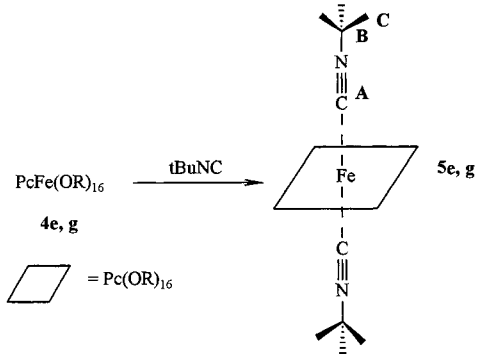
The nickel phthalocyanines with long side chains R = OC_6H_{13} **3a**, R = $OC_{10}H_{21}$ **3b** and R = $OC_{12}H_{25}$ **3c** exhibit unexpectedly low melting points (Table 1). The melting point decreases with increasing length of the side chains. Branching of the alkoxy chains as in $PcNi[O(2\text{-}EtC_6H_{12})]_{16}$ **(3d)** leads to a drastic increase in the melting point. The nickel phthalocyanines **3e** and **3g** do not melt up to 300 °C (Table 1).

Table 1. Melting Points of **3a–e** and **3g**

Compound	Melting Point [°C]
3a	81–82
3b	51–52
3c	39–40
3d	154–155
3e, 3g	> 300 (dec.)

Liquid crystalline properties of the compounds **3a–d** were not observed, in analogy to 1,4-octaalkoxy-substituted phthalocyanines $(RO)_8PcM$.[9] However, 2,3-octaalkoxy-substituted phthalocyanines with linear long side chains show liquid crystalline behaviour.[10]

Hexadecaalkoxy-substituted iron phthalocyanines with fluorinated alkoxy chains R = OCH_2CF_3 **4e** and R = $OCH_2CF_2CF_3$ **4f** were prepared from the tetraalkoxyphthalodinitriles **2e,f** by reaction with $FeSO_4 \cdot H_2O$ in DMAE. They show good solubility in polar organic solvents, e.g. acetone, methanol or tetrahydrofuran, but partial decomposition in solution was observed after several hours. No decomposition occurs in the solid state. Phthalodinitriles with nonfluorinated alkoxy side chains, e.g. R = OC_6H_{13} **2a** also react with $FeSO_4 \cdot H_2O$ under the same conditions to form the corresponding phthalocyanines, as observed by an initial colour change of the reaction mixture to green, but they all decompose during workup. The reaction of nonfluorinated tetraalkoxyphthalodinitriles, e.g. **2a** and $Fe(OAc)_2$ in hexan-1-ol with a catalytic amount of DBU, was also unsuccessful. Attempts to stabilize the iron phthalocyanines in the reaction mixture by bisaxial coordination with *tert*-butyl isocyanide or pyridine failed.[1,2] The low stability of the nonfluorinated iron phthalocyanines is probably due to their high sensitivity towards oxidation caused by the sixteen electron-donating substituents. The phenoxy-substituted phthalodinitrile **2g** gave the corresponding iron phthalocyanine **4g** in low yield, but this compound was also rather unstable. However, the iron phthalocyanine **4g** could be stabilized by bisaxial coordination with *tert*-butyl isocyanide similar to the fluorinated derivatives, e.g. $PcFe(OCH_2CF_3)_{16}$ **(4e)**, by reaction with an excess of *tert*-butyl isocyanide at 50 °C (Scheme 2).[11]



Scheme 2

UV/vis spectra of the phthalocyanines **3a–g**, **5e** and **5g** in dichloromethane and **4e,f** in acetone show the typical pattern, mainly the π–π*transition of the heteroaromatic 18-π electron system: a large, intensive $Q_{(0.0)}$ band in the visible region, accompanied by more or less resolved weak satellite bands [$Q_{(1.0)}$ and $Q_{(2.0)}$]. All phthalocyanines prepared show also the characteristic Soret or B band in the ultraviolet region. Peripheral substitution of the phthalocyanines with alkoxy groups leads to a bathochromic shift of the Q band caused by the electron-donating alkoxy chains depending on the number and the positions of the substituents. The Q band is more red shifted by substituents at the 1,4-positions than by those at the 2,3-positions.[12]

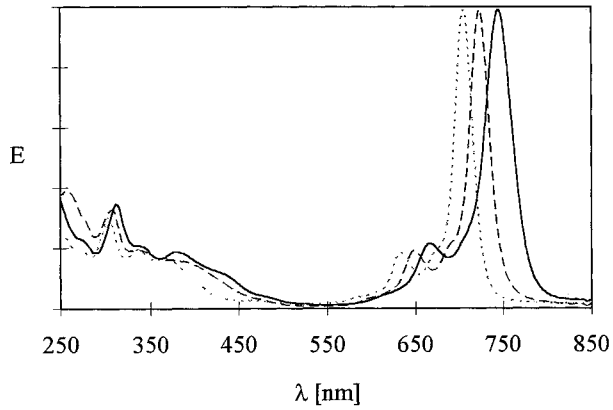


Figure 2. UV/vis spectra of **3d**(—), **3g**(– – –) and **3e**(....) in CH_2Cl_2.

The bathochromic shift of the Q band of the prepared nickel phthalocyanines **3a–c** is smaller compared to the bathochromic shift observed for the 1,4-octasubstituted analogues[13] (Table 2). Varying the chain length of the substituents as in **3a–c** has no effect on the position of the Q band, whereas, PcNi[O(2-EtC_6H_{12})]$_{16}$ **(3d)** with branched alkoxy chains shows the highest red shift of the Q band even slightly higher than the 1,4-octasubstituted analogue.[13] The phenoxy-substituted derivative **3g** exhibits the smallest red shift of the nonfluorinated compounds. Fluorine substitution in the side chains lowers the bathochromic shift of the Q band. PcNi(OCH_2CF_3)$_{16}$ **(3e)** shows the Q band at 705 nm compared to 723–745 nm for the other compounds depicted in Figure 2. Similar behaviour has been observed for PcZn(OCH_2CF_3)$_{16}$ and PcH_2(OCH_2CF_3)$_{16}$.[6,14] A lower bathochromic shift of the Q band was also observed for tetraalkoxy-substituted phthalocyanines containing fluorine.[15]

Table 2. UV/vis Data of Hexadeca(alkoxy)phthalocyanines

Compound	λ_{max} [nm]				
3a[a]	731	656	376	338	309
3b[a]	731	656	380	338	309
3c[a]	731	656	377	338	309
3d[a]	745	666	380	337	311
3e[a]	705	633	369	337	303
3g[a]	723	649	369	337	307
PcNi(OC_6H_{13})$_8$[b]	734	659	439	327	304
PcNi[O(2-EtC_6H_{12})$_8$][b]	739	663	443	327	305
PcNi(OC_5H_{11})$_8$[c]	670	641	410	312	
4e[d]	686	621		335	
4f[d]	689	623	430	335	
5e[a]	690	623		324	
5g[a]	700	630		334	

[a] In CH_2Cl_2.
[b] Substituents in 1,4-position, in toluene, ref.[13]
[c] Substituents in 2,3-position, in toluene, ref.[13]
[d] In acetone.

The UV/vis spectroscopic data (Table 2) support the structure of the obtained iron phthalocyanines **4e,f** ruling out the formation of μ-oxo-dimers which is the case for tetra- or octasubstituted iron phthalocyanines.[16] Compounds **4e,f** show Q bands at about 690 nm in non-coordinating solvents such as acetone (Table 2). No significant hypsochromic shift of the Q band was observed in pyridine which would be typical for the reduction of the iron(III) centers in μ-oxo-dimers to form hexacoordinated low spin phthalocyaninatoiron(II) complexes.[16] PcFe(OCH_2CF_3)$_{16}$ **(4e)** exhibits an additional absorption band at 748 nm in chloroform which increases with time while the absorption band at about 690 nm decreases simultaneously. This is a further support that **4e** is not a μ-oxo-dimer, however oxidation to the μ-oxo-dimer takes place in this solvent. The absorption band at 748 nm disappears by addition of pyridine to a chloroform solution of **4e**, due to reduction of the μ-oxo-dimer to the bisaxially pyridine coordinated system. The relative stability of the iron phthalocyanines substituted with fluorinated alkoxy chains in comparison to the nonfluorinated derivatives is due to the lower energies of the HOMOs caused by electron-withdrawing fluorine substitution.

The UV/vis spectrum of the bisaxially coordinated compound PcFe(OCH_2CF_3)$_{16}$[*t*-BuNC]$_2$ **(5e)** in dichloromethane shows the Q band at 690 nm. In this case the bathochromic shift is comparable to the 1,4-octasubstituted analogue.[15] The coordinated phenoxy-substituted complex PcFe(OC_6H_3[$C(CH_3)_3$]$_2$)$_{16}$[*t*-BuNC]$_2$ **(5g)** also exhibits a bathochromic shift of the Q band in CH_2Cl_2 to 700 nm (Table 2).

Cyclic voltammetric studies of PcFe(OCH_2CF_3)$_{16}$[*t*-BuNC]$_2$ **(5e)** were carried out to confirm the stabilizing effect of fluorine substitution in the alkoxy chains. Two oxidation steps were observed. In accordance with earlier studies,[12] the first step is assigned to the oxidation of the phthalocyanine ring and the second step is assigned to the oxidation of the central metal atom. The midpoint potential for the first oxidation step in dichloromethane/Bu_4NPF_6 is 0.93 V and for the second oxidation step is 1.39 V (vs. SCE). These values are remarkably higher than those of octaalkoxy-substituted species containing no fluorine, e.g. PcFe(OC_8H_{17})$_8$[*t*-BuNC]$_2$ [12] (Table 3), i.e. the electron-withdrawing effect of fluorine in the side chains predominates over the +M effect of the alkoxy chains. In particular, the value for the first oxidation step is quite high due to the lower electron density in the macrocycle which makes its oxidation more difficult.

Table 3. Midpoint Potentials of **5e** in CH_2Cl_2/Bu_4NPF_6 (V *vs.* SCE)

Compound	E_{Ox1}	E_{Ox2}
5e	0.93	1.39
PcFe[*t*-BuNC]$_2$[a]	0.50	1.40
PcFe(OC_8H_{17})$_8$[*t*-BuNC]$_2$[b]	0.22	0.77
PcFe(OC_8H_{17})$_8$[*t*-BuNC]$_2$[c]	0.38	1.16

[a] Ref.[12]
[b] Substituents in 1,4-position, ref.[12]
[c] Substituents in 2,3-position, ref.[12]

The ^{1}H NMR spectra of the nickel phthalocyanines **3a–e** (see experimental part) show the resonances of the aliphatic protons of the side chains at lower field than the corresponding phthalodinitriles **2a–e**. This is due to the aromatic ring current of the heteroaromatic systems. This effect influences mostly the methylene protons H-1 (Figure 1) leading to a larger shift to lower field. The protons of the 1,4-substituents are closer to the ring frame than those of the 2,3-substituents and therefore more affected by ring-current effects. This is in analogy to the corresponding 1,4- and 2,3-octasubstituted phthalocyanines.[13] Therefore the difference in the chemical shift of the two species of nonequivalent methylene protons at C-1 is enhanced. In the case of the bisaxially coordinated compounds **5e** and **5g**, the protons of the axial ligand show a diamagnetic ring-current shift to higher field.

The ^{13}C NMR spectra of the nickel phthalocyanines **3a–g** and the coordinated iron phthalocyanines **5e** and

5g show the resonances of the heteroaromatic carbon atoms at low field. The aliphatic carbon atoms of the alkoxy chains in 1,4-positions and 2,3-positions show more or less resolved signals for the individual carbon atoms of the chains depending on its position. In the case of the phenoxy-substituted derivatives **3g** and **5g** two resonances for each carbon atom of the substituents are observed according to the different positions of the phenoxy-substituents in the macrocycle. ^{19}F, ^{13}C-coupling of the aliphatic carbon atoms was observed for the fluorinated derivatives $PcNi(OCH_2CF_3)_{16}$ **(3e)** and $PcFe(OCH_2CF_3)_{16}[t\text{-BuNC}]_2$ **(5e)**.

Two different resonances were observed in the ^{19}F NMR spectra of the fluorinated macrocycles **3e** and **5e** due to chemical nonequivalency of the trifluoromethyl groups in these compounds. The chemical shift of the fluorine atoms is not significantly influenced by the heteroaromatic system. This is concluded by comparing the chemical shifts of **3e** and **5e** with the phthalodinitrile **2e**.

The IR spectra of the bis(*tert*-butyl isocyanide) coordinated compounds **5e** and **5g** are remarkable. In general, ν_{NC} of bis(*tert*-butyl isocyanide)phthalocyaninatoiron complex occurs at higher frequency as compared to the free ligand (Table 4).[7] This is in accordance with the predominance of the σ-donation, from the antibonding σ-orbital of the ligand to the metal ion, over the back donation from the metal ion to the antibonding π-orbital of the ligand. A significantly higher ν_{NC} was found for the fluorinated species $PcFe(OCH_2CF_3)_{16}[t\text{-BuNC}]_2$ **(5e)** than for the nonfluorinated compound $PcFe\{OC_6H_3[C(CH_3)_3]_2\}_{16}[t\text{-BuNC}]_2$ **(5g)** and the known nonfluorinated octaalkoxy-substituted compounds, e.g. $PcFe(OC_8H_{17})_8[t\text{-BuNC}]_2$ [12] as well as the unsubstituted complex $PcFe[t\text{-BuNC}]_2$ [7] as shown in Table 4, i.e. the strength of the NC-bond in **5e** is enhanced. This is caused by a weaker back donation from the iron center into the antibonding π-orbitals of the ligand due to the electron-withdrawing fluorine in the side chains which reduce the electron density in the macrocycle. Similar behaviour was observed for $PcFeF_{16}[t\text{-BuNC}]_2$, [17] where the electron-withdrawing fluorine is directly attached to the phthalocyanine ring. In this case the value for the NC-vibration is also significantly higher compared to nonfluorinated species (Table 4).

Table 4. IR-absorption of the NC-vibration of Bisaxially Coordinated Iron Phthalocyanines

Compound	ν [cm^{-1}]
5e	2166
5g	2146
$PcFe[t\text{-BuNC}]_2$[a]	2150
$PcFeF_{16}[t\text{-BuNC}]_2$[b]	2176
$PcFe(OC_8H_{17})_8[t\text{-BuNC}]_2$[c]	2143
$PcFe(OC_8H_{17})_8[t\text{-BuNC}]_2$[d]	2145
free ligand *t*-BuNC	2138

[a] Ref.[7]
[b] Ref.[17]
[c] Substituents in 1,4-position, ref.[12]
[d] Substituents in 2,3-position, ref.[12]

In summary, for the first time a systematic study of hexadecaalkoxy-substituted metal phthalocyanines is reported. The compounds were characterized and their spectral properties discussed.

Tetrafluorophthalodinitrile **(1)** is purchased from ABCR, D-76151 Karlsruhe. IR spectra: Bruker IFS 48, NMR spectra: Bruker AC 250 (^1H: 250 MHz; ^{13}C: 62.9 MHz, ^{19}F: 235.4 MHz), Mass spectra: Finnigan MAT ISQ (EI, 70 eV) and Finnigan MAT 711A (FD), UV/vis spectra: Shimadzu UV 2102 PC. Melting points were determined in open capillaries and are uncorrected.

Nonfluorinated 1,2-Dicyano-3,4,5,6-tetra(alkoxy)benzenes 2a–d; General Procedure:

Tetrafluorophthalodinitrile **(1)** (1.0 g, 5 mmol) was dissolved in anhyd DMF (30 mL). The corresponding alcohol (60 mmol) and K_2CO_3 (8.3 g, 60 mmol) were added with stirring and the mixture was heated to 100 °C [120 °C **(2d)**] over 24 h in a dry N_2 atmosphere. The cooled mixture was poured into H_2O (300 mL) and extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O, dried and the solvent evaporated. The remaining oily residue was further purified by column chromatography over silica gel (eluent: toluene).

1,2-Dicyano-3,4,5,6-tetra(hexyloxy)benzene **(2a)**:

Yield: 1.7 g (64%), viscous oil.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.8 (br, 44 H, $OCH_2C_5H_{11}$), 4.06 (t, J = 6.7 Hz, 4 H, OCH_2), 4.10 (t, J = 6.7 Hz, 4 H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.90 (C-6), 22.45/22.49 (C-5), 25.35/25.46 (C-3), 29.95/30.05 (C-2), 31.45 (C-4), 74.82/75.71 (C-1), 104.42 (C-c), 113.12 (C-d), 151.35 (C-a), 153.14 (C-b).

IR (NaCl, neat): ν = 2232 cm^{-1} (C≡N).

MS (EI, 70 eV); m/z (%) = 528.4 (3) [M^+].

$C_{32}H_{52}N_2O_4$ (528.9): calc. C 72.67 H 9.92 N 5.30
found 72.03 10.13 5.47

1,2-Dicyano-3,4,5,6-tetra(decyloxy)benzene **(2b)**:

Yield: 2.3 g (61%), viscous oil.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.8 (br, 76 H, $OCH_2C_9H_{19}$), 4.06 (t, J = 6.7 Hz, 4 H, OCH_2), 4.11 (t, J = 6.7 Hz, 4 H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.07 (C-10), 22.66 (C-9), 25.75/25.87 (C-3), 29.32, 29.35/29.38, 29.56, 29.59 (C-4–C-7), 30.04/30.16 (C-2), 31.88 (C-8), 74.85/75.78 (C-1), 104.51 (C-c), 113.16 (C-d), 151.36 (C-a), 153.18 (C-b).

IR (NaCl, neat): ν = 2232 cm^{-1} (C≡N).

MS (FD, toluene); m/z (%) = 752.5 (100) [M^+].

$C_{48}H_{84}N_2O_4$(753.2): calc. C 76.54 H 11.24 N 3.24
found 76.29 11.86 3.54

1,2-Dicyano-3,4,5,6-tetra(dodecyloxy)benzene **(2c)**:

Yield: 2.7 g (62%), viscous oil.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.8 (br, 92 H, $OCH_2C_{11}H_{23}$), 4.06 (t, J = 6.7 Hz, 4 H, OCH_2), 4.11 (t, J = 7.0 Hz, 4 H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.05 (C-12), 22.67 (C-11), 25.76/25.88 (C-3), 29.34, 29.39, 29.54, 29.61, 29.64, 29.66 (C-4–C-9), 30.05/30.17 (C-2), 31.90 (C-10), 74.86/75.79 (C-1), 104.54 (C-c), 113.15 (C-d), 151.36 (C-a), 153.18 (C-b).

IR (NaCl, neat): ν = 2233 cm^{-1} (C≡N).

MS (FD, toluene); m/z (%) = 865.2 (100) [M^+].

$C_{56}H_{100}N_2O_4$(865.4): calc. C 77.72 H 11.65 N 3.24
found 77.42 12.11 3.30

1,2-Dicyano-3,4,5,6-tetra(2-ethylhexyloxy)benzene **(2d)**:

Yield: 2.0 g (62%), viscous oil.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.8 (br, 60 H, $OCH_2C_7H_{15}$), 3.94 (d, J = 6.1 Hz, 4 H, OCH_2), 4.00 (d, J = 5.8 Hz, 4 H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.01 (C-8), 14.01 (C-6), 22.97/23.02 (C-5), 23.46 (C-7), 29.07 (C-4), 30.06/30.14 (C-3), 40.34/40.44

(C-2), 77.99/78.61 (C-1), 104.26 (C-c), 113.23 (C-d), 151.64 (C-a), 153.33 (C-b).

IR (NaCl, neat): $\nu = 2232\ cm^{-1}$ (C≡N).

MS (FD, toluene); *m/z* (%) = 640.6 (100) [M^+].

$C_{40}H_{68}N_2O_4$(641.0): calc. C 74.95 H 10.69 N 4.37
found 74.78 10.83 4.32

1,2-Dicyano-3,4,5,6-tetra(2,2,2-trifluoroethyloxy)benzene (2e); Typical Procedure:

Tetrafluorophthalodinitrile **(1)** (2.0 g, 10 mmol) was dissolved in DMF (30 mL). 2,2,2-Trifluoroethanol (10.0 g, 100 mmol) and K_2CO_3 (13.8 g, 100 mmol) were added. The mixture was stirred at r.t. for 4 h under a dry N_2 atmosphere. Then the mixture was poured into H_2O (300 mL). The precipitate was suction filtered, washed with H_2O and dried in vacuo. Yield: 4.8 g (92%) of a white powder, mp 133–134°C.

^{1}H NMR (250 MHz, acetone-d_6): $\delta = 4.90$ (q, $J_{HF} = 8.4$ Hz, 4H), 4.93 (q, $J_{HF} = 8.4$ Hz, 4H).

^{13}C NMR (62.9 MHz, acetone-d_6): $\delta = 71.05$ (q $J_{CF} = 36$ Hz, C-1), 71.34 (q, $J_{CF} = 36$ Hz, C-1′), 107.33 (C-c), 112.28 (C-d), 124.04 (q, $J_{CF} = 277$ Hz, C-2), 124.10 (q, $J_{CF} = 277$ Hz, C-2′), 149.68 (C-a), 152.07 (C-b).

^{19}F NMR (235.4 MHz, acetone-d_6): $\delta = -75.7$ (t, $J_{FH} = 8.6$ Hz, 6F), −75.8 (t, $J_{FH} = 8.6$ Hz, 6F).

IR (KBr): $\nu = 2237\ cm^{-1}$ (C≡N).

MS (EI, 70 eV); *m/z* (%) = 520.0 (50) [M^+].

$C_{16}H_8F_{12}N_2O_4$ (520.2): calc. C 36.94 H 1.55 N 5.38
found 37.01 1.73 5.59

1,2-Dicyano-3,4,5,6-tetra(2,2,3,3,3-pentafluoropropyloxy)benzene **(2f)**:

Compound **2f** was synthesized from 2,2,3,3,3-pentafluoropropanol as described for **2e**. Yield: 5.8 g (81%) of a white powder, mp 105–107°C.

^{1}H NMR (250 MHz, acetone-d_6): $\delta = 4.97$ (t, $J_{HF} = 13$ Hz, 4H), 5.02 (t, $J_{HF} = 13$ Hz. 4H).

^{13}C NMR (62.9 MHz, acetone-d_6): $\delta = 70.23$ (t $J_{CF} = 25$ Hz, C-1), 70.49 (t, $J_{CF} = 25$ Hz, C-1′), 107.74 (C-c), 109–122 (m, C-2, C-3), 112.18 (C-d), 149.81 (C-a), 151.93 (C-b).

^{19}F NMR (235.4 MHz, acetone-d_6): $\delta = -84.8$ (s, 6F), −85.0 (s, 6F), −125.4 (t, $J_{FH} = 15$ Hz, 4F), −125.6 (t, $J_{FH} = 15$ Hz, 4F).

IR (KBr): $\nu = 2241\ cm^{-1}$ (C≡N).

MS (EI, 70 eV); *m/z* (%) = 720.0 (50) [M^+].

$C_{20}H_8F_{20}N_2O_4$ (720.3): calc. C 33.35 H 1.12 N 3.89
found 32.86 1.23 4.09

1,2-Dicyano-3,4,5,6-tetra(3,5-di-tert-butylphenyloxy)benzene **(2g)**:

Compound **2g** was obtained from tetrafluorophthalodinitrile **(1)** (1.0 g, 5 mmol), 3,5-di-*tert*-butylphenol (6.2 g, 30 mmol) and K_2CO_3 (8.3 g, 60 mmol) by the procedure used for preparation of **2a–d** (reaction temperature: 80°C). Yield: 3.9 g (82%) of a white solid, mp 181–182°C.

^{1}H NMR (250 MHz, acetone-d_6): 1.15 (s, 36H, 6-H), 1.22 (s, 36H, 6′-H), 6.47 (d, $J = 1.5$ Hz, 4H, 2-H), 6.81 (d, $J = 1.7$ Hz, 4H, 2′-H), 7.07 (t, $J = 1.7$ Hz, 2H, 4-H), 7.19 (t, $J = 1.5$ Hz, 2H, 4′-H).

^{13}C NMR (62.9 MHz, acetone-d_6): $\delta = 31.63$ (C-6), 35.40/35.52 (C-5), 108.33 (C-c), 110.82/111.53 (C-2), 113.44 (C-d), 118.22/118.70 (C-4), 147.08 (C-a), 150.17 (C-b), 152.79/153.38 (C-3), 155.82/157.39 (C-1).

IR (KBr): $\nu = 2237\ cm^{-1}$ (C≡N).

MS (FD, acetone); *m/z* (%) = 944.9 (100) [M^+].

$C_{64}H_{84}N_2O_4$ (945.4): calc. C 81.31 H 8.96 N 2.96
found 82.96 9.34 2.98

Hexadeca(alkoxy)phthalocyaninatonickels 3a–g; General Procedure:

A mixture of the corresponding dinitrile (1.0 mmol) and $NiCl_2$ (0.33 mmol) in freshly distilled DMAE (10 mL) was refluxed for 48 h under a dry N_2 atmosphere. The product was precipitated by adding brine (150 mL), washed with H_2O (100 mL), MeOH (100 mL) [H_2O **(3e)**], collected and purified by column chromatography [silica gel, toluene/hexane (1/1) **(3a)**, toluene/hexane (1/3) **(3b–d)**, hexane/CH_2Cl_2 (1/1) **(3e)**, toluene/hexane (1/2) **(3g)**]. After evaporation of the solvent, the product was dried for 6 h at 50°C in vacuo.

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadeca(hexyloxy)-phthalocyaninatonickel **(3a)**:

Yield: 95 mg (17%), mp 81–82°C.

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.8–2.2$ (br, 176H, $OCH_2C_5H_{11}$), 4.44 (t, $J = 6.7$ Hz, 16H, OCH_2), 4.75 (t, $J = 7.0$ Hz, 16H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.08/14.14$ (C-6), 22.79 (C-5), 25.99/26.02 (C-3), 30.34/30.70 (C-4), 31.95/32.05 (C-2), 75.04/75.97 (C-1), 125.1, 144.81, 146.21, 148.86 (heteroaromatic C).

MS (FD, toluene); *m/z* (%) = 2173.7 (100) [M^+].

$C_{128}H_{208}N_8NiO_{16}$ (2173.8): calc. C 70.72 H 9.64 N 5.15
found 71.19 9.89 5.15

1,2,3,4,8,9,10,11,15,16,17,18,22,24,34,25-Hexadeca(decyloxy)-phthalocyaninatonickel **(3b)**:

Yield: 70 mg (9%), mp 51–52°C.

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.8–2.2$ (br, 304H, $OCH_2C_9H_{19}$), 4.34 (t, $J = 6.7$ Hz, 16H, OCH_2), 4.74 (t, $J = 7.0$ Hz, 16H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.50/14.56$ (C-10), 23.10/23.17 (C-9), 26.84 (C-3), 29.87/29.92, 30.18/30.23, 30.29/30.32, 30.37 (C-4–C-7), 30.84/31.21 (C-2), 32.37/32.42 (C-8), 75.48/76.37 (C-1), 125.54, 145.22, 146.63, 149.26 (heteroaromatic C).

MS (FD, toluene); *m/z* (%) = 3072.7 (100) [M^+], 1536.5 (100) [M^{2+}].

$C_{192}H_{336}N_8NiO_{16}$ (3071.5): calc. C 75.08 H 11.03 N 3.65
found 75.06 11.15 4.23

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadeca(dodecyloxy)-phthalocyaninatonickel **(3c)**:

Yield: 130 mg (15%), mp 39–40°C.

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.8–2.2$ (br, 368H, $OCH_2C_{11}H_{23}$), 4.43 (t, $J = 6.7$ Hz, 16H, OCH_2), 4.74 (t, $J = 7.0$ Hz, 16H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.07/14.11$ (C-12), 22.68/22.72 (C-11), 26.43 (C-3), 29.41/29.46, 29.73, 29.78, 29.82, 29.89, 29.91/29.95 (C-4–C-9), 30.43/30.79 (C-2), 31.93/31.99 (C-10), 75.05/75.96 (C-1), 125.13, 144.81, 146.22, 148.85 (heteroaromatic C).

MS (FD, toluene); *m/z* (%) = 3519.8 (100) [M^+].

$C_{224}H_{400}N_8NiO_{16}$ (3520.4): calc. C 76.43 H 11.45 N 3.18
found 76.48 11.75 3.60

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadeca(2-ethylhexyloxy)phthalocyaninatonickel **(3d)**:

Yield: 120 mg (18%), mp 154–155°C.

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.6–2.3$ (br, 240H, $OCH_2C_7H_{15}$), 4.30 (d, $J = 6.0$ Hz, 16H, OCH_2), 4.61 (br, 16H, OCH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 11.01/11.20$ (C-8), 14.03/14.20 (C-6), 23.19/23.30 (C-5), 23.62/23.73 (C-7), 29.12/29.40 (C-4), 30.29/30.50 (C-3), 40.29/40.80 (C-2), 78.39/79.39 (C-1), 124.30, 144.72, 146.41, 148.65 (heteroaromatic C).

MS (FD, toluene); *m/z* (%) = 2623.3 (100) [M^+].

$C_{160}H_{272}N_8NiO_{16}$ (2622.7): calc. C 73.28 H 10.45 N 4.27
found 73.24 10.50 4.94

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadeca(2,2,2-trifluoroethyloxy)phthalocyaninatonickel **(3e)**:

Yield: 65 mg (12%).

^{1}H NMR (250 MHz, acetone-d_6): $\delta = 5.14$ (q, $J_{HF} = 8.7$ Hz, 16H, OCH_2), 5.63 (q, $J_{HF} = 8.7$ Hz, 16H, OCH_2).

^{13}C NMR (62.9 MHz, acetone-d_6): $\delta = 70.86$ (q $J_{CF} = 35.6$ Hz, C-1), 72.93 (q, $J_{CF} = 35.1$ Hz, C-1′), 124.63 (q, $J_{CF} = 278$ Hz, C-2),

125.09 (q, J_{CF} = 278 Hz, C-2'), 125.77, 145.71, 145.77, 147.57 (heteroaromatic C).

^{19}F NMR (235.4 MHz, acetone-d_6): δ = −75.3 (t, J_{FH} = 8.6 Hz, 24 F), −75.7 (t, J_{FH} = 8.6 Hz, 24 F).

MS (FD, acetone); *m/z* (%) = 2138.5 (100) [M^+].

$C_{64}H_{32}F_{48}N_8NiO_{16}$ (2139.6): calc. C 35.93 H 1.51 N 5.24
found 35.84 1.75 5.57

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadeca(3,5-di-tert-butylphenyloxy)phthalocyaninatonickel **(3g)**:

Yield: 150 mg (16%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.62 (s, 144 H, 6-H), 1.83 (s, 144 H, 6'-H), 6.66 (d, J = 1.2 Hz, 16 H, 2-H), 6.79 (t, J = 1.2 Hz, 8 H, 4-H), 6.91 (d, J = 1.2 Hz, 16 H, 2'-H), 6.92 (t, J = 1.2 Hz, 8 H, 4'-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.24/31.38 (C-6), 34.49/34.62 (C-5), 111.07/111.43 (C-2), 115.16/116.35 (C-4), 126.14, 141.52, 144.50, 144.66 (heteroaromatic C), 150.59/151.24 (C-3), 156.94/157.76 (C-1).

MS (FD, toluene); *m/z* (%) = 3841.0 (100) [M^+].

$C_{256}H_{336}N_8NiO_{16}$ (3840.2): calc. C 80.07 H 8.82 N 2.92
found 79.09 9.15 3.03

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadeca(2,2,2-trifluoroethyloxy)phthalocyaninatoiron **(4e)**:

A mixture of 1,2-dicyano-3,4,5,6-tetra(2,2,2-trifluoroethyloxy)benzene **(2e)** (3.0 g, 5.8 mmol) and $FeSO_4 \cdot H_2O$ (0.32 g, 1.9 mmol) in freshly distilled DMAE (20 mL) was refluxed for 48 h under a dry N_2 atmosphere. The product was precipitated by adding H_2O, collected and purified by column chromatography [silica gel, acetone/hexane (1/1)]. After evaporation of the solvent, the product was dried for 6 h at 50 °C in vacuo. Yield: 0.6 g (19%).

MS (FD, acetone); *m/z* (%) = 2136.1 (100) [M^+].

$C_{64}H_{32}F_{48}FeN_8O_{16}$ (2136.8): calc. C 35.98 H 1.51 N 5.24
found 36.11 1.74 5.25

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadeca(2,2,3,3,3-pentafluoropropyloxy)phthalocyaninatoiron **(4f)**:

Compound **4f** was obtained from 1,2-dicyano-3,4,5,6-tetra(2,2,3,3,3-pentafluoropropyloxy)benzene **(2f)** (3.0 g, 4.2 mmol) and $FeSO_4 \cdot H_2O$ (0.24 g, 1.4 mmol) by the procedure used for the preparation of **4e**. Yield: 0.6 g (19%).

MS (FD, acetone); *m/z* (%) = 2938.6 (100) [M^+], 1469.1 (10) [M^{2+}].

$C_{80}H_{32}F_{80}FeN_8O_{16}$ (2936.9): calc. C 32.72 H 1.10 N 3.82
found 35.54 2.04 3.51

Bis(*tert*-butyl isocyanide)[1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadeca(2,2,2-trifluoroethyloxy)phthalocyaninato]iron(II) (5e):
Compound **4e** (200 mg, 0.09 mmol) was stirred in *tert*-butyl isocyanide (2 mL) for 3 days at 50 °C. The excess of the ligand was evaporated and the product was purified by column chromatography [silica gel, hexane/CH_2Cl_2 (1/1)]. After evaporation of the solvent, the product was dried for 6 h at 50 °C in vacuo. Yield: 80 mg (39%).

^{1}H NMR (250 MHz, acetone-d_6): δ = −0.28 (s, 18 H, H^C), 5.12 (q, J_{HF} = 8.5 Hz, 416 H, OCH_2), 5.75 (q, J_{HF} = 8.5 Hz, 16 H, OCH_2).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 28.59 (C-C), 56.99 (C-B), 71.38 (q J_{CF} = 35 Hz, C-1), 72.88 (q, J_{CF} = 35 Hz, C-1'), 124.71 (q, J_{CF} = 278 Hz, C-2), 125.20 (q, J_{CF} = 278 Hz, C-2'), 129.47, 144.85, 145.69, 145.97 (heteroaromatic C).

^{19}F NMR (235.4 MHz, acetone-d_6): δ = −75.2 (t, J_{FH} = 8.6 Hz, 24 F), −75.7 (t, J_{FH} = 8.6 Hz, 24 F).

IR (KBr): ν = 2166 cm^{-1} (N≡C).

$C_{74}H_{50}F_{48}FeN_{10}O_{16}$ (2303.0): calc. C 38.59 H 2.19 N 6.08
found 38.98 2.55 5.85

Bis(*tert*-butyl isocyanide)[1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadeca(3,5-di-*tert*-butylphenyloxy)phthalocyaninato]iron(II) (5g):
Compound **5g** was obtained from 1,2-dicyano-3,4,5,6-tetra(3,5-di-*tert*-butylphenyloxy)benzene **(2g)** (0.95 g, 1 mmol) and $FeSO_4 \cdot H_2O$ (0.055 g, 0.33 mmol) by the procedure used for the preparation of **4e**. The crude product was dissolved in *tert*-butyl isocyanide (3 mL). The further preparation is analogous to **5e**. [chromatographic purification: silica gel; eluent: toluene/hexane (1/2)]. Yield: 25 mg (3%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.58 (s, 18 H, H^C), 0.90 (s, 144 H, 6-H), 1.08 (s, 144 H, 6'-H), 6.55 (d, J = 1.5 Hz, 16 H, 2-H), 6.76 (t, J = 1.5 Hz, 8 H, 4-H), 6.86 (t, J = 1.5 Hz, 8 H, 4'-H), 7.33 (d, J = 1.5 Hz, 16 H, 2'-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 28.77 (C—C), 31.43/31.46 (C-6), 34.57/34.62 (C-5), 55.17 (C—B), 110.77/113.68 (C-2), 115.39/115.91 (C-4), 130.56, 142.09, 142.45, 145.39 (heteroaromatic C), 150.22/150.87 (C-3), 156.84/158.84 (C-1).

IR (KBr): ν = 2146 cm^{-1} (N≡C).

MS (FD, CH_2Cl_2): *m/z* (%) = 3838.0 (100) [M^+-2 *t*-BuNC].

$C_{266}H_{354}FeN_{10}O_{16}$ (4003.6): calc. C 79.80 H 8.91 N 3.50
found 77.77 9.51 3.39

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