Soluble Substituted μ-Oxo(phthalocyaninato)iron(III) Dimers

Reinhold Dieing, Gabriele Schmid, Elisabeth Witke, Carola Feucht, Michael Dreßen, Jörg Pohmer, and Michael Hanack*

Institut für Organische Chemie, Universität Tübingen,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received November 25, 1994

Key Words: μ-Oxobis(phthalocyaninato)iron / μ-Oxo dimers / Mössbauer spectroscopy / Iron complexes / Phthalocyanines

Attempts to prepare various peripheral tetra- and octasubstituted (phthalocyaninato)iron derivatives R_nPcFe [$n = 4$: R = CH_2OEt (**6e**), CO_2Et (**6h**), CO_2-n-C_6H_{13} (**6i**), O(2-Et-n-C_6H_{13}) (**6j**), $OCH_2C(CH_3)_3$ (**6k**), $OCH_2C(CH_3)_2CH_2Ph$ (**6l**); $n = 8$: R = $CH_2CH(CO_2Me)CH(CO_2Me)CH_2$ (**6f**), $CH_2CH(CO_2Et)$-$CH(CO_2Et)CH_2$ (**6g**), O-n-C_8H_{17} (**6m**), O(2-Et-n-C_6H_{13}) (**6n**)] by starting from the corresponding substituted phthalonitriles led to substituted (μ-oxo)bis[(phthalocyaninato)iron(III)] compounds $[R_nPcFe]_2O$. The *tert*-butyl- and ethyl-substituted systems $[tBu_4PcFe]_2O$ (**6c**) and $[Et_4PcFe]_2O$ (**6d**) were reinvestigated. UV/Vis, FD mass, Mössbauer, NMR as well as ESR spectroscopy was used to characterize the complexes $[R_nPcFe]_2O$ to furnish evidence for the presence of Fe–O–Fe moieties in $[R_nPcFe]_2O$. The UV/Vis data reported for $[R_nPcFe]_2O$ as well as their spectral behavior in pyridine correspond to unsubstituted $[PcFe]_2O$. Mössbauer spectra of $[R_nPcFe]_2O$ show that the complexes were obtained as a mixture of two isomeric μ-oxo compounds **A** ($\delta_{Fe} = 0.22$ mm s^{-1}, $\Delta E_Q = 1.33-1.39$ mm s^{-1}) and **B** ($\delta_{Fe} = 0.33-0.36$ mm s^{-1}, $\Delta E_Q = 0.39-0.53$ mm s^{-1}), whose Mössbauer parameters are comparable to $[PcFe]_2O$ μ-oxo(2) and μ-oxo(1), respectively. Mössbauer spectral data of $[R_nPcFe]_2O$ indicate high-spin ($S = 5/2$) Fe^{III} centers. NMR-spectra of $[R_nPcFe]_2O$ ($n = 4$: R = tBu, Et, O(2-Et-n-C_6H_{13}), $OCH_2C(CH_3)_2CH_2Ph$; $n = 8$: R = O-n-C_8H_{17}, O(2-Et-n-C_6H_{13}) give further evidence for μ-oxo bridged structures.

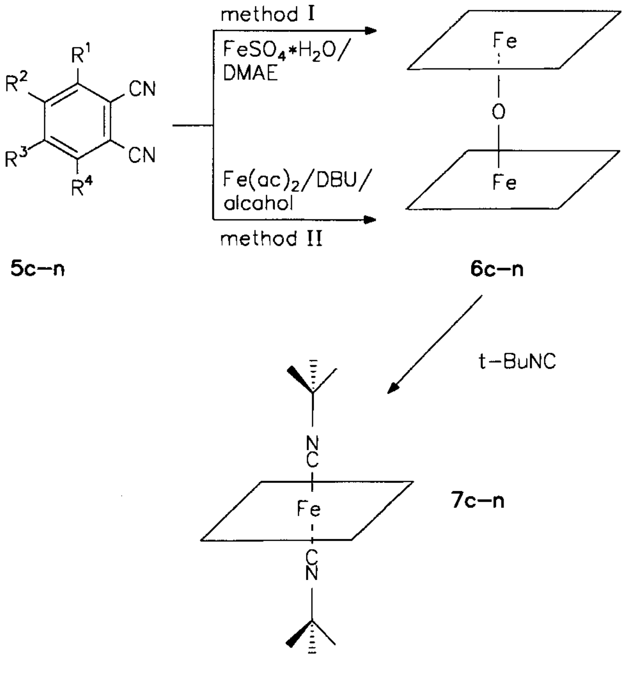
Introduction

The μ-oxo-diiron(III) structure is well-known in coordination chemistry and several reviews are available which summarize the chemistry of the Fe–O–Fe unit[1–4]. μ-Oxo dimers of porphyrins are important elements in biological processes occurring in the active centers of e.g. hemeproteins and cytochrome P450[5]. μ-Oxo-bis(phthalocyaninato)iron(III) $[PcFe]_2O$ has been synthesized and investigated as representative example of a synthetic analog of the porphyrin core in these systems.

Two isomers of $[PcFe]_2O$ were prepared and characterized: μ-oxo(1) (**6a**) was obtained from PcFe[6] or from $PNP[PcFe(OH)_2]$[7], μ-oxo(2) (**6b**) was synthesized from PcFe or μ-oxo(1) (**6a**)[5,6b,f]. Compounds **6a** and **6b** can be distinguished by X-ray powder patterns, IR and Mössbauer spectral data, and by their different magnetic behavior. For both isomers, by means of Mössbauer and magnetic susceptibility data, the presence of antiferromagnetically coupled Fe^{III} high-spin centers ($S = 5/2$, $S = 5/2$) was established[6b,f,7b]. Ercolani et al. suggested a bent Fe–O–Fe arrangement for μ-oxo(1) (**6a**) and a quasi-linear for μ-oxo(2) (**6b**)[6b,f,5]. While $[PcFe]_2O$ was studied in detail there are only few reports about substituted analogs.

In recent years we have studied the electrical and nonlinear optical properties of soluble bridged phthalocyaninato metal compounds of the type $[R_nPcFe(L)]_m$ ($n = 4$, 8), L being a bidentate ligand, e.g. pyrazine (pyz), tetrazine (tz) and 1,4-diisocyanobenzene (dib)[8,9]. Both R_nPcFe and $[R_nPcFe]_2O$ may be used as starting materials for the preparation of the oligomers $[R_nPcFe(L)]_m$. In order to vary the properties of the bridged oligomers various tetra- and octasubstituted (μ-oxo)bis[phthalocyaninato)iron] complexes **6c–n** (Figure 1) have been prepared. In this paper we present analytical data which establish μ-oxodiiron(III) structures for the compounds **6c–n**.

Scheme 1. Synthesis of (μ-oxo)bis[(phthalocyaninato)iron(III)] complexes $[R_nPcFe]_2O$ **6c–n** and corresponding bis(*tert*-butyl isocyanide) complexes $R_nPcFe(tBuNC)_2$ **7c–n**



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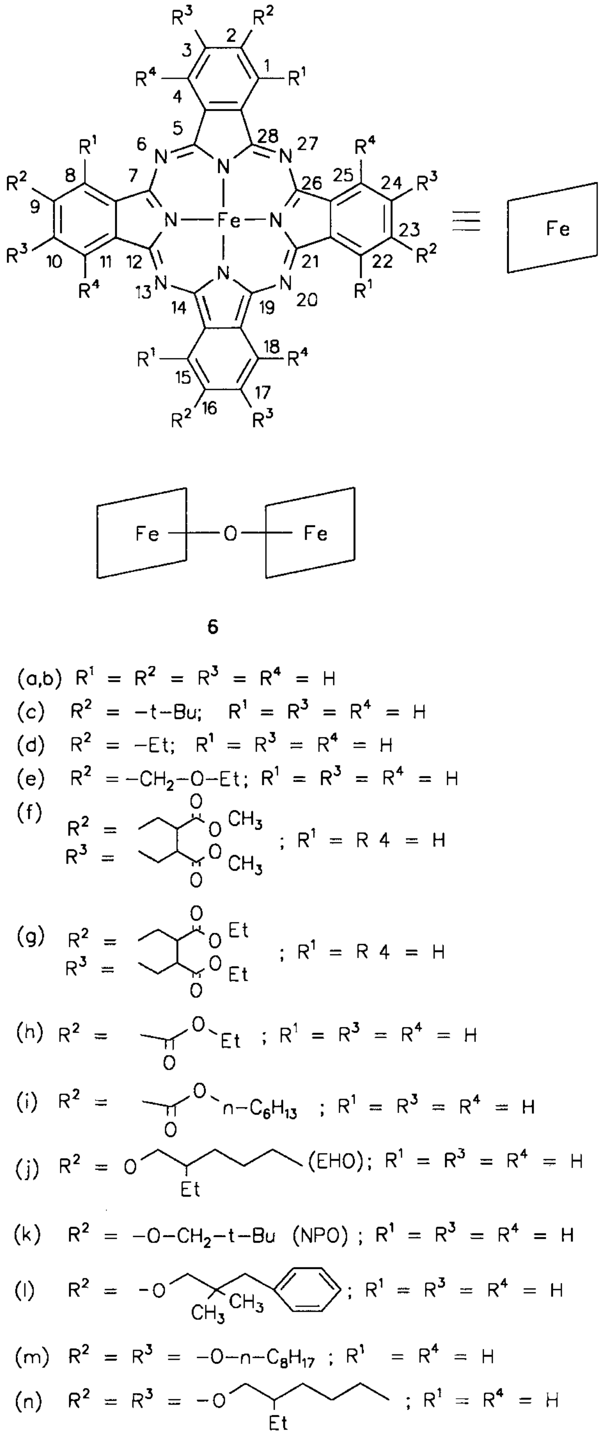
Results and Discussion

The μ-oxo dimers **6c–n** (Figure 1) were obtained by reacting the corresponding substituted phthalonitriles **5c–n** with $FeSO_4 \cdot H_2O$ in *N*,*N*-dimethylaminoethanol (method I: **6c**, **d**, **j–n**) or with iron(II) acetate in an alcohol in the presence of a catalytic amount of DBU (method II: **6e–i**) (Scheme 1).

Figure 1. Schematic representation of (μ-oxo)bis[(phthalocyaninato)iron(III)] complexes $[R_nPcFe]_2O$ **6a–n**



Because of their good solubility in common organic solvents, e.g. dichloromethane, chloroform or toluene, the complexes **6c–n** could be purified by column chromatography. If traces of acids which cleave the μ-oxo dimers are absent in the solvent, the products are practically free of monomeric high-spin impurities which is a common feature of unsubstituted $[PcFe]_2O$[6f,7b].

During the statistical synthesis of the tetrasubstituted phthalocyanines leading to the μ-oxo dimers **6c**, **d**, **e**, **h**, **i**, **j**, **k**, and **6l** (Figure 1) a mixture of four constitutional isomers[10,11] may be obtained. Each of these isomers can form μ-oxo dimers leading to a large number of isomeric octasubstituted (μ-oxo)bis[(phthalocyaninato)iron] compounds during synthesis.

IR, UV/Vis, and Mass Spectra

Absorptions occurring at 852 and 824 cm^{-1} in the IR spectrum of $[PcFe]_2O$ (**6a**) were attributed to the antisymmetric Fe–O–Fe stretching vibration (ν_3) by means of ^{18}O labeling[6a,b]. In the case of μ-oxo(2) (**6b**), however, ν_3 could not be observed[6b]. IR spectroscopy cannot be used to establish μ-oxodiiron units in the peripherally substituted complexes **6c**[12,13]–**n** described here because the antisymmetric stretching mode of the Fe–O–Fe moiety (ν_3) interferes with absorptions of the substituents in the phthalocyanine ring. This can be seen by comparing the IR spectra of the μ-oxo dimers **6c–n** with spectra of equally substituted (phthalocyaninato)nickel or cobalt complexes.

Solution UV/Vis spectra of $[PcFe]_2O$ in 1-chloronaphthalene exhibit main absorptions at 365, 600 and 695 nm. Both μ-oxo(1) (**6a**) and μ-oxo(2) (**6b**) show the same UV/Vis spectra. The broad band at 695 nm has a shoulder at 710 nm[7a,14]. The UV/Vis spectra of dimeric μ-oxosiliconphthalocyanines[15], e.g. $\{PcSi[OSiMe(OSiMe_3)_2]\}_2O$ [λ_{max}(Q) = 630 nm, in cyclohexane], show a characteristic blue shift of the Q band compared to the monomeric species $PcSi[OSiMe(OSiMe_3)_2]_2$ (λ_{max}(Q) = 665 nm, in cyclohexane] due to exciton coupling[15a]. However, there is no hypsochromic shift of the Q band of $[PcFe]_2O$ when compared to both monomeric pentacoordinated (phthalocyaninato)iron(III) complexes, e.g. PcFeCl [λ_{max}(Q) = 655 nm, in 1-chloronaphthalene], and hexacoordinated low-spin (phthalocyaninato)iron(III) complexes such as $PNP[PcFe(CN)_2]$ [λ_{max}(Q) = 685 nm, in 1-chloronaphthalene][7]. Similar spectral data as for $[PcFe]_2O$ have been reported for $[t\text{Bu}_4PcFe]_2O$ (**6c**) which also shows a split Q band near 700 nm[12,13]. The UV/Vis spectra of compounds **6d–n** exhibit essentially the same characteristics namely split or broad Q bands (Table 1).

Both $[PcFe]_2O$ **6a** and **6b** give the same initial UV/Vis spectrum when dissolved in pyridine, with the main absorption located at 620 nm, indicating a reaction with pyridine[6b]. The species formed was formulated as a μ-oxo adduct [(py)PcFe–O–PcFe(py)] and this was confirmed by the crystal structure determination of an analogous 1-methylimidazole adduct. After some time the μ-oxo bridge in [(py)PcFe–O–Fe(py)] is cleaved and the bis(pyridine) complex $PcFe(py)_2$ is formed. The same behavior has been

Table 1. UV/Vis data of substituted (μ-oxo)bis[(phthalocyaninato)iron(III)] complexes

	λ_{max} [nm] (rel. absorbance)	λ_{max} (Q) [nm] (in pyridine)[d]
6c	363 (0.93), 590 (0.37), 687 (1.00), 704 (0.89, sh)[a]	627[e]
6d	363 (0.85), 588 (0.20), 687 (1.00), 703 (0.90, sh)[a]	624[e]
6e	290 (0.98), 358 (0.92), 600 (0.29), 692 (1.00), 704 (0.97, sh)[b]	630
6f	288 (1.35), 354 (1.07), 604 (0.31), 693 (1.00), 709 (0.88, sh)[b]	
6g	291 (1.02), 356 (0.97), 604 (0.20), 697 (1.00), 709 (0.89, sh)[b]	
6h	345 (1.24), 586 (0.49), 690 (1.00), 710 (0.91, sh)[b]	635
6i	285 (1.12), 350 (1.04), 586 (0.35), 697 (1.00), 710 (0.97, sh)[b]	636
6j	300 (1.16), 370 (0.79), 410 (0.55), 610 (0.24), 715 (1.00)[b]	635
6k	295 (1.22), 368 (0.87), 400 (sh), 610 (0.22), 711 (1.00)[b]	635
6l	289 (1.1), 367 (0.9), 593 (0.3), 697 (1.0), 709 (sh)[a,c]	631[e]
6m	300 (1.02), 360 (0.81), 425 (0.55), 600 (0.15), 670 (sh), 714 (1.00)[b]	635
6n	300 (1.42), 360 (0.97), 425 (0.59), 600 (sh), 670 (sh), 714 (1.00)[b]	635

[a] In toluene. – [b] In $CHCl_3$. – [c] In parentheses: 10^{-5} ε/l mol^{-1} cm^{-1}. – [d] Initial spectrum. – [e] In pyridine/toluene (1:1).

reported for $[t\mathrm{Bu_4PcFe}]_2O$ (**6c**)[12] and is also observed for **6d**, **e**, **h**–**n** which is clearly indicative of μ-oxo-bridged structures. The intermediates initially formed when the μ-oxo dimers **6c**–**e**, **h**–**n** are dissolved in pyridine exhibit Q bands located between 624 and 645 nm (Table 1).

Compounds **6c**–**n** are soluble in common organic solvents and hence they could be studied by mass spectroscopy using the FD technique. Most of the complexes do not show the molecular peak for the μ-oxo dimer but just the mass peak of the monomer R_nPcFe. However, in the case of $[t\mathrm{Bu_4PcFe}]_2O$ (**6c**), $[\mathrm{Et_4PcFe}]_2O$ (**6d**), $[(\mathrm{NPO})_4\mathrm{PcFe}]_2O$ (**6k**), and $[(\mathrm{PPO})_4\mathrm{PcFe}]_2O$ (**6l**) the M^+ peak of the μ-oxo dimer (**6c**: *m*/*z* = 1601.7; **6d**: *m*/*z* = 1376.0; **6k**: *m*/*z* = 1841.9; **6l**: *m*/*z* = 2450.3), accompanied by the mass peaks of the monomers R_4PcFe, was observed. The FD mass spectra of $[(\mathrm{NPO})_4\mathrm{PcFe}]_2O$ (**6k**) and $[(\mathrm{PPO})_4\mathrm{PcFe}]_2O$ (**6l**) exhibit additional signals that can be attributed to multiply charged aggregates of the μ-oxo dimers, $[2\,M]^+$, $[2\,M]^{3+}$, $[3\,M]^{2+}$, and $[4\,M]^{3+}$. In earlier studies of $[t\mathrm{Bu_4PcFe}]_2O$ (**6c**) the molecular peak of the μ-oxo-diiron dimer has not been found[12,13].

In order to exclude the possibility that the μ-oxo dimers might be produced in the mass spectrometer, bis(isocyanide) complexes of **6c**, **k**, **l** $t\mathrm{Bu_4PcFe}(t\mathrm{BuNC})_2$ (**7c**), $(\mathrm{NPO})_4\mathrm{PcFe}(t\mathrm{BuNC})_2$ (**7k**), and $(\mathrm{PPO})_4\mathrm{PcFe}(t\mathrm{BuNC})_2$ (**7l**) were investigated by FD mass spectroscopy. Compounds **7c**, **k**, **l** were easily prepared by reaction of **6c**, **k**, **l** with an excess of *tert*-butyl isocyanide at 60 °C (Scheme 1)[16]. The spectra of **7c**, **k**, **l** exhibit the mass peaks of the corresponding monomers R_4PcFe only, because the axially coordinated isocyanide ligands are split off in the spectrometer and no mass peaks that would indicate the presence of μ-oxo dimers **6c**, **k**, **l** were found.

^{57}Fe-Mössbauer Spectra

The Mössbauer parameters obtained for compounds **6c**–**n** are given in Table 2. The spectra of $[t\mathrm{Bu_4PcFe}]_2O$ (**6c**) and $[\mathrm{Et_4PcFe}]_2O$ (**6d**) are shown in Figure 2. To our knowledge $[t\mathrm{Bu_4PcFe}]_2O$ (**6c**) (δ_{Fe} = 0.22 mm s^{-1}, ΔE_Q = 1.38 mm s^{-1}, T = 90 K)[17] and $[(C_5H_{11}O)_8\mathrm{PcFe}]_2O$ (δ_{Fe} = 0.18 mm s^{-1}, ΔE_Q = 1.21 mm s^{-1}, T = 143 K)[8] are the only examples of substituted (μ-oxo)bis[(phthalocyaninato)iron] complexes which have been studied by Mössbauer spectroscopy so far. In both cases we reported only one doublet. The Mössbauer spectra octained now for **6c**–**n** could be fitted with two doublets that are referred to as **A** and **B** in the following (Table 2). Thus, the compounds given in Table 2 are mixtures of two different species. The Mössbauer parameters of **A** and **B**, however, are very similar for the different μ-oxo complexes **6c**–**n** (**A**: δ_{Fe} = 0.22 mm s^{-1}, ΔE_Q = 1.33–1.39 mm s^{-1}, **B**: δ_{Fe} = 0.33–0.36 mm s^{-1}, ΔE_Q = 0.39–0.53 mm s^{-1}). Moreover, the parameters of **A** are similar to the values reported for $[\mathrm{PcFe}]_2O$ (**6b**) [μ-oxo(2); δ_{Fe} = 0.25 mm s^{-1}, ΔE_Q = 1.26 mm s^{-1}, T = 77 K][6f] and the Mössbauer data of **B** are very similar to the parameters given for $[\mathrm{PcFe}]_2O$ (**6a**) [μ-oxo(1); δ_{Fe} = 0.36 mm s^{-1}, ΔE_Q = 0.44 mm s^{-1}, T = 77 K][7b]. Therefore, we conclude that compounds **6c**–**n** are formed as a mixture of two isomeric μ-oxo dimers during synthesis, corresponding to μ-oxo(1) (**6a**) and μ-oxo(2) (**6b**). The Mössbauer spectral data are indicative of high-spin (S = 5/2) Fe^{III} centers[18].

As the Debye-Waller factors might be different for the two isomers belonging to pattern **A** and **B** the ratio of area must not be taken for the ratio of isomers in the mixture. However, provided the species belonging to **A** and **B** have similar geometric structures at least in compounds **6c**–**n** the relative ratio of area of different complexes may be compared.

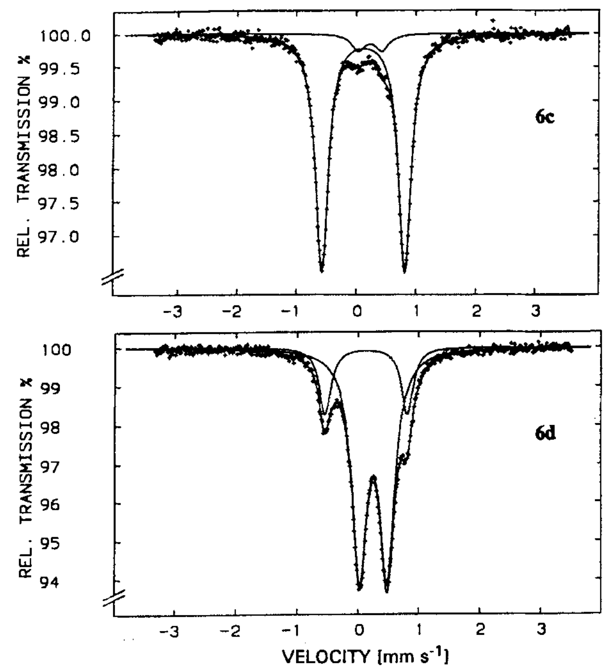
The relative ratio of doublets, **A** and **B**, is not dependent on the method of preparation (I and II, Scheme 1). For example, both $[t\mathrm{Bu_4PcFe}]_2O$ (**6c**) and $[\mathrm{Et_4PcFe}]_2O$ (**6d**) were prepared by method I. Yet, species **A** predominates in **6c** whereas **B** predominates in **6d**.

Table 2. Mössbauer data of substituted (μ-oxo)bis[(phthalocyaninato)iron(III)] complexes

Compound		T, K	δ_{Fe}[a] mm s^{-1}	ΔE_Q mm s^{-1}	Γ[b] mm s^{-1}	area,[c] %
6a		77	0.36[d]	0.44	0.16	
6b		77	0.25[e]	1.26	0.14	
6c		90	0.22[f]	1.38	-	-
	A	82	0.22	1.39	0.13	93
	B		0.33	0.39	0.14	7
6d	**A**	82	0.22	1.35	0.12	20
	B		0.35	0.45	0.15	80
6e	**A**	100	0.22	1.34	0.13	13
	B		0.35	0.43	0.15	87
6f	**A**	82	0.22	1.39	0.14	65
	B		0.34	0.46	0.16	35
6g	**A**	82	0.22	1.38	0.14	72
	B		0.33	0.45	0.16	28
6h	**A**	82	0.22	1.35	0.14	95
	B		0.33	0.41	0.12	5
6i	**A**	82	0.22	1.35	0.13	79
	B		0.33	0.53	0.16	21
6j	**A**	83	0.22	1.33	0.13	28
	B		0.36	0.45	0.15	72
6k	**B**	82	0.35[g]	0.41	0.17	-
6l	**A**	82	0.22	1.34	0.14	87
	B		0.36	0.41	0.14	13
$[(C_5H_{11}O)_8PcFe]_2O$		143	0.18[h]	1.21	-	-
6m	**A**	82	0.22	1.34	0.12	55
	B		0.34	0.52	0.15	45
6n	**B**	82	0.36[j]	0.52	0.15	-

[a] Relative to metallic iron. – [b] Half-width at half-height. – [c] Area estimated by: area ≈ intensity × Γ. – [d] Ref.[7b]. Additional doublet present: δ_{Fe} = 0.25 mm s^{-1}, ΔE_Q = 1.35 mm s^{-1} (9% of area). Assigned to $PcFe(OH_2)OH$. – [e] Ref.[6f] **6a** present (1% of area). – [f] Ref.[17]. – [g] Additional doublet present: δ_{Fe} = 0.20 mm s^{-1}, ΔE_Q = 2.28 mm s^{-1}, Γ = 0.42 mm s^{-1}. Site **A** is present but could not be fitted properly. – [h] Ref.[8]. – [j] Additional doublet present: δ_{Fe} = 0.14 mm s^{-1}, ΔE_Q = 2.10 mm s^{-1}, Γ = 0.35 mm s^{-1}.

Figure 2. Mössbauer spectra of $[tBu_4PcFe]_2O$ (**6c**) and $[Et_4PcFe]_2O$ (**6d**) at 82 K [isomer shift relative to $^{57}Co(Rh)$ source]



A comparison of the alkyl-substituted $[tBu_4PcFe]_2O$ (**6c**) and $[Et_4PcFe]_2O$ (**6d**) or alkoxy-substituted $[(EHO)_4$-$PcFe]_2O$ (**6j**) and $[(PPO)_4PcFe]_2O$ (**6l**) reveals that the electronic properties of the substituents do not dominate the relative ratios of **A** and **B**. And more importantly, the isomer shift δ_{Fe} and quadrupole splitting ΔE_Q of **A** and **B** for compounds **6c**–**n** seem to be almost indifferent towards the electronic and steric properties of the peripheral substituents.

Attempts were made to correlate the effects of electron-withdrawing[19] and electron-releasing[20] substituents with Mössbauer parameters by establishing so-called bonding parameters Σ and Π, calculated from Mössbauer data. Thus, the anomalous Mössbauer spectral data of $(NPO)_4PcFe$ (δ_{Fe} = 0.28 mm s^{-1}, ΔE_Q = 2.91 mm s^{-1}, T = 79 K) which was prepared by metalation of $(NPO)_4PcH_2$ with $FeCl_2$ in DMF were explained in terms of the electron-releasing effect of the neopentoxy group (for comparison: PcFe[21]: δ_{Fe} = 0.25 mm s^{-1}, ΔE_Q = 2.69 mm s^{-1}, T = 79 K). Such a correlation of the electronic properties of the substituents with Mössbauer data cannot be established for compounds **6c**–**n** as the Mössbauer parameters δ_{Fe} and ΔE_Q for alkyl-substituted **6c**–**g**, alkoxy-substituted **6j**, **k**, **l**, **f**, **n** as well as **6h** and **6i**, bearing electron-withdrawing ester groups, are quite similar. The influence of the steric requirements of the peripheral substituents on the relative proportion of **A** and **B** is difficult to rationalize. If the octasubstituted μ-oxo dimers **6c**, **d**, **e**, **h**–**l** are considered, non-flexible substituents, such as the *tert*-butyl (**6c**) or alkoxycarbonyl groups (**6h**, **6i**), seem to favor the structure belonging to **A**, whereas in compounds with conformationally flexible substituents, such as the ethyl (**6d**) and ethoxymethyl (**6e**) groups, species **B** dominates. However, it was not expected that the 2-ethylhexyloxy in **6j** and the neopentoxy group in **6k** have similar effects on the Mössbauer hyperfine parameters as the ethyl group in **6d**. Yet, both **6j** and **6k** and even hexadecasubstituted **6n** show a high proportion of isomer **B**. However, if the neopentoxy group is replaced by a phenyl ring, resulting in the PPO-substituted μ-oxo dimer **6l**, the form **A** predominates. The Mössbauer data of the pentyloxy-substituted $[(C_5H_{11}O)_8PcFe]_2O$[8] suggest the presence of mainly the isomer **B**. However, there are nearly equal amounts of **A** and **B** in the octyloxy homolog **6m**. The preceding considerations illustrate that it is so far not possible to correlate the nature of the substituents with the ratio of isomers **A** and **B**. Further systematic variations of the peripheral groups will be necessary to find out the factors that determine the ratio of isomers **A** and **B**. Based on Mössbauer spectral data, tetra(ethyl)phthalocyaninatoiron was formulated as a monomeric Fe^{II} complex Et_4PcFe ($\delta_{Fe} = 0.38$ mm s^{-1}, $\Delta E_Q = 2.57$ mm s^{-1}, $T = 293$ K)[9b]. The compound was prepared according to method I. However, UV/Vis spectra of the reaction mixture now give evidence for the formation of μ-oxo dimer **6d**. As described in ref.[9b] work-up was carried out by heating Et_4PcFe with dilute HCl. This suggests that the chloro complex $Et_4PcFeCl$ has been obtained because μ-oxo dimers are easily transformed into the chloro complexes by reaction with HCl[22]. Chromatography of $Et_4PcFeCl$ on neutral alumina results in the formation of the μ-oxo dimer **6d**.

ESR Spectra

ESR spectra of compounds $[tBu_4PcFe]_2O$ (**6c**), $[Et_4PcFe]_2O$ (**6d**), $[(EHO)_4PcFe]_2O$ (**6j**), and $[(PPO)_4PcFe]_2O$ (**6l**) were recorded from neat powders at 77 K. Frozen solution spectra of these compounds at 77 K only showed signals of low intensity. The powder spectra obtained for **6c**, **d**, **j**, and **6l** are very similar with regard to shape and position of the signals. The spectrum of **6l** shown in Figure 3 is a representative example and exhibits a well-resolved set of signals near $g \approx 2$.

Four lines occurring at $g_{min} = 2.017, 2.007, 2.000, 1.996$ have nearly the same g_{min} values in compounds **6c**, **d**, **j**, and **6l** and are superimposed by a broad signal which seems to have a fine structure as well. Signals emerging at $g \approx 4.3$ and $g \approx 6.2$ are negligible or of very low intensity, respectively. They are due to Fe^{III} high-spin impurities which are a common feature of $[PcFe]_2O$ (**6a**, **b**)[6f,7b]. However, if for example the μ-oxo dimer $[Et_4PcFe]_2O$ (**6d**) was dissolved in solvents containing traces of acid, intense signals at $g \approx 6.2$ and 4.3 emerged in the ESR spectra. The produced monomeric species could not be detected by Mössbauer spectroscopy which is less sensitive. ESR spectra of μ-oxodiiron(III) compounds are still poorly understood[7b,23]. The very similar spectra of **6c**, **d**, **j**, and **6l** suggest that the spectrum presented in Figure 3 is characteristic of an antiferromagnetically coupled moiety in (μ-oxo)bis[(phthalocyaninato)iron(III)] complexes (see magnetic measurements). The isomeric μ-oxo dimers **A** and **B** seem to have identical ESR properties which may be attributed to the fact that the ESR pattern of **6c** and **6l**, with a high proportion of **A** and that of **6d** and **6j**, with a dominating proportion of **B**, do not differ.

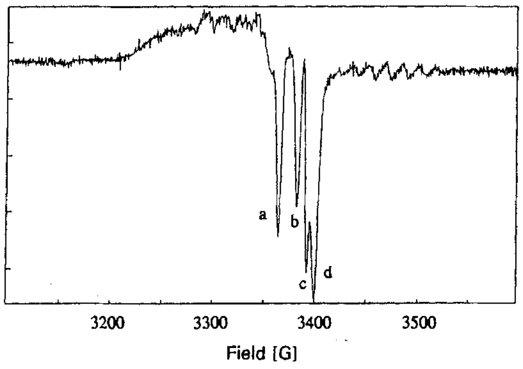


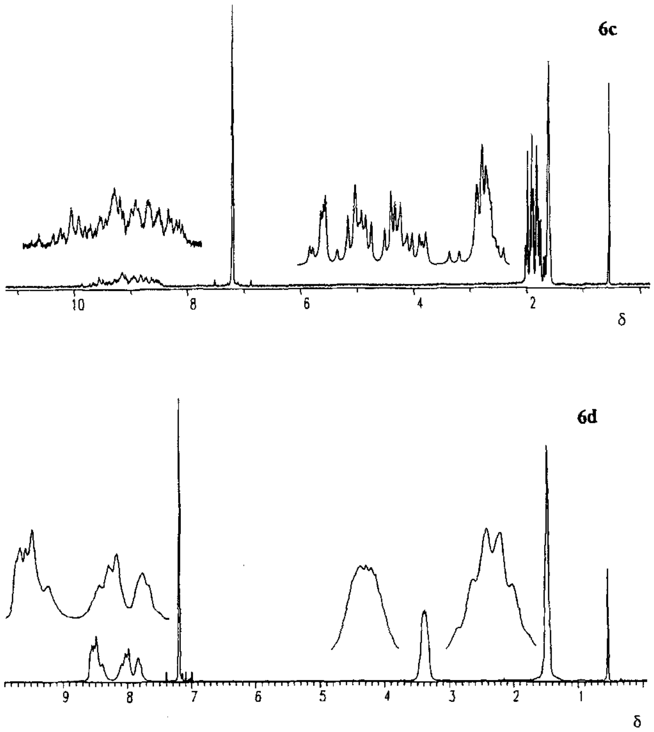
Figure 3. ESR spectrum of a powdered sample of $[(PPO)_4PcFe]_2O$ (**6l**) measured at 77 K microwave frequency of 9.502 GHz. g_{min} values (a−d) are marked (a: 2.017, b: 2.007, c: 2.000, d: 1.996)

^{1}H-NMR Spectra

$[tBu_4PcFe]_2O$ (**6c**), $[Et_4PcFe]_2O$ (**6d**), $[(EHO)_4PcFe]_2O$ (**6j**), $[(PPO)_4PcFe]_2O$ (**6l**), $[(C_8H_{17}O)_8PcFe]_2O$ (**6m**), and $[(EHO)_8PcFe]_2O$ (**6n**) were investigated by ^{1}H-NMR spectroscopy. The spectra show the absence of any ligands coordinated to the Fe−O−Fe moiety in **6c**, **d**, **j**, and **6l**. Compared to the corresponding bisaxially coordinated diamagnetic monomers R_nPcFeL_2 (L = tBuNC) (**7c**, **d**, **j**, **l**, **m**, and **7n**) compounds **6c**, **d**, **j**, **l**, **m**, and **6n** exhibit complex resonance patterns which can only be explained by assuming dimeric μ-oxo-bridged complexes. Figure 4 shows the ^{1}H-NMR spectra of $[tBu_4PcFe]_2O$ (**6c**)[24] and $[Et_4PcFe]_2O$ (**6d**). A large number of signals are observed between $\delta = 1.6-2.0$ (*tert*-butyl protons) and 8.5−9.8 (phthalocyanine protons) in the spectrum of **6c**. Compared to **6c** $[Et_4PcFe]_2O$ (**6d**) exhibits a much simpler spectrum with signals between $\delta = 1.4-1.5$ (CH_3), 3.3−3.5 (CH_2), and 7.7−8.6 (phthalocyanine protons) (the methylene protons are diastereotopic in octasubstituted μ-oxo dimers such as **6d**). As already mentioned several constitutional isomers must be considered for octasubstituted μ-oxo dimers formed by the combination of the four possible isomeric tetrasubstituted monomers. Thus, the large number of signals observed in the spectrum of **6c** are due to these isomers and also a result of rotational isomers caused by hindered rotation around the Fe−O−Fe bond. The much wider range of the proton resonances in $[tBu_4PcFe]_2O$ (**6c**) compared to $[Et_4PcFe]_2O$ (**6d**) is a consequence of the stronger interaction of the bulky, non-flexible *tert*-butyl substituents whereas the more narrow range of resonances in the spectrum of **6d** reflects the much higher conformational flexibility of the ethyl groups. Similar observations were made when the NMR spectra of the μ-oxosilicon compounds

$\{t\mathrm{Bu}_4\mathrm{PcSi[OSiMe_2}(t\mathrm{Bu})]\}_2\mathrm{O}$ and $\{\mathrm{Et_4PcSi[OSiMe_2}(t\mathrm{Bu})]\}_2\mathrm{O}$ were compared[15b].

Figure 4. ^{1}H-NMR spectra of $[t\mathrm{Bu_4PcFe]_2O}$ (**6c**) and $\mathrm{[Et_4PcFe]_2O}$ (**6d**) (250 MHz, [D$_8$]toluene)



Conclusions

Compounds **6c**–**n** represent examples of substituted μ-oxo-bridged (phthalocyaninato)iron(III) complexes. This was shown by means of UV/Vis spectroscopy as the UV/Vis spectra of **6c**–**n** exhibit essentially the same features as unsubstituted $\mathrm{[PcFe]_2O}$ (**6a**) and (**6b**). In addition, their spectral behavior in pyridine is clearly indicative of μ-oxo-bridged structures. For $[t\mathrm{Bu_4PcFe]_2O}$ (**6c**), $\mathrm{[Et_4PcFe]_2O}$ (**6d**), $\mathrm{[(NPO)_4PcFe]_2O}$ (**6k**), and $\mathrm{[(PPO)_4PcFe]_2O}$ (**6l**) the molecular peaks of the μ-oxo dimers **6c**, **d**, **j**, and **l** were detected in the mass spectra by using the FD technique. Mössbauer spectra of **6c**–**n** show two patterns **A** (δ_{Fe} = 0.22 mm s^{-1}, ΔE_Q = 1.33–1.39 mm s^{-1}, T = 82 K) and **B** (δ_{Fe} = 0.33–0.36 mm s^{-1}, ΔE_Q = 0.39–0.53 mm s^{-1}, T = 82 K) present in varying ratios. The Mössbauer spectral data of **A** can be related to the data of μ-oxo(2) (**6b**) and the Mössbauer parameters of **B** can be compared to the parameters found for μ-oxo(1) (**6a**). This suggest that patterns **A** and **B** correspond to isomeric μ-oxo dimers as in the case of $\mathrm{[PcFe]_2O}$ (**6a**) and (**6b**). The Mössbauer data are indicative of high-spin (S = 5/2) Fe$^{\mathrm{III}}$ centers. So far the varying ratios of isomer **A** and **B** in compounds **6c**–**n** as determined by Mössbauer spectroscopy cannot be simply explained in terms of electronic and steric factors extended by the peripheral substituents. The nature of the two isomeric μ-oxo compounds **A** and **B** still remains unknown. For unsubstituted $\mathrm{[PcFe]_2O}$ (**6a**) and (**6b**) a bent and a quasi-linear structure was suggested[6b] which is in accordance with the two different magnetic coupling constants J determined for **6a** and **6b**, since a linear Fe–O–Fe moiety should favor exchange coupling with respect to a bent moiety. Yet, there should be some doubts if a bent geometry of the Fe–O–Fe unit is possible when bulky substituents are present at the phthalocyanine macrocycle. The NMR spectrum of $[t\mathrm{Bu_4PcFe]_2O}$ (**6c**) indicates that there are interactions between substituents of the two phthalocyanine units. Very recently, NMR and UV/Vis studies of peripheral alkoxy-substituted μ-oxosilicon dimers $\{\mathrm{(RO)_8PcSi[OSiMe_2}(t\mathrm{Bu})]\}_2\mathrm{O}$ have given evidence for rotational isomers in these compounds[25]. One might also think of rotational isomers in the case of μ-oxo-bis(phthalocyaninatoiron) complexes. However, any model assumed should be able to explain the different Mössbauer parameters and magnetic coupling constants found for the two isomers. It remains to be seen whether the experimental data can be deduced by calculations from rotational isomers in the case of μ-oxoiron complexes.

We have also investigated a potential formation of μ-oxo dimers with 1,4,8,11,15,18,22,25-oxa(*n*-octyloxy)(phthalocyaninato)iron and 1,8,15,22-tetrakis(2-ethylhexyloxy)(phthalocyaninato)iron compounds (Figure 1). These systems, however, are completely different from the compounds **6c**–**n**. This will be published elsewhere[26].

We would like to express our gratitude to Dr. *A. Lange* and Dr. *B. Haas* for their help in operating the Mössbauer equipment.

Experimental

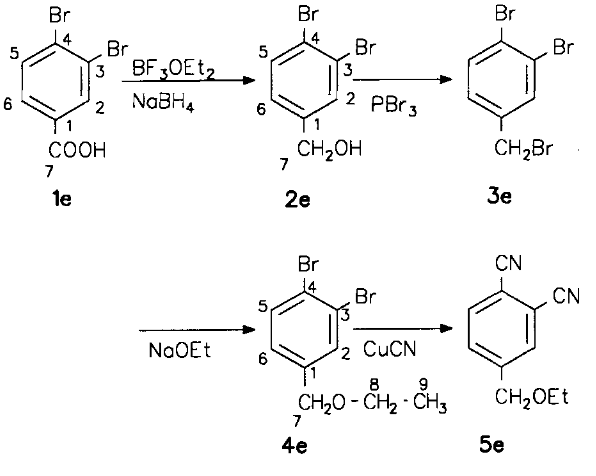
FT-IR: Bruker IFS 48. – UV/Vis: Shimadzu UV 365 and Perkin-Elmer Lambda 15 UV/Vis. – MS: Finnigan MAT ISQ 70 (EI, 70 eV) and Finnigan MAT 711A (modified) (FD). – NMR Bruker AC 250 (^{1}H: 250 MHz; ^{13}C: 62.9 MHz) and Bruker AMX 400 (^{1}H: 400 MHz; ^{13}C: 100.6 MHz). – Mössbauer spectra: Elscint AME-30 spectrometer equipped with a ^{57}Co(Rh) source (10 mCi) in conjunction with a CMTE MCD301/8k multi-channel analyzer. The spectrometer was calibrated with a metallic iron foil. Spectra were recorded in the constant acceleration mode and adapted to Lorentzian line shapes by least-squares techniques. – ESR: Bruker ESP 300. – Melting points are uncorrected. – The syntheses of phthalocyanines were carried out under nitrogen. – 1,2-Dicyano-4-*tert*-butylbenzene[27], 1,2-dicyano-4-neopentyloxybenzene[28], 1,2-dicyano-4-nitrobenzene[29], 1,2-dicyano-4,5-bis(*n*-octyloxy)benzene[30], and 1,2-dicyano-4,5-bis(2-ethylhexyloxy)benzene[31] were prepared according to literature procedures.

(μ-Oxo)bis[(tetra-tert-butylphthalocyaninato)iron(III)] (**6c**): A mixture of 1,2-dicyano-4-*tert*-butylbenzene (**5c**) (5.0 g, 27 mmol) and $\mathrm{FeSO_4 \cdot H_2O}$[32] (1.42 g, 9 mmol) in freshly distilled *N*,*N*-dimethylaminoethanol (50 ml) was heated under reflux for 12 h. The mixture was cooled and the product was precipitated and washed with MeOH/H$_2$O (1:1). The solid was dried and purified by column chromatography (neutral alumina, deactivated by 10% H$_2$O; eluent: toluene). To remove traces of toluene the product was dissolved in CH$_2$Cl$_2$ and reprecipitated by adding MeOH. Finally, it was dried at 80°C in vacuo for 6 h. Yield 2.8 g (52%). – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.6–2.0 [m, 36 H, C(CH$_3$)$_3$], 8.5–9.8 (m, 12 H, aromatic H). – MS (FD, CH$_2$Cl$_2$); *m/z* (%): 1601.7 (100) [M$^+$], 792.2 (85) [monomer]. – $\mathrm{C_{96}H_{96}Fe_2N_{16}O}$ (1601.6): calcd. C 71.99, H 6.04, N 13.99; found C 71.82, H 5.63, N 14.01.

(μ-Oxo)bis[(tetraethylphthalocyaninato)iron(III)] (**6d**): The synthesis was carried out according to lit.[9b]. The product was worked up as described for **6c**. – ^1H NMR (250 MHz, [D_6]benzene): δ = 1.4–1.5 (br, 3H, CH_3), 3.3–3.5 (br, 2H, $-CH_2-$), 7.7–8.6 (br, 3H, aromatic H). – MS (FD, CH_2Cl_2); *m/z* (%): 1376.0 (100) [M^+], 1029.2 (10), 679 (5) [monomer]. – $C_{80}H_{64}Fe_2N_{16}O$ (1377.19): calcd.C 69.77, H 4.68, N 16.27; found C 69.78, H 4.80, N 16.13.

1,2-Dibromo-4-(hydroxymethyl)benzene (**2e**; Scheme 2): Under nitrogen 3,4-dibromobenzoic acid[33] (**1e**) (16.7 g, 59.6 mmol) was added in portions to a stirred suspension of sodium borohydride (2.03 g, 53.7 mmol) in dry bis(2-methoxyethyl) ether (50 ml). Then a solution of freshly distilled $BF_3 \cdot Et_2O$ (8.8 ml, 71.6 mmol) in bis(2-methoxyethyl) ether (15 ml) was added over a period of 1 h. The mixture was stirred at room temp. and when there was no more 3,4-dibromobenzoic acid present the reaction mixture was poured on ice. The precipitate was suction filtered and dried in vacuo. Yield 14.7 g (93%), m.p. 61–63 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.12 (s, 1H, CH_2OH), 4.60 (s, 2H, CH_2OH), 7.12 (dd; *J* = 8.2, 2.0 Hz; 1H, 6-H), 7.56 (d, *J* = 8.2 Hz, 1H, 5-H), 7.60 (d, *J* = 2.0 Hz, 1H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 63.78 (C-7), 123.58 (C-4), 124.90 (C-3), 126.84 (C-6), 131.91 (C-2), 133.69 (C-5), 141.77 (C-1). – IR (KBr): ṽ = 3429 cm^{-1}, 2928–2854, 1656, 1462, 1447, 1393, 1192, 1111, 1045, 1013, 812. – MS (70 eV); *m/z* (%): 266 (100) [M^+]. – $C_7H_6Br_2O$ (265.93): calcd. C 31.62, H 2.27, Br 60.09; found C 31.30, H 2.09, Br 59.72.

Scheme 2. Synthesis of 1,2-dicyano-4-(ethoxymethyl)benzene (**5e**)



1,2-Dibromo-4-(bromomethyl)benzene (**3e**; Scheme 2)[34,35]: Freshly distilled phosphorus tribromide (14.3 ml, 19.8 mmol) in dry chloroform (30 ml) was added to a solution of 3,4-dibromo-4-(hydroxymethyl)benzene (**2e**) (57.6 g, 54.5 mmol) in chloroform (120 ml) at –10 °C. The reaction mixture was allowed to warm to room temp. and stirred until there was no more benzyl alcohol. Then the mixture was poured on ice and extracted several times with ether. The combined extract was washed with a potassium hydrogen carbonate solution and water. After evaporation of the solvent the product was purified by vacuum distillation. Yield 63.7 g (90%) of a white solid, m.p. 43–44 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 4.35 (s, 2H, CH_2Br), 7.15 (dd; *J* = 8.3, 2.1 Hz; 1H, 6-H), 7.55 (d, *J* = 8.3 Hz, 1H, 5-H), 7.62 (d, *J* = 2.1 Hz, 1H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.10 (C-7), 124.83 (C-4), 125.03 (C-3), 129.11 (C-6), 133.99 (C-5), 134.06 (C-2), 138.62 (C-1). – IR (NaCl, neat): ṽ = 1585 cm^{-1}, 1458, 1379, 1223, 1111, 1015, 852, 818, 700, 627. – MS (70 eV); *m/z* (%): 328 (10) [M^+]. – $C_7H_5Br_3$ (328.83): calcd. C 25.57, H 1.53, Br 72.90; found C 25.89, H 1.45, Br 72.71.

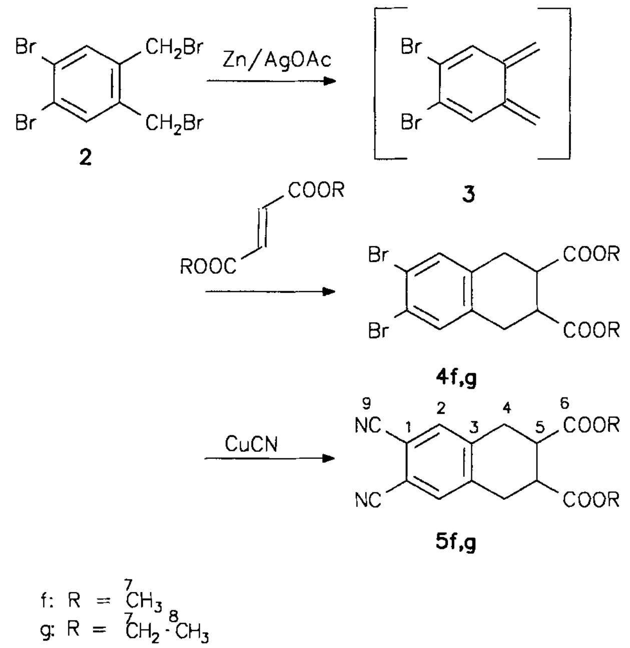
1,2-Dibromo-4-(ethoxymethyl)benzene (**4e**; Scheme 2): 1,2-Dibromo-4-bromomethylbenzene (**3e**) (63.7 g, 0.19 mol) was added in portions to a solution of sodium ethylate (0.33 mmol) (prepared from 7.5 g sodium) in ethanol at 60 °C. The mixture was stirred for 12 h and cooled to room temp. Then water was added and the pH adjusted to neutral by addition of diluted hydrochloric acid. The mixture was extracted several times with ether, the extract was washed with water and dried with $MgSO_4$. After evaporation of the solvent the residue was distilled in vacuo. Yield 55.8 g (98%) of a colorless liquid. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 3.57 (q, *J* = 7.0 Hz, 2H, CH_2CH_3), 4.46 (s, 2H, CH_2OCH_2), 7.16 (dd; *J* = 8.2, 2.0 Hz; 1H, 6-H), 7.60 (d, *J* = 8.2 Hz, 1H, 5-H), 7.64 (d, *J* = 2.0 Hz, 1H, 2-H). – ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 15.16 (C-9), 66.13 (C-8), 71.16 (C-7), 123.46 (C-4), 124.76 (C-3), 127.53 (C-6), 132.57 (C-2), 133.53 (C-5), 139.85 (C-1). – IR (NaCl, neat): ṽ = 2975–2866 cm^{-1}, 1462, 1385, 1346, 1258, 1200, 1108, 1014, 812. – MS (70 eV); *m/z* (%): 294 (33) [M^+].

1,2-Dicyano-4-(ethoxymethyl)benzene (**5e**): A mixture of 1,2-dibromo-4-ethoxymethylbenzene (**4e**) (20.0 g, 68 mmol) and copper(I) cyanide (13.4 g, 0.20 mol) was stirred in dry DMSO (320 ml) at 130 °C under nitrogen. When there was no more dibromo compound the reaction mixture was cooled to room temp. and poured into concentrated ammonia solution (150 ml). After bubbling of a stream of air through the suspension for 12 h the mixture was extracted several times with toluene. The combined extract was washed with water and dried with $MgSO_4$. After evaporation of the solvent the residue was distilled at 140 °C in vacuo (0.04 mbar) and purified by flash chromatography (silica gel, eluent: dichloromethane). Sublimation of the product afforded a white solid. Yield 3.8 g (30%), m.p. 66–68 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 3.60 (q, *J* = 7.0 Hz, 2H, CH_2CH_3), 4.58 (s, 2H, $CH_2OCH_2CH_3$), 7.68 (dd; *J* = 8.1, 1.5 Hz; 1H, 6-H), 7.75 (d, *J* = 8.1 Hz, 1H, 5-H), 7.80 (d, *J* = 1.5 Hz, 1H, 2-H). – ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 15.07 (C-9), 66.85 (C-8), 70.54 (C-7), 114.39/115.45 (C–3/4/10/11), 131.29 (C-2), 131.70 (C-6), 133.48 (C-5), 145.74 (C-1). – IR (NaCl, neat): ṽ = 3112 cm^{-1}, 3045, 2976–2895, 2233 (ν_{CN}), 1604, 1462, 1409, 1377, 1356, 1161, 1120, 900, 839. – MS (70 eV); *m/z* (%): 186 (4) [M^+]. – $C_{11}H_{10}N_2O$ (186.21): calcd. C 70.95, H 5.41, N 15.04; found C 71.57, H 5.99, N 15.02.

(μ-Oxo)bis{[tetrakis(ethoxymethyl)phthalocyaninato]iron(III)} (**6e**): 1,2-Dicyano-4-ethoxymethylbenzene (**5e**) (2.88 g, 15.5 mmol), iron(II) acetate (672 mg, 3.9 mmol), and two drops of DBU were heated in dry hexanol (120 ml) at 150 °C until all the dinitrile had reacted (TLC). The mixture was cooled and the solvent was removed under reduced pressure. The residue was washed with methanol and purified by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: $CHCl_3$). Yield 0.98 g (32%). – MS (FD, $CHCl_3$); *m/z* (%): 800 (100) [monomer]. – $C_{88}H_{80}Fe_2N_{16}O_9$ (1617.40): calcd. C 65.35, H 4.99, N 13.86; found C 66.09, H 5.39, N 13.65.

6,7-Dibromo-2,3-bis(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**4f**; Scheme 3): Preparation of Zn/AgOAc: Zn dust (7.5 g) was stirred in 10% hydrochloric acid (50 ml) for 4 min. The liquid was decanted and the residue washed with acetone (50 ml) and ether (50 ml). Silver(I) acetate (0.3 g) in boiling acetic acid (100 ml) was added. After the mixture had been stirred for 1 min the solution was decanted and the solid was washed with acetic acid (25 ml) and four times with ether (50 ml). Finally, the Zn/AgOAc was dried in stream of dry nitrogen. – A mixture of dimethyl fumarate (5.5 g, 38 mmol) and Zn/AgOAc (0.12 g) in dry DMF (75 ml) was stirred at 80 °C. 4,5-Dibromo-1,2-bis(bromomethyl)benzene (**2**) (5.4 g, 12.5 mmol) in DMF (20 ml) was added over a period of 6 h. Zn/AgOAc (0.3 g) was added every hour. The mixture was cooled, filtered through kieselgur into 1% hydrochloric acid (150 ml), and extracted several times with chloroform. The combined extract was washed with a sodium carbonate solution and dried with $MgSO_4$. After evaporation of the solvent the residue was crystallized from *n*-hexane. Yield 2.2 g (42%), m.p. 157 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.8–3.1 (m, 6H, $CH_2CHCOOCH_3$), 3.72 (s, 6H, $COOCH_3$), 7.34 (s, 2H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 30.4 (C-4), 41.3 (C-5), 52.2 (C-7), 122.2 (C-1), 133.3 (C-2), 134.9 (C-3), 174.1 (C-6). – IR (KBr): $\tilde{\nu}$ = 3011 cm^{-1}, 2960, 2896, 1739, 1731, 1466, 1438, 1341, 1304, 1176, 1162, 1152. – MS (70 eV); *m/z* (%): 406 (30) [M^+]. – $C_{14}H_{14}Br_2O_4$ (405.93): calcd. C 41.4, H 3.5, Br 39.4; found C 41.6, H 3.6, Br 40.0.

Scheme 3. Synthesis of 6,7-dicyano-2,3-bis(alkoxycarbonyl)-1,2,3,4-tetrahydronaphthalenes **5f, g**



6,7-Dicyano-2,3-bis(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**5f**): A mixture of 6,7-dibromo-2,3-bis(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**4f**) (2.2 g, 5.4 mmol) and copper(I) cyanide (1.45 g, 16.2 mmol) in dry DMF (20 ml) was stirred at 150 °C for 6 h under nitrogen. After cooling to room temp. the mixture was poured into concentrated ammonia solution. A stream of air was bubbled through the suspension for 12 h. The solid material was collected and washed with water. Column chromatography of the product (silica gel, eluent: chloroform) afforded white crystals after evaporation of the solvent. Yield 0.8 g (49%), m.p. 163 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.0–3.2 (m, 6H, $CH_2CHCOOCH_3$), 3.66 (s, 6H, $COOCH_3$), 7.49 (s, 2H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 30.2 (C-4), 40.3 (C-5), 52.4 (C-7), 113.4 (C-1), 115.1 (C-9), 133.6 (C-2), 140.5 (C-3), 173.1 (C-6). – IR (KBr): $\tilde{\nu}$ = 3037 cm^{-1}, 2953, 2943, 2233 (ν_{CN}), 1744, 1722, 1556, 1497, 1431, 1377, 1367, 1331, 1300, 1285, 1254, 1242, 1201, 1184, 1171, 1159. – MS (70 eV); *m/z* (%): 298 (15) [M^+]. – $C_{16}H_{14}N_2O_4$ (298.14): calcd. C 64.4, H 4.7, N 9.3; found C 64.5, H 4.8, N 9.1.

(μ-Oxo)bis{[1,2,3,4,10,11,12,13,19,20,21,22,28,29,30,31-hexadecahydro-2,3,11,12,20,21,29,30-octakis(methoxycarbonyl)-naphthalocyaninato]iron(III)} (**6f**): 6,7-Dicyano-2,3-bis(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**5f**) (0.80 g, 27 mmol), iron(II) acetate (0.16 g, 13 mmol) and one drop of DBU were dissolved in dry methanol and the solution was heated at 150 °C for 8 h in an autoclave. The solid was collected, washed with methanol, and purified by column chromatography (neutral alumina, deactivated with 10% H_2O; eluent: $CHCl_3$). The product was dried at 80 °C in vacuo. Yield 270 mg (32%). – $C_{128}H_{112}Fe_2N_{16}O_{33}$ (2584.80): calcd. C 61.18, H 4.49, N 8.92; found C 60.4, H 4.5, N 8.3.

6,7-Dibromo-2,3-bis(ethoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**4g**; Scheme 3): The synthesis was carried out as described for the methoxy analog starting from dimethyl fumarate. Crystallization from chloroform at –20 °C and washing with *n*-hexane afforded white crystals. Yield 40%, m.p. 107 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.2 (t, 6H, CH_2CH_3), 2.8 (m, 2H, CH_2CHCOO), 3.0 (m, 4H, CH_2CHCOO), 4.1 (q, 4H, CH_2CH_3), 7.3 (s, 2H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.2 (C-8), 30.6 (C-4), 41.5 (C-5), 61.1 (C-7), 122.1 (C-1), 133.3 (C-2), 135.1 (C-3), 173.6 (C-6). – IR (KBr): $\tilde{\nu}$ = 3035 cm^{-1}, 2940, 1730, 1470, 1450. – MS (70 eV); *m/z* (%): 434 (30) [M^+]. – $C_{16}H_{18}Br_2O_4$ (434.12): calcd. C 44.3, H 4.2, Br 36.8; found C 44.9, H 4.6, Br 36.6.

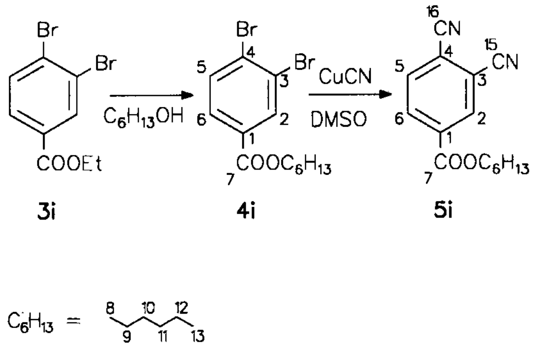
6,7-Dicyano-2,3-bis(ethoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**5g**): A mixture of 6,7-dibromo-2,3-di(ethoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**4g**) (2.0 g, 4.6 mmol) and copper(I) cyanide (1.65 g, 18 mmol) was heated in dry DMF (15 ml) for 4 h at 150 °C. After cooling the mixture was poured into water. The precipitate was filtered, dried, and extracted with toluene in a Soxhlet apparatus. After evaporation of the solvent the product was purified by column chromatography [silica gel, eluent: *n*-hexane/ethyl acetate, 7:3]. Yield 1.3 g (87%), m.p. 149–150 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.2 (t, 6H, CH_2CH_3), 3.1 (m, 6H, CH_2CHCOO), 4.2 (q, 4H, CH_2CH_3), 7.5 (s, 2H, aromatic H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (C-8), 30.9 (C-4), 40.6 (C-5), 61.4 (C-7), 113.5 (C-1), 115.2 (C-9), 133.7 (C-2), 140.9 (C-3), 172.7 (C-6). – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2980, 2235 (ν_{CN}), 1730, 1480, 1465. – MS (70 eV); *m/z* (%): 326 (10) [M^+]. – $C_{18}H_{18}N_2O_4$ (325.35): calcd. C 66.3, H 5.5, N 8.6; found C 64.9, H 5.6, N 7.5.

(μ-Oxo)bis{[2,3,11,12,20,21,29,30-octakis(ethoxycarbonyl)-1,2,3,4,10,11,12,13,19,20,21,22,28,29,30,31-hexadecahydro-naphthalocyaninato]iron(III)} (**6g**): 6,7-Dicyano-2,3-di(ethoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**5g**) (1.0 g, 31 mmol), iron(II) acetate (0.18 g, 15 mmol), and one drop of DBU were dissolved in dry ethanol and the solution was heated at 150 °C for 8 h in an autoclave. The product was worked up as described for **6f**. Yield 410 mg (38%). – $C_{144}H_{144}Fe_2N_{16}O_{33}$ (2738.37): calcd. C 63.16, H 5.30, N 8.18; found C 63.3, H 5.8, N 8.3.

(μ-Oxo)bis{[tetrakis(ethoxycarbonyl)phthalocyaninato]iron(III)} (**6h**): 1,2-Dicyano-4-(ethoxycarbonyl)benzene[36] (1.0 g, 5 mmol), iron(II) acetate (217 mg, 1.25 mmol), and 3 drops of DBU were dissolved in 50 ml of dry ethanol and the solution was heated at 150 °C for 8 h in an autoclave. The product was precipitated by adding methanol, collected and purified by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: $CHCl_3$). Yield 340 mg (32%). – MS (FD, $CHCl_3$); *m/z* (%): 856 (100) [monomer]. – $C_{88}H_{64}Fe_2N_{16}O_{17}$ (1729.32): calcd. C 61.12, H 3.73, N 12.96; found C 61.07, H 3.83, N 12.89.

1,2-Dibromo-4-(hexyloxycarbonyl)benzene (**4i**; Scheme 4): 1,2-Dicyano-4-(ethoxycarbonyl)benzene (**3i**) (10.0 g, 33 mmol) in dry hexanol (120 ml) and 10 drops of concentrated sulfuric acid were heated under reflux for 48 h. After cooling of the reaction mixture ether (300 ml) was added. The mixture was then washed with a sodium hydrogen carbonate solution and water, and dried with $MgSO_4$. After evaporation of the solvent the residue was distilled in vacuo to afford a colorless oil. Yield 8.3 g (70%). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.9 Hz, 3H, $[CH_2]_5CH_3$), 1.28–1.46 (m, 6H, $[CH_2]_2[CH_2]_3CH_3$), 1.79 (m, 2H, OCH_2CH_2), 4.32 (t, J = 6.7 Hz, 2H, OCH_2CH_2), 7.67 (d, J = 8.3 Hz, 1H, 5-H), 7.79 (dd; J = 8.3, 2.0 Hz; 1H, 6-H), 8.23 (d, J = 2.0 Hz, 1H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.02 (C-14), 22.55 (C-13), 25.66 (C-10), 28.60 (C-9), 31.44 (C-11), 65.82 (C-8), 125.02 (C-3), 129.25 (C-6), 130.20 (C-4), 131.03 (C-1), 133.73 (C-5), 134.57 (C-2), 164.78 (C-7). – IR (NaCl, neat): $\tilde{\nu}$ = 2957 cm^{-1}, 2930, 2858, 1724, 1583, 1556, 1458, 1373, 1283, 1244, 1103, 1016, 758. – MS (70 eV); m/z (%): 364 (4) $[M^+]$.

Scheme 4. Synthesis of 1,2-dicyano-4-(hexyloxycarbonyl)benzene (**5i**)

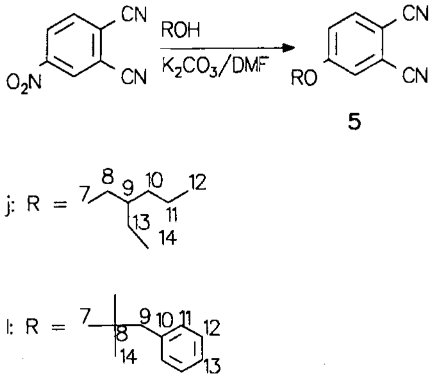


1,2-Dicyano-4-(hexyloxycarbonyl)benzene (**5i**; Scheme 4): 1,2-Dibromo-4-(hexyloxycarbonyl)benzene (**4i**) (5.0 g, 13.7 mmol) and copper(I) cyanide (3.4 g, 38 mmol) were stirred in dry DMSO (70 ml) at 150 °C under nitrogen until the starting material had disappeared (TLC). After cooling to room temp., a mixture of iron(III) chloride hexahydrate (7.5 g) in water (10 ml) and concentrated hydrochloric acid (0.25 ml) was added. The mixture was stirred at 70 °C for 10 min, cooled, poured into water (200 ml), and extracted several times with chloroform. The combined extract was washed with water and dried with $MgSO_4$. After evaporation of the solvent the product was purified by sublimation (100 °C/0.04 mbar). Yield 2.0 g (57%), m.p. 41–43 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, J = 6.8 Hz, 3H, CH_3), 1.36–1.49 (m, 6H, $[CH_2]_2[CH_2]_3CH_3$), 1.78 (m, 2H, OCH_2CH_2), 4.42 (t, J = 6.6 Hz, 2H, OCH_2CH_2), 7.95 (d, J = 8.1 Hz, 1H, 5-H), 8.40 (dd; J = 8.1, 1.2 Hz; 1H, 6-H), 8.48 (d, J = 1.2 Hz, 1H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.99 (C-13), 22.51 (C-12), 25.93 (C-10), 28.50 (C-9), 31.38 (C-11), 66.84 (C-8), 114.68, 114.75 (C-15/16), 116.43 (C-3), 119.21 (C-4), 133.75 (C-5), 133.84 (C-2), 134.28 (C-6), 135.10 (C-1), 163.15 (C-7). – IR (NaCl, neat): $\tilde{\nu}$ = 2959 cm^{-1}, 2932, 2860, 2237 (ν_{CN}) 1730, 1468, 1410, 1294, 1263, 1207, 1180, 1117, 766. – MS (70 eV); m/z (%): 257 (9) $[M^+ + 1]$, 256 (1) $[M^+]$. – $C_{15}H_{16}N_2O_2$ (256.31): calcd. C 70.30, H 6.30, N 10.93; found C 70.04, H 6.57, N 10.31.

(μ-Oxo)bis{[tetrakis(hexyloxycarbonyl)phthalocyaninato]iron(III)} (**6i**): 1,2-Dicyano-4-(hexyloxycarbonyl)benzene (1.0 g, 3.9 mmol), iron(II) acetate (170 mg, 1 mmol), and 3 drops of DBU in dry hexanol (50 ml) were heated at 150 °C for 10 h. The mixture was cooled and the solvent was removed under reduced pressure. The residue was washed with methanol and finally purified by column chromatography (neutral alumina, deactivated with 4% water; eluent: $CHCl_3$). Yield 310 mg (29%). – MS (FD, $CHCl_3$); m/z (%): 1081.4 (100) [monomer]. – $C_{120}H_{128}Fe_2N_{16}O_9$ (2178.14): calcd. C 66.17, H 5.92, N 10.29; found C 66.69, H 6.09, N 10.21.

1,2-Dicyano-4-(2-ethylhexyloxy)benzene (**5j**; Scheme 5): 1,2-Dicyano-4-nitrobenzene[29] (2.5 g, 14.5 mmol), 2-ethylhexanol (4.7 ml, 36.2 mmol) and anhydrous potassium carbonate (5 g, 36 mmol) were stirred in dry DMF (20 ml) at room temperature under nitrogen for 4 d. The reaction mixture was poured into water (50 ml) and extracted several times with toluene. The combined organic extract was dried with $MgSO_4$. After evaporation of the solvent and excess 2-ethylhexanol in vacuo, the residue was purified by column chromatography (silica gel; eluent: *n*-hexane/diethyl ether, 1:1; R_f = 0.47). Evaporation of the solvent afforded a greenish oil. Yield 3 g (81%). – ^1H-NMR (250 MHz, $CDCl_3$): δ = 0.85–0.96 (m, 6H, CH_3), 1.25–1.53 (m, 8H, H-9/10/11/13), 1.63–1.79 (m, 1H, OCH_2CH), 3.91 (d, J = 5.6 Hz, 2H, OCH_2CH), 7.17 (dd, J = 8.8, 2.5 Hz; 1H, 5-H), 7.25 (d, J = 2.5 Hz, 1H, 6-H), 7.68 (d, J = 8.8 Hz, 1H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.02 (C-14), 14.03 (C-12), 22.94 (C-11), 23.66 (C-13), 28.95 (C-10), 30.28 (C-9), 39.09 (C-8), 71.75 (C-7), 106.88 (C-1), 115.34/115.80 (C-15/16), 117.36 (C-2), 119.34/119.61 (C-3/5), 135.19 (C-6), 162.45 (C-4). – IR (nujol): $\tilde{\nu}$ = 2960 cm^{-1}, 2932, 2232 (ν_{CN}), 1599, 1323, 1310, 1292, 1254. – MS (70 eV); m/z (%): 256.2 (2) $[M^+]$. – $C_{16}H_{20}N_2O$ (256.35): calcd. C 74.97, H 7.86, N 10.93; found C 74.88, H 7.81, N 10.30.

Scheme 5. Synthesis of 1,2-dicyano-4-alkoxybenzenes **5j, l**



(μ-Oxo)bis{[tetrakis(2-ethylhexyloxy)phthalocyaninato]iron(III)} (**6j**): A mixture of 1,2-dicyano-4-(2-ethylhexyloxy)benzene (**5j**) (1.0 g, 3.9 mmol) and $FeSO_4 \cdot H_2O$ (192 mg, 1.1 mmol) in freshly distilled *N,N*-dimethylaminoethanol (15 ml) was refluxed for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (neutral alumina; eluent: $CHCl_3$). The product was dried at 50 °C in vacuo for 6 h. Yield 600 mg (57%). – ^1H NMR (250 MHz, $[D_6]$benzene): δ = 1.1–2.1 (br, 15H, $OCH_2C_7H_{15}$), 3.3–4.4 (br, 2H, $-OCH_2$), 7.5–9.0 (br, 3H, aromatic H). – MS (FD, $CHCl_3$); m/z: 1081.5 [monomer]. – $C_{128}H_{160}Fe_2N_{16}O_9$ (2178.48): calcd. C 70.90, H 7.44, N 10.34; found C 70.03, H 7.67, N 9.74.

(μ-Oxo)bis{[tetrakis(neopentyloxy)phthalocyaninato]iron(III)} (**6k**): This compound was obtained from 1,2-dicyano-4-(neopentyloxy)-benzene (**5k**) (1.0 g, 4.7 mmol) and $FeSO_4 \cdot H_2O$ (230 mg, 1.35 mmol) by the procedure used for the preparation of **6j**. Yield 620 mg (58%). – MS (FD, $CHCl_3$); m/z (%): 3684.5 (10) $[2\ M^+]$, 2763.5 (15) $[3\ M^{2+}]$, 2456.0 (20) $[4\ M^{3+}]$, 1841.9 (100) $[M^+]$, 1228.2 (15) $[2\ M^{3+}]$. –

$C_{104}H_{112}Fe_2N_{16}O_9$ (1841.88): calcd. C 67.82, H 6.13, N 12.17; found C 66.98, H 6.03, N 12.08.

1,2-Dicyano-4-(2,2-dimethyl-3-phenylpropoxy)benzene (**5l**; Scheme 5): 1,2-Dicyano-4-nitrobenzene[29] (14.6 g, 84.3 mmol), 2,2-dimethyl-3-phenylpropanol (36.1 g, 220 mmol), and potassium carbonate (29 g) were stirred under nitrogen atmosphere in dry DMF (85 ml) at 60°C for 20 h. The mixture was cooled and poured into water (1 l). The product was extracted several times with ether and the combined extract was dried with $MgSO_4$. The solvent was evaporated and excess alcohol was removed in vacuo. The residue was crystallized from methanol. In order to remove formed phthalocyanine the crystals were dissolved in ether. The solution was filtered and the solvent evaporated. Yield 19 g (77%), m.p. 98–99°C. – ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 1.05 [s, 6H, $C(CH_3)_2$], 2.75 (s, 2H, CH_2Ph), 3.83 (s, 2H, OCH_2), 7.13–7.28 (m, 5H, aromatic H of Ph), 7.49 (dd, J = 8.8, 2.6 Hz, 1H, 5-H), 7.66 (d, J = 2.6 Hz, 1H, 3-H), 7.96 (d, J = 8.7 Hz, 1H, 6-H). – ^{13}C NMR (62.9 MHz, [D$_6$]acetone): δ = 24.57 (C-14), 36.10 (C-8), 45.12 (C-9), 76.99 (C-7), 107.60 (C-1), 116.25/116.66 (C-15/16), 117.90 (C-2), 120.68 (C-3), 120.83 (C-5), 126.94 (C-13), 128.70 (C-11), 131.25 (C-12), 136.37 (C-6), 138.94 (C-10), 163.39 (C-4). – IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1}, 2976, 2935, 2230 (ν_{CN}), 1597, 1487, 1325, 1252, 1094, 1024, 706. – MS (70 eV); m/z (%): 290.1 (10) [M$^+$]. – $C_{19}H_{18}N_2O$ (290.37): calcd. C 78.59, H 6.25, N 9.65; found C 78.64, H 6.11, N 9.55.

(μ-Oxo)bis{[tetrakis(2,2-dimethyl-3-phenylpropoxy)phthalocyaninato]iron(III)} (**6l**): 1,2-Dicyano-4-(2,2-dimethyl-3-phenylpropoxy)benzene (**5l**) (1.16 g, 4 mmol) and $FeSO_4 \cdot H_2O$ (204 mg, 1.2 mmol) in distilled *N,N*-dimethylaminoethanol (15 ml) were heated under reflux for 16 h. The mixture was worked up as described for **6c**: Yield 500 mg (41%). – ^{1}H NMR (250 MHz, [D$_8$]toluene): δ = 1.1–1.6 [br, 6H, $-C(CH_3)_2$], 3.0–3.3 (br, 2H, CH_2Ph), 3.9–4.3 (br, 2H, OCH_2), 7.4–7.7 (br, 5H, aromatic H of Ph), 8.1–9.3 (3H, aromatic H of Pc). – MS (FD, CH_2Cl_2); m/z (%): 3266.2 (10) [4 M^{3+}], 2450.3 (100) [M$^+$], 1632.8 (20) [2 M^{3+}], 1224.8 (30) [M^{2+}]. – $C_{152}H_{144}Fe_2N_{16}O_9$ (2450.61): calcd. C 74.50, H 5.92, N 9.15; found C 74.09, H 6.14, N 8.80.

(μ-Oxo)bis{[2,3,9,10,16,17,23,24-octakis(n-octyloxy)phthalocyaninato]iron(III)} (**6m**): Compound **6m** was obtained from 1,2-dicyano-4,5-bis(*n*-octyloxy)benzene (**5m**) (1.0 g, 2.6 mmol) and $FeSO_4 \cdot H_2O$ (144 mg, 0.85 mmol) by the procedure described for **6j**. The product was purified by column chromatography (silica gel, eluent: toluene/diethyl ether 1:1). Yield 550 mg (53%). – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.0–2.3 (br, 30H, $-OCH_2C_7H_{15}$), 4.2–4.5 (br, 4H, $-OCH_2$), 8.7 (br, 2H, aromatic H). – MS (FD, $CHCl_3$); m/z: 1594.0 [monomer]. – $C_{192}H_{288}Fe_2N_{16}O_{17}$ (3204.22): calcd. C 71.97, H 9.06, N 6.99; found C 71.46, H 8.93, N 6.83.

(μ-Oxo)bis{[2,3,9,10,16,17,23,24-octakis(2-ethylhexyloxy)phthalocyaninato]iron(III)} (**6n**): This compound was obtained from 1,2-dicyano-4,5-bis(2-ethylhexyloxy)benzene (**5n**) by the procedure used for the preparation of **6m**. Yield 400 mg (38%). – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.0–2.2 (br, 30H, $-OCH_2C_7H_{15}$), 4.3–4.6 (br, 4H, $-OCH_2$), 9.3 (br, 2H, aromatic H). – MS (FD, $CHCl_3$); m/z: 1594.0 [monomer]. – $C_{192}H_{288}Fe_2N_{16}O_{17}$ (3204.22): calcd. C 71.97, H 9.06, N 6.99; found C 71.45, H 8.89, N 6.75.

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[23] Ref.[4] and references cited therein.

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