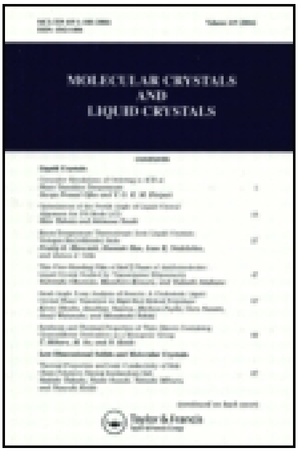

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Synthesis and Characterization of Soluble Phthalocyanines: Structure-Property Relationship

Michael Hanack [a], Ahmet Gül [a b], Andreas Hirsch [a], Braja K. Mandal [a], L. R. Subramanian [a] & Elisabeth Witke [a]

[a] Institut für Organische Chemie, Lehrstuhl II, Universität Tubingen, Auf der Morgenstelle 18, D-7400, Tübingen, Federal Republic of Germany

[b] Technical University of Istanbul, Istanbul, Turkey

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SYNTHESIS AND CHARACTERIZATION OF SOLUBLE PHTHALOCYANINES: STRUCTURE-PROPERTY RELATIONSHIP[1]

MICHAEL HANACK*, AHMET GÜL+, ANDREAS HIRSCH,
BRAJA K. MANDAL, L.R. SUBRAMANIAN, ELISABETH WITKE
Institut für Organische Chemie, Lehrstuhl II, Universität Tübingen, Auf der
Morgenstelle 18, D-7400 Tübingen, Federal Republic of Germany

Abstract (μ-Oxo)bis[octakis(alkoxy)phthalocyaninatoiron (III)] 6a-c are obtained by treatment of the cyclotetramerisation product of 4,5-bis(alkoxy)-phthalonitriles in lithium pentanolate with iron(II) acetate. Compounds 6a-c are reduced to bisaxially coordinated octaalkoxyphthalocyaninatoiron(II) in the presence of ligands such as pyridine and t-butylisocyanide. Reaction of 6a with bidentate bridging ligands (e.g. pyrazine, 1,4-diisocyanobenzene) yields the bridged complexes 8a and 9a. The Mößbauer spectroscopic data are described and compared with the analogous unsubstituted phthalocyaninatoiron derivatives.

INTRODUCTION

Over the last decade soluble phthalocyanines have attracted special interest, because of their conducting,[2,3] catalytic,[4,5] photovoltaic,[6,7] liquid-crystalline,[8,9] LB film,[10,11] and electrochromic[12] properties. Much of the recent work in this area has centered on attempts to tune the properties of the related complexes by changing the substituents on the macrocycles. Further fine tuning of the absorption bands has recently been reported by preparing peripheral 1,4- and 2,3-substituted phthalocyanines.[13] In continuation of our studies on several types of phthalocyanines, we have obtained electrical conductivity of such molecules as high as 0.30 $S \cdot cm^{-1}$ in the undoped state[15] and synthesized several soluble phthalocyanines and related bridged complexes.[14-19]

It has been understood that minor changes in the position of the side groups or altering the size of the groups or central metal atom affect appreciably the physical and the chemical properties of phthalocyanines. Long chain alkoxy substituted phthalocyanines continue to be the subject of increasing research activity, because of their

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+On leave from the Technical University of Istanbul, Istanbul, Turkey.

discotic mesophase and LB film forming behavior in addition to their solubility and stability in common organic solvents. Synthesis of several such molecules have been reported recently.[13,20-22] In this paper we describe a modified synthetic route for alkoxy substituted metal-free $(RO)_8PcH_2$ 5a and iron phthalocyanines $[(RO)_8PcFe]_2O$ 6a-c with R = C_5H_{11}, C_8H_{17} and $C_{12}H_{25}$. For the phthalocyanine macrocycles with iron as the central metal atom, bridged systems with dib and pyz ligands and a hexacoordinated complex with t-buNC are also reported. Structure-property relationship of these compounds is emphasized from the results of IR, UV/VIS, and ^{57}Fe-Mößbauer spectroscopy.

RESULTS AND DISCUSSION

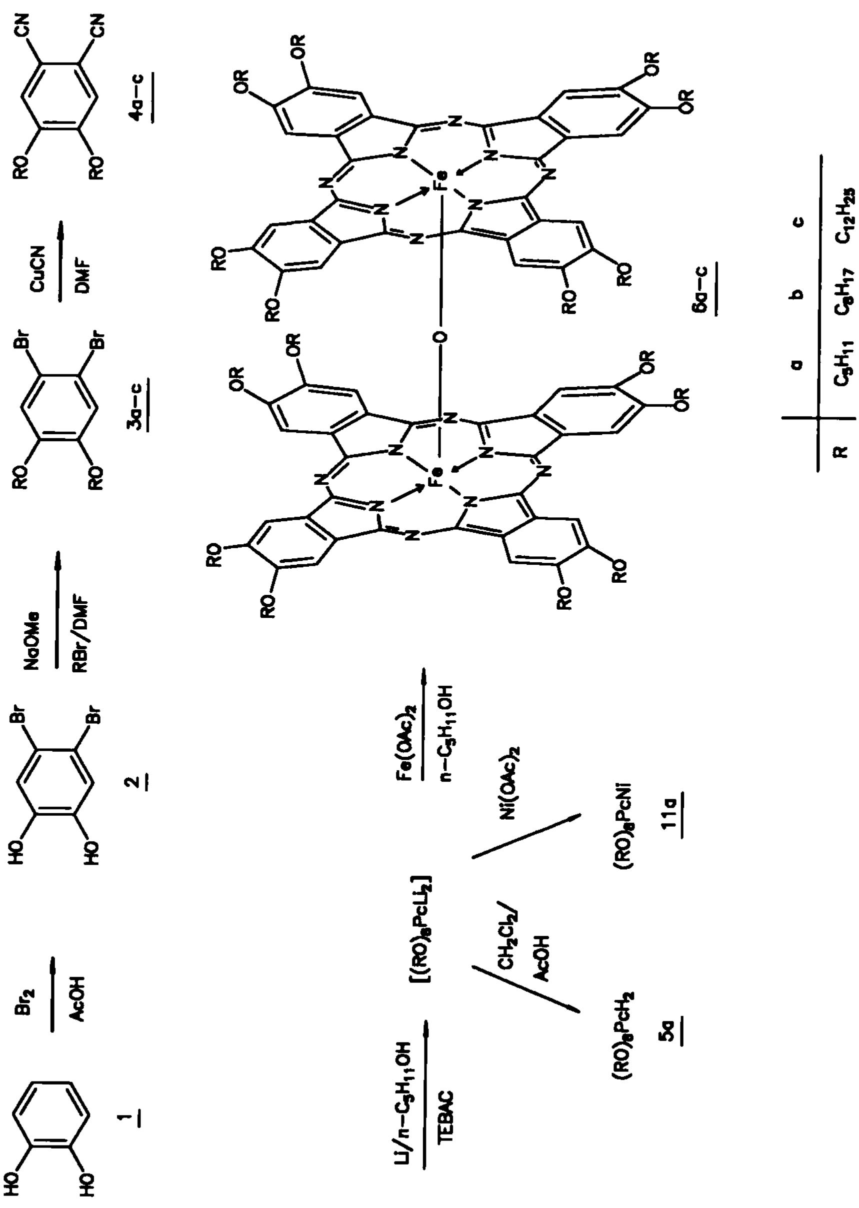
The synthesis of the new compounds is shown in Scheme 1 and Scheme 2. Peripherally substituted phthalocyanines have been obtained from phthalonitriles with desired substituents. Several chemical pathways are known for the synthesis of dialkoxyphthalonitriles.[16,21,23] The present synthetic route involves bromination of catechol (1)[24] in the first step (Scheme 1). O-alkylation of 4,5-dibromocatechol (2) was performed almost quantitatively by reacting the disodium salt of 2 with alkylbromide in DMF.[25] Dialkoxyphthalonitriles 4a-c were obtained from the corresponding dialkoxydibromo compounds 3a-3c by Rosenmund-von-Braun reaction.

Cyclic tetramerization of phthalonitrile derivatives can be performed by several ways.[26-28] However, the yield of the reaction is strongly dependent on the substituents on the benzene rings and the central metal atom. For instance, PcFe is prepared in fairly high yield by reacting $Fe(CO)_5$ with phthalonitrile in 1-chloronaphthalene at elevated temperature.[28] However, when the same method was applied for making long chain alkoxy substituted phthalocyanines, a mixture of compounds with very low yield was obtained.

$PcLi_2$ is known to be an efficient starting material to prepare various metal phthalocyanines under mild conditions.[29] In some recent reports, it was used to prepare phthalocyanines of lanthanides and actinides with fairly good yields.[30] In these reactions, the choice of a suitable solvent which can dissolve both $PcLi_2$ and the metal salt or complex is very important.[30] The reaction of o-dicyano compounds with lithium pentanolate in pentanol has also been applied to prepare some substituted metal-free phthalocyanines.[13,31]

In the present work, the cyclotetramerization has been carried out by treating the phthalonitriles 4a-c with lithium pentanolate. For this reaction pentanol is found to be a versatile solvent for phthalocyanines having chain lengths upto $C_{18}H_{37}$.[32] The yield can be further improved to a great extent by using a catalytic amount of a phase-transfer-catalyst such as TEBAC (triethylbenzylammonium chloride) especially for those with longer alkoxy chains. Since $PcLi_2$ derivatives are very sensitive to water and acids, they can be easily converted into metal-free phthalocyanines 5a-c by treating them with water or acetic acid.

SCHEME 1



In order to insert transition metal ions into the macrocycles, we tried both the reaction of metal-free phthalocyanines 5a-c with the metal acetate in pentanol and direct treatment of the reaction mixture containing $PcLi_2$ derivative with the metal acetate. Though the same products with comparable yields have been obtained after chromatographic separation in both cases [silica gel, toluene/diethyl ether (1:1)], we preferred the latter since we could neglect the isolation of the intermediate $(C_5H_{11}O)_8PcH_2$ (5a). The reaction products with iron(II) acetate were the trivalent μ-oxo dimers 6a-c and they can be easily reduced in the presence of ligands (e.g. py, pyz, dib) to divalent state which is required to form bridged polymers 8a-9a. Since it is known that in the presence of solvents such as DMF, DMA, THF or dioxane (μ-oxo)bis[(phthalocyaninato)iron(III)] has been prepared by exposure to air,[33-36] the formation of a similar compound in a basic pentanol solution can be also expected while the presence of traces of oxygen cannot be excluded during the synthesis or the separation processes. We have encountered a similar μ-oxo dimer structure by the reaction of 4-tert-butylphthalonitrile with $Fe(CO)_5$.[37] To verify the applicability of this method for various phthalocyaninatometal compounds, we have prepared $(C_5H_{11}O)_8PcNi$ (11a) by following the same procedure applied for the phthalocyaninatoiron compounds and obtained the monomeric divalent state, because of the sufficient stability of Ni(II) under the reaction conditions. The basic advantage of the synthetic route reported here applicable to many soluble phthalocyanines is the low reaction temperature (~150°C) which might be especially important for some thermally less stable substituted derivatives.

Elemental analyses results do not permit to make a decision between the monomer or the μ-oxo dimer 6a-c structures. FD mass spectra always showed the molecular ion for the monomers, but even in the case of dimers, similar spectra could be obtained.[37] The most important difference expected between the monomer and the dimer in the IR spectra is the absorption of Fe-O-Fe moiety of the dimer which appears at 890, 850, and 820 cm^{-1} in $(PcFe)_2O$,[33-37] but for the alkoxy substituted phthalocyanines this region is screened by the vibrations of the alkyl groups.

UV/VIS measurements in coordinating and non-coordinating solvents are very efficient to identify the valence-state of the central metal ion. The effect of substituents on the absorption bands is very small, so we have obtained similar spectra for three iron phthalocyanines with substituents of varying chain length. In halogenated hydrocarbons, they showed maximum absorption around 700 nm with a shoulder at ~670 nm (see Table 1). These values very closely follow those for $(PcFe)_2O$[38] and its tetra-t-butyl derivative.[37] The Q-band region is reported to be very sensitive to metal oxidation in iron phthalocyanines and the absorption bands for Fe(III) are at longer wavelenths than those for Fe(II).[39]

Aggregation of divalent planar phthalocyanines in concentrated solutions is characterized by blue shift and broadening for the Q-band.[39] When the products 6a-c are tested for this property, no blue shift is observed and the absorption band at 706 nm completely disappears in dilute solutions especially when dichloromethane is used as the solvent (see Figure 1). These results indicate that the product is not in divalent state.

The absorption spectra in coordinating solvents (e.g. pyridine) show the typical Q-band at 658 nm for the axially coordinated Fe(II)phthalocyanines and this absorption is not also affected from the peripheral substitution. These spectra denote that 6a-c can be easily reduced to the divalent state. When pyridine is added in excess to a solution of 6a in chloroform, the band at 706 nm starts to decrease in intensity and in about 0.5 h the spectrum is identical with that of $(C_5H_{11}O)_8PcFe(py)_2$ (7a).

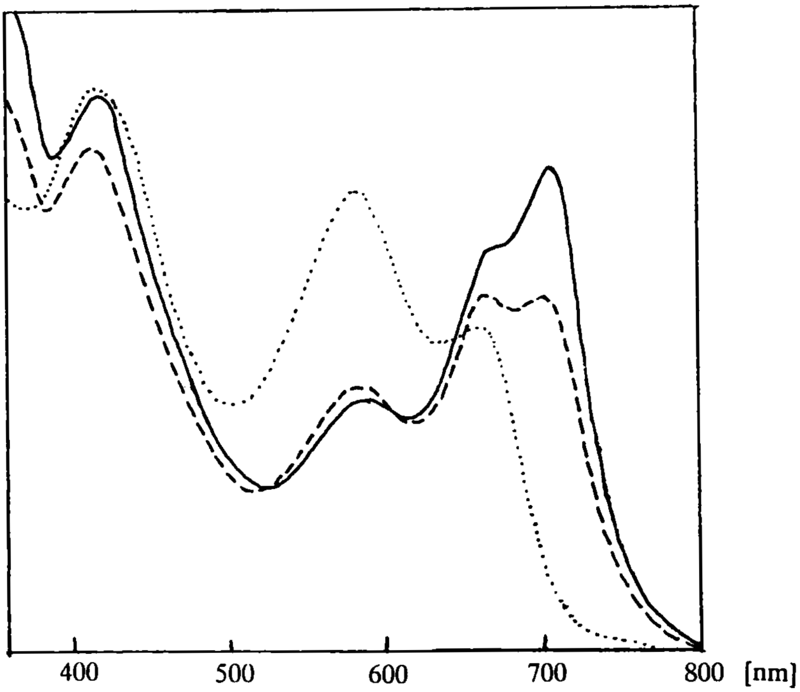


FIGURE 1 Optical absorption spectra of 6a; solvent: CH_2Cl_2, λ_{max} in [nm]; concentration a___> b_ _ _> c ....

TABLE 1 UV/VIS data for the phthalocyanines 5a-11a, solvent: CH_2Cl_2; λ_{max} in [nm]

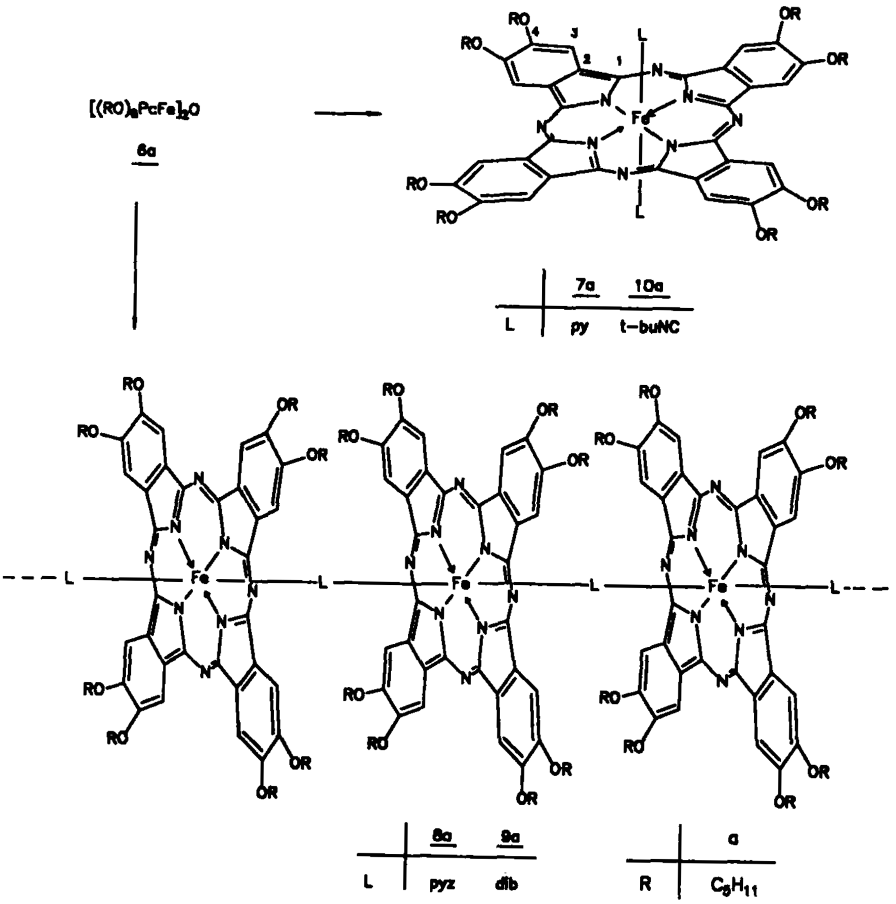
Compound	λ_{max} in [nm]				
$(C_5H_{11}O)_8PcH_2$ (5a)	703	665	640 (sh)	600	420
$[(C_5H_{11}O)_8PcFe]_2O$ (6a-c)	706	666 (sh)	586	414	
$(C_5H_{11}O)_8PcFe(py)_2$ (7a)	655	630 (sh)	595 (sh)	415	332
$[(C_5H_{11}O)_8PcFe(dib)]_n$ (9a)	684	612 (sh)	462 (sh)	404 (sh)	
$(C_5H_{11}O)_8PcFe(t\text{-}buNC)_2$ (10a)	657	601	342		
$(C_5H_{11}O)_8PcNi$ (11a)	675	620 (sh)	386	308 (sh)	290

Mößbauer spectrum is extremely important to decide on the valency of the central metal ion in the solid state.[40] Though the measurements for 6a at room temperature gave poorly resolved spectrum, at 143°K a doublet with parameter values $\delta = 0.18\ mm{\cdot}s^{-1}$ and $\Delta E_Q = 1.211\ mm{\cdot}s^{-1}$ is observed (see Table 2). These values are very close to those reported for (μ-oxo)bis[(phthalocyaninato)iron(III)][34] in the second crystalline form denoted as μ-oxo 2[34,35] (see Table 2). While μ-oxo 1 was tentatively assigned to be in bent structure by the same authors, μ-oxo 2 was assumed to be linear.[35] The bulky substituents on 6a might force a linear conformation in the case of μ-oxo-dimerization.

Bridged Systems

Phthalocyanines having transition metal ion, e.g. iron(II), in the centre are of special interest while they form "shish kebab" type axially coordinated bridged complexes with bidentate coordinating ligands.[3,14] As described above, 6a-c can be easily reduced to axially coordinated 7a-c in the presence of ligands such as pyridine. We have prepared bridged systems with pyz and dib and an axially coordinated monomer with t-buNC (see Scheme 2). While dib and t-buNC can react with 6a in chlorobenzene solutions, we could accomplish the reaction with pyz only in melted excess ligand and in contrast to our expectations the product is a bridged system (not bisaxially coordinated monomer).

SCHEME 2



The identification of isocyanide complexes is best carried out by IR spectroscopy.[14] The bridged compound 9a shows the $N{\equiv}C$ absorption at 2096 cm^{-1} compared to 2130 cm^{-1} of the free ligand. The monomeric compound 10a obtained from monodentate ligand t-buNC shows the same absorption at relatively higher frequency (2145 cm^{-1}) compared to the free ligand (2138 cm^{-1}). This is due to the fact that in case of the model compound 10a, the coordination occurs mostly by σ-donation through carbon atom of t-buNC. The dib complexes, in addition to σ-donation, allow favorable metal-ligand back donation which is greatly stabilized by the aryl ring of dib through π-delocalization and hence confer strong absorption at lower frequency.

The electronic spectra of the axially coordinated compounds show the reduction of metal ion to divalent state by large shift (~20-30 nm) of Q absorptions to shorter wavelength (see Table 1).[37-39] Even though the solubility of octa-alkoxy substituted phthalocyaines in various organic solvents have been extremely increased, it is not sufficient in the case of the bridged systems 8a, 9a to obtain ^{1}H-NMR spectra in solution.

Mößbauer spectroscopy has been proven to be a powerful tool to give an inside in the electronic structure and the coordination state of the central iron in phthalocyanines and porphyrines.[40,41] The Mößbauer parameters, namely the isomer shift (δ) and the quadrupole splitting (ΔE_Q) of hexacoordinated PcFe(II)-systems are very much dependent on the nature of the axial ligand.[42-45] According to the values of the hyperfine parameters δ and ΔE_Q three categories of PcFe(L)$_2$ compounds can be defined. That is PcFeL$_2$ (L = N- or S-donor ligand), δ_{Fe} = 0.25 - 0.29 mm/S, ΔE_Q = 1.77 - 2.34 mm/S;[40,46] PcFeCO(L) (L = N-, S-, O-donor ligand), δ_{Fe} = 0.09 - 0.12 mm/S, ΔE_Q = 1.02 - 1.82 mm/S[45] and PcFeL$_2$ (L = CN-R, CO), δ_{Fe} = 0.06 - 0.15 mm/S, ΔE_Q = 0.58 - 1.48 mm/S.[45,47] These limits enable us to verify the hexacoordinated structure of 8a, 9a, and 10a (see Table 2). The isomer shift δ is a measure of the s-electron density around the iron nucleus. A high s-electron density leads to a decrease of δ. Therefore increasing the σ-donor and the π-acceptor power of the axial ligands will both decrease the isomer shift (δ). The smaller isomer shifts of PcFe(II) complexes coordinated with isocyanide ligands being strong σ-donors and π-acceptors (see Table 2) compared to those of N-donor ligand complexes like 9a are therefore easily explainable.

TABLE 2 ^{57}Fe-Mößbauer data for iron phthalocyanines

Compound	T [K]	δ [mm·s^{-1}]	ΔE_Q [mm·s^{-1}]	Ref.
(PcFe)$_2$O [μ-oxo (1)]	295	0.26	0.42	34
(PcFe)$_2$O [μ-oxo (2)]	295	0.18	1.04	34
[(C$_5$H$_{11}$O)$_8$PcFe]$_2$O (6a)	143	0.18	1.21	
[PcFe(pyz)]$_n$	298	0.25	2.01	14
[(C$_5$H$_{11}$O)$_8$PcFe(pyz)]$_n$ (8a)	295	0.27	2.26	
[PcFe(dib)]$_n$	295	0.12	0.67	49
[PcFe(me$_4$dib)]$_n$	295	0.14	0.69	43
[(C$_5$H$_{11}$O)$_8$PcFe(dib)]$_n$ (9a)	295	0.09	0.57	
PcFe(t-buNC))$_2$	293	0.16	0.79	43
(C$_5$H$_{11}$O)$_8$PcFe(t-buNC)$_2$ (10a)	295	0.19	0.64	

For $PcFe(L)_2$ complexes (L = N-donor ligand and isocyanide ligand) the principle component of the electric field gradient (EFG) V_{zz} has shown to be positive[41,47] with the asymmetric parameter $\eta \simeq 0$. The positive value of V_{zz} indicate a higher occupation of the 3d-orbitals with x- and y components compared to those with z components in the phthalocyanine system. Therefore coordination with axial ligands lowers ΔE_Q with respect to PcFe by increasing the electron density along the z-axis.[41] Increasing the π-acceptor power of the axial ligand should also lead to an increased quadrupole splitting ΔE_Q due to the decrease of electron density of the iron $3d_{xz}$ and $3d_{yz}$ orbitals. This is in contrast to the experimental observations[45,47] (see Table 2).

In order to explain the smaller ΔE_Q values for the bis(isocyanide) compounds when compared to those with N-donor ligands, Fe-L bond lengths should be taken into account. While the Fe-L bond length was reported to be 204 pm for $PcFe(4\text{-}mepy)_2$,[48] it was 191.1 pm for $1{,}2\text{-}NcFe(c\text{-}HxNC)_2$.[49] For the latter, Fe-C bond was also shorter than the Fe-N bonds in the macrocycle plane. Since such shortening of the axial bonds will increase the electron density near iron along the z-axis, lower ΔE_Q values will be observed for bis(isocyanide) compounds as in the case of $PcFe(CO)_2$.[45]

EXPERIMENTAL SECTION

Instrumentation: IR: Bruker IFS 48. - ^1H-NMR and ^{13}C-NMR: Bruker AC 250 (250 MHz for ^1H, 62.5 MHz for ^{13}C). - MS: Varian MAT 711 (70 eV). - UV/VIS: Perkin Elmer Lambda 5. - ^{57}Fe-Mößbauer: Elscint AME-30, LMTE MCD 301/8k. - Elemental analyses: Carlo-Erba-Elemental-Analyser 1104, 1106.

Materials: Commercially available catechol (1) was purified by recrystallization from toluene. Bromine (Fluka), 1-pentanol (Aldrich), 1-bromopentane (Aldrich), 1-bromooctane (Aldrich), 1-bromododecane (Aldrich) were used without further purification. Dimethylformamide was vacuum destilled from barium oxide before use.

1,2-Dibromo-4,5-bis(pentyloxy)benzene (3a)

$NaOCH_3$ (10.8 g, 0.2 mol) was dissolved in 30 ml of freshly distilled DMF and cooled to room temperature. To this solution 4,5-dibromocatechol (2) (26.8 g, 0.1 mol) was added and stirred for 1 h under a nitrogen atmosphere. 1-Bromopentane (25 ml, 0.2 mol) in 30 ml of dry DMF was added dropwise in 30 min and the mixture

was stirred at 110°C for 3 h. The brown solution was cooled and poured into 600 ml water. The product was extracted with diethyl ether and dried (Na_2SO_4). Evaporation of the solvent gave an oil which was distilled(156°C/$2 \cdot 10^{-2}$ Torr) giving a colorless liquid, which turned into colorless crystals in a few days.
Yield: 36.7 g (90%), m.p. 31°C.
IR (film): ν = 2955, 2932, 2870 (CH_2, CH_3), 1251, 1202 (C-O), 652 cm^{-1} (C-Br).
^{1}H-NMR ($CDCl_3$): δ = 0.87 (t, 6H, CH_3), 1.31 (m, 8H, CH_2), 1.73 (tt, 4H, ß-CH_2), 3.98 (t, 4H, OCH_2), 6.98 ppm (s, 2H, ArH).
^{13}C-NMR ($CDCl_3$): δ = 14.01 (CH_3), 22.42, 28.04, 28.71, 69.67 (CH_2), 114.72 (CBr), 118.20 (C=C), 149.14 ppm (CO).
MS (EI): m/e = 408 (M^+), 338, 268.
Anal. Calcd. for $C_{16}H_{24}O_2Br_2$ (408): C, 47.06; H, 5.88; Br, 39.22. Found: C, 46.55; H, 6.07; Br, 38.90.

1,2-Dibromo-4,5-bis(octyloxy)benzene (3b)

Compound 3b was prepared following the same procedure as described for 3a with 1-bromooctane (38.6 g, 0.2 mol) as the alkylbromide. The crude product was recrystallized from ethanol, giving a white solid.
Yield: 45.9 g (93.3%), m.p. 38°C.
IR (KBr): ν = 2927, 2855 (CH_2, CH_3), 1249, 1202 (C-O), 652 cm^{-1} (C-Br).
^{1}H-NMR ($CDCl_3$): δ = 0.88 (t, 6H, CH_3); 1.28 (b, 20H, CH_2); 1.80 (tt, 4H, ß-CH_2); 3.94 (t, 4H, OCH_2); 7.06 ppm (s, 2H, ArH).
^{13}C-NMR ($CDCl_3$): δ = 14.09 (CH_3), 22.67, 25.95, 28.80, 29.31, 31.81, 69.60 (CH_2), 114.70 (CBr), 118.13 (C=C), 149.10 ppm (CO).
MS (EI): m/e = 492 (M^+), 380, 268.
Anal. Calcd. for $C_{22}H_{36}Br_2O_2$ (492): C, 53.66; H, 7.32; Br, 32.52. Found: C, 53.71; H, 7.57; Br 32.44.

1,2-Dibromo-4,5-bis(dodecyloxy)benzene (3c)

Compound 3c was prepared following the same procedure as described for 3a with 1-bromododecane (49.8 g, 0.2 mol) as the alkylbromide. The crude product was recrystallized from ethanol giving a white solid.
Yield: 48.0 g (79.5%); m.p. 50.9°C.
IR (KBr): ν = 2955, 2918, 2873 (CH_2, CH_3); 1250, 1200 (C-O); 650 cm^{-1} (C-Br).
^{1}H-NMR ($CDCl_3$): δ = 0.88 (t, 6H, CH_3); 1.26 (b, 36H, CH_2); 1.80 (tt, 4H, ß-CH_2); 3.94 (t, 4H, O-CH_2); 7.06 ppm (s, 2H, ArH).

^{13}C-NMR ($CDCl_3$): δ = 14.12 (CH_3), 22.71, 25.96, 29.10, 29.49, 29.68, 30.16, 31.95, 69.71 (CH_2), 114.73 (CBr), 118.21 (C=C), 149.14 ppm (CO).

MS (EI): m/e 604 (M^+), 436, 368.

Anal. Calcd. for $C_{30}H_{52}Br_2O_2$ (604): C, 59.60; H, 8.61; Br, 26.49. Found: C, 58.84; H, 9.17; Br, 26.30.

1,2-Dicyano-4,5-bis(pentyloxy)benzene (4a)

A mixture of 3a (10 g, 25 mmol) and CuCN (6.7 g, 75 mmol) in freshly distilled DMF (60 ml) was stirred under nitrogen for 5 h at 150°C. The resulting green solution was cooled and poured into conc. ammonia solution (600 ml). Air was bubbled through the reaction mixture for 6 h. The precipitate was filtered, washed thoroughly with water until neutral and dried. The product was extracted with methanol for 12 h in a Soxhlet apparatus and after evaporation of the solvent, the pure product was isolated by column chromatography (silica gel, diethyl ether/toluene 1:9) and recrystallized from ethanol as white needles.

Yield: 2.66 g (35.5%); m.p. 123°C.

IR (KBr): ν = 2957, 2935, 2873 (CH_2, CH_3); 2228 ($C\equiv N$), 1292, 1231 cm^{-1} (CO).

^{1}H-NMR ($CDCl_3$): δ = 0.94 (t, 6H, CH_3); 1.43 (b, 8H, CH_2); 1.87 (tt, 4H, ß-CH_2); 4.06 (t, 4H, OCH_2); 7.14 ppm (s, 2H, ArH).

^{13}C-NMR ($CDCl_3$): δ = 13.95 (CH_3), 22.34, 28.04, 28.46, 69.82 (CH_2), 108.52 (C=C), 111.97 (CN, CH), 152.59 ppm (CO).

MS (EI): m/e 300 (M^+), 231, 161.

Anal. Calcd. for $C_{18}H_{24}N_2O_2$ (300): C, 72.0; H, 8.0; N, 9.33. Found: C, 72.35; H, 8.48; N, 9.10.

1,2-Dicyano-4,5-bis(octyloxy)benzene (4b)

Compound 4b was prepared following the same procedure as described for the preparation of 4a starting from 3b (10 g, 20.33 mmol) and CuCN (5.46 g, 61 mmol), the title compound was obtained as white flakes.

Yield: 4.22 g (54.1%); m.p. 107.5°C.

IR (KBr): ν = 2956, 2923, 2852 (CH_2, CH_3), 2229 ($C\equiv N$), 1297, 1228 cm^{-1} (CO).

^{1}H-NMR ($CDCl_3$): δ = 0.94 (t, 6H, CH_3); 1.43 (n, 8H, CH_2); 1.86 (n, 4H, ß-CH_2); 4.05 (t, 4H, OCH_2); 7.12 ppm (s, 2H, ArH).

^{13}C-NMR ($CDCl_3$): δ = 14.09 (CH_3), 22.66, 25.86, 28.76, 29.22 , 31.78, 69.80 (CH_2), 108.45 (C=C), 115.94 (CN, CH), 152.56 ppm (CO).

MS (EI): m/e 384 (M^+), 273, 161.

Anal. Calcd. for $C_{24}H_{36}N_2O_2$ (384): C, 75.0; H, 9.38; N, 7.29. Found: C, 74.89; H, 10.03; N, 7.08.

1,2-Dicyano-4,5-bis(dodecyloxy)benzene (4c)

Compound 4c was prepared following the same procedure as described for the preparation of 4a starting from 3c (15 g, 24.84 mol) and CuCN (6.67 g, 74.5 mmol) the title compound was obtained as white flakes.

Yield: 5.47 g (66.7%); m.p. 102°C.

IR (KBr): ν = 2956, 2921, 2850 (CH_3, CH_2), 2229 ($C\equiv N$), 1298, 1230 cm^{-1} (CO).

^{1}H-NMR ($CDCl_3$): δ = 0.88 (t, 6H, CH_3); 1.27 (m, 8H, CH_2); 1.86 (m, 4H, ß-CH_2); 4.05 (t, 4H, OCH_2); 7.12 ppm (s, 2H, ArH).

^{13}C-NMR ($CDCl_3$): δ = 14.12 (CH_3), 22.70, 25.84, 28.73, 29.26, 29.36, 29.55, 29.67, 31.93, 69.75 (CH_2), 108.40 (C=C), 115.83 (CH), 115.97 (CN), 152.50 ppm (CO).

MS (EI): m/e 496 (M^+), 329, 161.

Anal. Calcd. for $C_{32}H_{52}N_2O_2$ (496): C, 77.42; H, 10.48; N, 5.65. Found: C, 77.64; H, 10.18; N, 5.39.

2,3,9,10,16,17,23,24-Octakis(pentyloxy)phthalocyanine (5a)

1.13 g (3.76 mmol) 4a and 0.1 g TEBAC (0.44 mmol) was added into a solution of Li metal (0.7 g, 100 mmol) in 1-pentanol (20 ml) and the mixture was refluxed under nitrogen for 2 h. After cooling, 100 ml of acetic acid was added and heated at 100°C for 15 min. Then the bulk of the solvent was removed under reduced pressure and the green residue dissolved in 150 ml of dichloromethane. This solution was washed first with HCl solution (10%), then with brine and dried over Na_2SO_4. After evaporating the solvent, the residue was chromatographed (silica gel, toluene/diethyl ether 1:1).

Yield: 0.56 g (49.5%).

IR (KBr): ν = 2958, 2933, 2872, 1385, 1279, 1199, 1101, 1055, 849, 739 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = -3.05 (b, NH), 1.12 (t, 24H, CH_3); 1.66 (b, 32H, CH_2); 2.21 (b, 16H, ß-CH_2), 4.56 (b, 16H, OCH_2), 8.42 ppm (s, 8H, ArH).

^{13}C-NMR ($CDCl_3$): δ = 14.28 (CH_3), 22.88, 28.93, 29.51, 69.52 (CH_2), 104.92 (C-2, C-3), 129.69 (C-1), 151.52 ppm (C-4).

UV/VIS (CH_2Cl_2): λ = 703, 665, 640 (sh), 600, 420 nm.

MS (FD): m/e 1202 (M^+).

Anal. Calcd. for $C_{72}H_{98}O_8N_8$ (1202): C, 71.88; H, 8.15; N, 9.32. Found: C, 71.62; H, 7.69; N, 9.04.

(μ-Oxo)bis[2,3,9,10,16,17,23,24-octakis(pentyloxy)phthalocyaninatoiron(III)] (6a)

Lithium metal (0.35 g, 50.88 mmol) was dissolved in pentanol (15 mol) by heating the mixture at 100°C under nitrogen. The solution was then cooled, 4a (1.57 g, 5.23 mmol) and TEBAC (0.1 g, 0.44mmol) in pentanol (10 ml) was added and the mixture was refluxed for 2 h. After cooling, iron(II) acetate (1.96 g, 11.32 mmol) in pentanol (15 ml) was added and refluxed further 4 h under nitrogen. The cooled solution was poured into methanol/water 3:1 (100 ml) and the precipitate was centrifugated, dried and dissolved in dichloromethane. The insoluble parts were separated by filtration and then the solvent was evaporated. Further purification was done by column chromatography [silica gel, diethyl ether/toluene (1:1)] giving a green product.

Yield: 0.45 g (27.3%).

IR (nujol) ν = 1282, 1201, 1106, 1059, 1026, 802, 743 cm^{-1}.

UV/VIS (CH_2Cl_2):λ = 706, 666 (sh), 586, 414 nm.

MS (FD): m/e = 1256 (M^+ for$(C_5H_{11}O)_8$PcFe).

Anal. Calcd. for $C_{144}H_{192}N_{16}O_{17}Fe_2$ (2528): C, 68.35; H, 7.59; N, 8.86. Found: C, 67.82; H, 7.15; N, 8.34.

(μ-Oxo)bis[2,3,9,10,16,17,23,24-octakis(pentyloxy)phthalocyaninatoiron(III)] (6b)

Compound 6b was prepared following the same procedure as described for the preparation of 6a starting from lithium (0.38 g, 56.04 mmol), 4b (2.22 g, 5.78 mmol) and iron(II) acetate (2.25 g, 12.91 mmol) the title compound was obtained as a green semisolid.

Yield: 0.75 g (32.6%).

IR (nujol): ν = 1282, 1203, 1106, 1056, 801, 744 cm^{-1}.

UV/VIS (CH_2Cl_2): λ = 706, 666 (sh), 586, 414 nm.

Anal. Calcd. for $C_{192}H_{288}N_{16}O_{17}Fe_2$ (3200): C, 72.0; H, 9.0; N, 7.0. Found: C, 71.46; H, 9.37; N, 6.61.

(μ-Oxo)bis[2,3,9,10,16,17,23,24-octakis(dodecyloxy)phthalocyaninatoiron(III)] (6c)

Compound 6c was prepared following the same procedure as described for the preparation of 6a starting from lithium (0.48 g, 70 mmol), 4c (3.5 g, 7.06 mmol) and iron(II) acetate (1.9 g, 10.87 mmol) the title compound was obtained as green semisolid.

Yield: 1.8 g (49.9%).

IR (nujol): ν = 1281, 1203, 1102, 1056, 805, 743 cm^{-1}.

UV/VIS (CH_2Cl_2): λ = 706, 666 (sh), 586, 414 nm.
Anal. Calcd. for $C_{256}H_{416}N_{16}O_{17}Fe_2$ (4096): C, 75.0; H, 10.15; N, 5.47. Found: C, 75.92; H, 10.64; N, 5.08.

2,3,9,10,16,17,23,24-Octakis(pentyloxy)phthalocyaninatonickel(II) (11a)
Compound 11a was prepared following the same procedure as described for the preparation of 6a starting from lithium (0.42 g, 60 mmol), 4a (1,3 g, 4.33 mmol) and nickel(II) acetatetetrahydrate (1.5 g, 6 mmol) the title compound was obtained as dark green powder.
Yield: 0.45 g (33%).
IR (nujol): ν = 1281, 1203, 1110, 1064, 847, 748 cm^{-1}.
UV/VIS (CH_2Cl_2): λ = 675, 620 (sh), 386, 308 (sh), 290 nm.
^{1}H-NMR ($CDCl_3$): δ = 1.16 (t, 24H, CH_3); 1.66 (m, 16H, C^4H_2); 1,82 (n, 16H, C^3H_2), 2.20 (m, 16H, C^2H_2); 4.45 (t, 16H, -OCH_2); 7.95 ppm (s, 8H, Ar-H).
^{13}C-NMR: δ = 14.28 (CH_3); 22.96, 28.80, 29.63, 69.28 (CH_2); 103.84 (C-2, C-3); 129.92 (C-1); 150.94 (C-4).
Anal. Calcd. for $C_{72}H_{96}N_8O_8Ni$ (1259): C, 68.62; H, 7.63; N, 8.90. Found: C, 68.27; H, 8.07; N, 8.37.

μ-(1,4-Pyrazine)2,3,9,10,16,17,23,24-octakis(pentyloxy)phthalocyaninatoiron(II) (8a)
6a (0.60 g, 0.24 mmol) and pyrazine (2.0 g, 25 mmol) were mixed and melt at 80°C under nitrogen and this mixture was kept at 60°C for 36 h. Then the excess pyrazine was sublimed under high vacuum at 60°C for 24 h. The yield of dark-blue colored product was almost quantitative (0.62 g).
IR (KBr): ν = 2957, 2932, 2872, 1460, 1420, 1349, 1272, 1114, 1102, 1057 cm^{-1}.
UV/VIS (CH_2Cl_2): λ = 676, 612 (sh), 462 (sh), 404 (sh) nm.
Anal. Calcd. for $(C_{76}H_{100}N_{10}O_8Fe)_n$ (1336): C, 68.26; H, 7.48; N, 10.48. Found: C, 69.85; H, 8.31; N, 9.12.

μ-(1,4-Diisocyanobenzene)2,3,9,10,16,17,23,24-octakis(pentyloxy)phthalocyaninato-iron(II) (9a)
A mixture of 6a (0.4 g, 0.16 mmol), 1,4-diisocyanobenzene (0.045 g, 0.35 mmol) and chlorobenzene (3.5 ml) was stirred for 24 h at 65°C under nitrogen. After cooling to room temperature, the solution was poured into methanol/water (3:1) (150 ml), the precipitate was centrifuged, washed with methanol/water (3:1) until the washing solution was colorless to obtain a bluish green powder.

Yield: 0.3 g (68.6%).

IR (nujol): ν = 2928, 2856, 2096 (N≡C), 1505, 1458, 1420, 1379, 1351, 1275, 1201, 1104, 1058, 920, 886, 848, 751, 736 cm^{-1}.

UV/VIS (CH_2Cl_2): λ = 684, 612 (sh), 462 (sh), 404 (sh) nm.

Anal. Calcd. for $[C_{80}H_{100}O_8N_{10}Fe]_n$ ($[1384]_n$): C, 69.36; H, 7.32; N, 10.12. Found: C, 70.08; H, 7.46; N, 9.92.

2,3,9,10,16,17,23,24-Octakis(pentyloxy)phthalocyaninatobis-(t-butylisocyanide)-iron(II) (10a)

Compound 10a was prepared following the same procedure as described for the preparation of 9a starting from 6a (1 g, 0.4 mmol) and tert-butylisocyanide (0.6 g, 7.23 mmol) the title compound was obtained as bluish green powder.

Yield: 0,83 g (73%).

IR (nujol): ν = 2149, 1274, 1203, 1110, 1058, 849, 735 cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = -0,48 (s, 18H, $C(CH_3)_3$); 1,07 (t,24H, CH_3); 1,67 (m, 32H, CH_2); 2,15 (m, 16H, ß-CH_2); 4,59 (t, 16H, O-CH_2); 8,77 ppm (s, 8H, ArH) .

^{13}C-NMR ($CDCl_3$): δ = 14,16 (CH_3); 22,64, 28,54, 29,33, 69,82 (CH_2); 28,81 ($C(\underline{C}H_3)_3$); 54,73 ($\underline{C}(CH)_3)_3$; 105,13 (C-2, C-3); 134,88 (C-1); 146,35 (-N≡C); 150,39 ppm (C-4).

UV/VIS ($CHCl_3$): λ = 657, 601, 342 nm.

Anal. Calcd. for $C_{82}H_{114}N_{10}O_8Fe$ (1922): C, 69.20; H, 8.02; N, 9.85. Found: C, 68.55; H, 7.23; N, 8.93.

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