Synthesis of Nickel Phthalocyanines with One Aldehyde Group and Preparation of a Bisvinylene-Phenylene-Bridged Bisphthalocyanine

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Dedicated to Professor Günther Wulff on the occasion of his 65th birthday

Keywords: Nickel / Phthalocyanines / Aldehydes / Wittig reactions / Nickel tribenzonaphthoporphyrazines / Bisvinylene-phenylene-bridged dimers

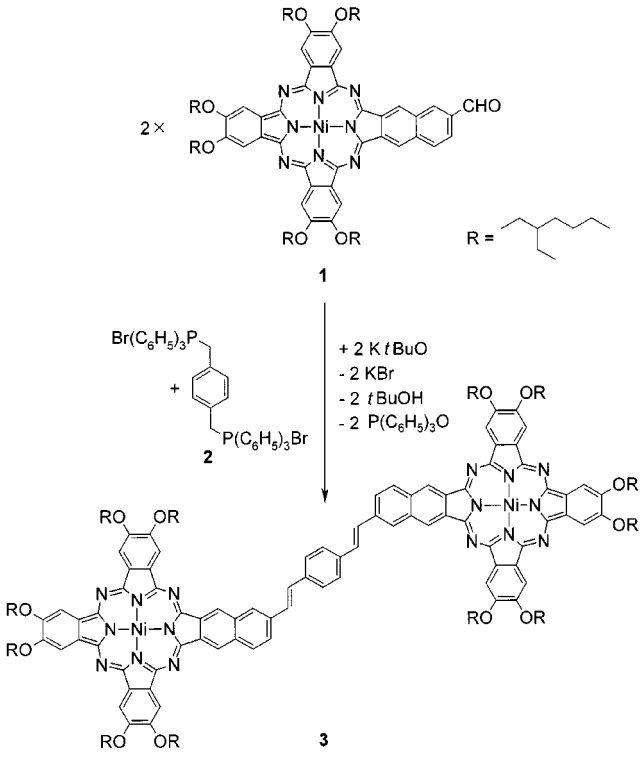
The synthesis and characterization of two soluble, unsymmetrical nickel phthalocyanines with one aldehyde group in the α- (**10b**) and β-position (**10a**), respectively, is reported. The β-functionalized phthalocyanine (Pc) (**10a**) was used in a Wittig reaction to afford the first "real" bisvinylene-phenylene-bridged bisphthalocyanine **11**. The properties of the new Pcs are compared with those of the corresponding tribenzonaphthoporphyrazino (TBNP) nickel analogues **1** and **3**.

Introduction

Because of their special electronic and optical properties and good processibility, substituted phthalocyanines (Pcs) have established themselves in many applied fields.[1] *Un*symmetrical Pcs with only one reactive substituent are desirable or even essential for various applications: for example as Langmuir−Blodgett (L−B) films,[2] as sensitizers for photodynamic cancer therapy (PDT),[3] for the preparation of chemically modified electrodes[4] or as precursors for the synthesis of ladder polymers.[5] There are only a few reports on monofunctionalized Pcs and tribenzonaphthoporphyrazines (TBNPs) bearing one nitro,[6,7] amino,[7−9] sulfo,[7,8] carboxy,[8,10] ester[11] or hydroxy group,[12] due not least to difficulties in preparation and purification. To the best of our knowledge, no phthalocyanine monoaldehyde has yet been described. However, the aldehyde group in particular is able to undergo various chemical reactions (Wittig or Knoevenagel reactions, for example), which should enable Pc aldehydes to act as building blocks for the preparation of new Pc-based materials.

The phthalocyanine monoaldehyde **10a** can be obtained in a convenient statistical cyclocondensation of two different appropriately substituted phthalonitriles. It represents a useful building block for new phthalocyanine derivatives, as shown by the preparation of the first bisvinylene-phenylene-bridged dimer **11** by a Wittig reaction.

In the context of our work on oligomer analogues of poly(*p*-phenylenevinylene) (PPV) and polymers with Pc moieties incorporated into the molecular backbone, we recently reported the synthesis of a substituted tribenzonaphthoporphyrazine with one aldehyde group attached to the naphthalene moiety (**1**, Scheme 1).[13] A suitable unsymmetrical precursor Pc,[5a] was subjected to a Diels−Alder reaction with acrolein (with a reactive isobenzofuran derivative formed in situ) to give the corresponding acrolein adduct. Subsequent dehydration with *p*-toluenesulfonic acid afforded the TBNP aldehyde **1** in good yield.



Scheme 1. Synthesis of the TBNP dimer **3** by a Wittig reaction

The reactivity of this compound was demonstrated in a Wittig reaction, resulting in the bisvinylene-phenylene-bridged dimer **3**.[13] The synthesis of **3** represented a first step towards the preparation of a phthalocyanine-PPV containing Pc subunits, attached either end-on or within the polymer backbone. In the TBNP derivatives **1** and **3**, how-

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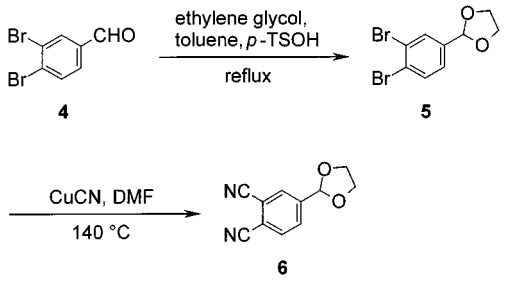
ever, one and two additional aromatic rings, respectively, are annulated within the macrocyclic system as compared to their Pc analogues.

In this paper, we report on the synthesis and characterization of two "real" Pc monoaldehydes with one aldehyde group attached to the macrocycle in the α- (**10b**) and β- (**10a**) position, respectively (Scheme 3). The Pc aldehyde **10a** was treated with *p*-xylylene-bis(triphenylphosphonium bromide) (**2**)[14] to give the first bisvinylene-phenylene-bridged Pc dimer **11** (Scheme 4).

Results and Discussion

For the preparation of the unsymmetrical Pcs, a mixed condensation of two different, appropriately substituted phthalonitriles in the presence of a metal salt was applied. For this purpose, the phthalonitriles **6** and **8** (see Scheme 3) were synthesized, bearing one aldehyde group protected as an ethylene acetal or a dimethylhydrazone, respectively. We found that the aldehyde function is unstable to the severe reaction conditions of the phthalocyanine condensation, and so prior protection is necessary. It was therefore necessary first to find a method of preparing suitable phthalonitriles bearing one masked aldehyde group. Reacting 3,4-dibromobenzaldehyde (**4**)[15] with ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid in toluene yielded the dioxolane derivative **5** (Scheme 2).



Scheme 2. Synthesis of the phthalonitrile **6**

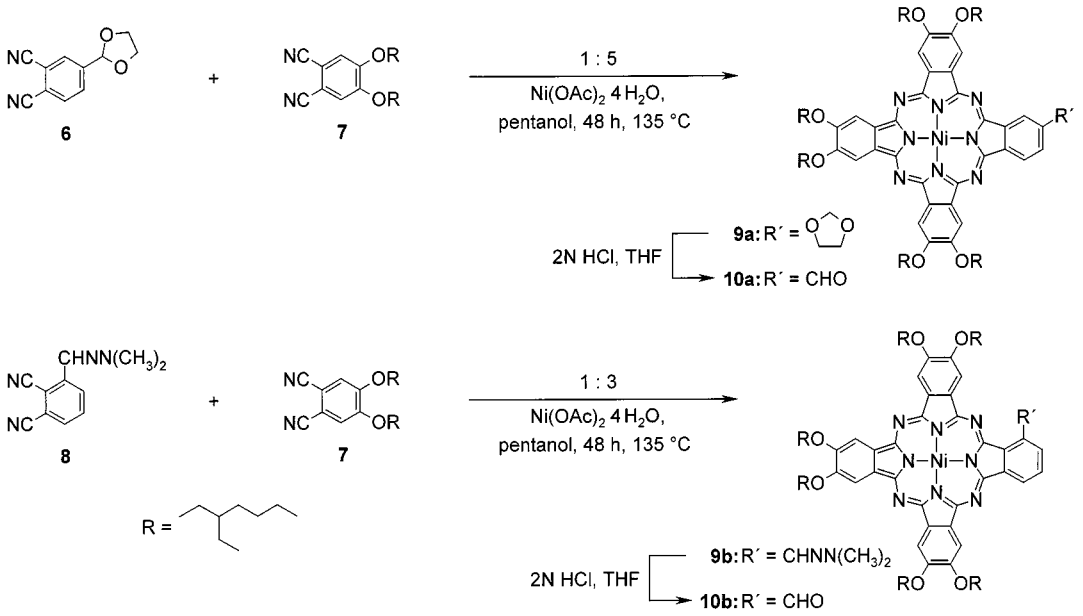
Compound **5** was converted into the desired phthalonitrile **6** by a Rosenmund−von Braun reaction[16] with copper cyanide in dry DMF. The dimethylhydrazone derivative **8** (Scheme 3) has previously been described in the literature[17] and is obtained in a one-pot reaction of commercially available 2-furaldehyde-*N*,*N*-dimethylhydrazone with fumarodinitrile in chloroform. The next step was to combine **6** or **8** in a statistical cyclotetracondensation with a further phthalonitrile bearing solubilizing substituents. We chose 4,5-bis(2′-ethylhexyloxy)benzene-1,2-dinitrile (**7**),[18] since the ethylhexyloxy groups provide for excellent solubility of the resulting Pcs in common organic solvents such as dichloromethane, toluene or THF. The new β-functionalized Pc **9a** was obtained by reaction of a mixture of **6** and **7** with nickel(II) acetate tetrahydrate in pentanol using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst (Scheme 3).

A 1:5 ratio of **6** and **7** was found to be the most appropriate. This method of statistical synthesis afforded a mixture of differently substituted Pcs, from which **9a** could be separated by silica gel column chromatography as the second fraction, with toluene as eluent. The product was further purified by extracting it with hot methanol. In an analogous manner, mixed condensation of **8** and **7** in a 1:3 ratio afforded the α-functionalized Pc **9b**. Compound **9b** was separated and purified by column chromatography (silica gel) with a 1:2 mixture of toluene/cyclohexane and subsequent extraction with hot methanol.

The new unsymmetrical phthalocyanines **9a** and **9b** were identified by their mass and NMR spectra. The [M^+] peaks in the FD mass spectra were found at m/z = 1410.4 and 1408.3, respectively. The dioxolane group of **9a** is evident in the ^{1}H NMR spectrum by a singlet signal at δ = 6.42. The signals of the OCH_2 protons of this group are hidden beneath those of the 2-ethylhexyloxy chains. In the ^{13}C NMR spectrum, the corresponding carbon atoms can be identified by singlets at δ = 104.3 and 65.5. In the ^{1}H NMR spectrum of **9b**, a broad signal at δ = 6.31 originates from the single hydrogen substituent attached to the hydrazone carbon, and a broad singlet signal at δ = 3.02 from the *N*-methyl protons. The signals for the corresponding carbon atoms can be found in the ^{13}C NMR spectrum at δ = 128.5 and 42.8, respectively. All other data are in agreement with the proposed structures.

The monofunctionalized phthalocyanines **9a** and **9b** are precursors for the target molecules **10a** and **10b**. To obtain the latter, the masked aldehyde groups in **9a** and **9b** had to be deprotected, which was achieved by cleavage with 2 N hydrochloric acid in THF at room temperature. After column chromatography (silica gel, toluene) and subsequent extraction with hot methanol, compounds **10a** and **10b** could be isolated as dark-green solids, with excellent solubility in common organic solvents. The Pc monoaldehydes are characterized by their [M^+] peak at m/z = 1368.1 (**10a**) and 1366.4 (**10b**) in the FD mass spectra. In the IR spectra, the carbonyl bands appear at 1693 and 1682 cm^{-1}, respectively. To simplify the interpretation of the NMR spectra of **10a** and **10b** (and also that of **9a** and **9b**), additional H,C-COSY experiments were performed on **10a** and **10b**. The carbonyl groups are characterized by ^{1}H NMR singlet signals at δ = 10.05 (**10a**) and 11.68 (**10b**) and by ^{13}C NMR signals at δ = 191.9 and 192.1, respectively.

In the UV/Vis spectra of Figure 1 and 2, the Pc aldehyde **10a** (689, 664 nm) exhibits a slight bathochromic shift of the Q-band compared with the parent molecule **9a** (670 nm), whereas for Pc aldehyde **10b** (675, 612 nm) this signal is hypsochromically shifted compared with **9b** (681, 619 nm). As expected, the Q-band maxima of the TBNP aldehyde **1** (692, 632 nm) are located at longer wavelengths than those of the Pc derivatives **10a** and **10b**, because of the more extended aromatic system. The difference in the Q-band position between **10a** and **10b** is negligible. In the case of **10a** the band is split, in contrast to **1** and **10b**. In general, such a splitting is observed when going from a Pc with, for example, D_{4h} symmetry to one with D_{2h} symmetry.[19] This



Scheme 3. Synthesis of the unsymmetrical phthalocyanines **9a** and **9b** by statistical cyclotetramerization and formation of the phthalocyanine aldehydes **10a** and **10b**

lowering in symmetry abolishes the degeneracy of the two LUMO levels, leading to a splitting of the Q-band into a Q_x-part (at longer wavelength) and a Q_y-part (at shorter wavelength). One might conclude in the case of **10a** that the nickel atom had perhaps been replaced by two hydrogen atoms in the cleavage reaction with hydrochloric acid, because metal-free Pcs (PcH_2) nearly always exhibit a splitting in their electronic spectra. However, the mass spectrum of **10a** clearly proved that a nickel atom was complexed in the macrocycle. In the ^1H NMR spectrum there is no evidence for highfield-shifted signals caused by inner-ring hydrogens. Nevertheless, since none of the aldehydes **1**, **10a** and **10b** has D_{4h} symmetry it is more surprising that none of their UV/Vis spectra show a split Q-band like that of **10a**. The reasons for these differences remain unclear.

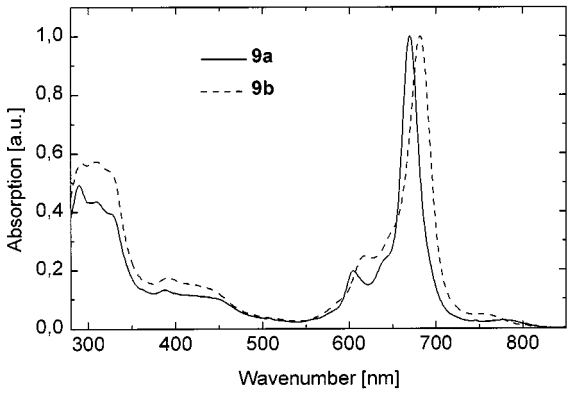


Figure 1. UV/Vis spectra of **9a** and **9b** (in CH_2Cl_2 solution)

Since the preparation of **3** had demonstrated the suitability of this route for the synthesis of bisvinylene-phenylene-bridged TBNP dimers by a Wittig reaction, the method was also applied to prepare the analogous Pc derivative **11**. For this purpose, compound **10a** was treated with 0.5 equivalents of *p*-xylylene-bis(triphenylphosphonium bromide) (**2**) in dry THF to yield the bisvinylene-phenylene-bridged dimer **11** in 27% yield (Scheme 4).

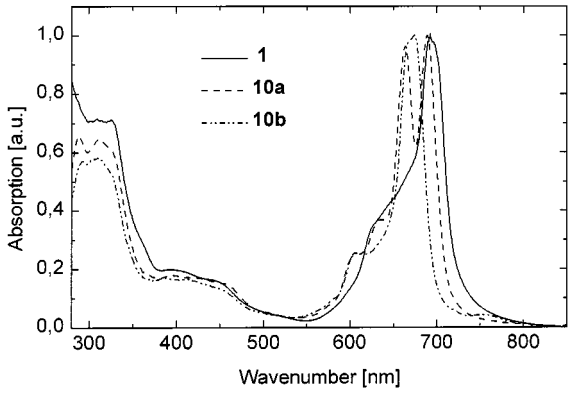
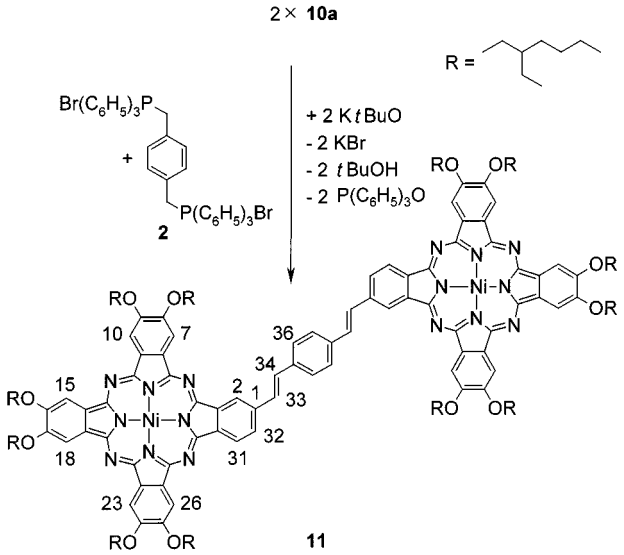


Figure 2. UV/Vis spectra of the Pc aldehydes **10a** and **10b** and the TBNP aldehyde **1** (in CH_2Cl_2 solution)

The moderate yield (for comparison, 50% of **3** was obtained) could be due to **10a** having a lower reactivity than **1**. The [M^+] peak for dimer **11** is found in the FAB mass spectrum at m/z = 2804.7. The IR spectrum shows a weak band at 960 cm^{-1}, which is not observed in the spectrum of **10a** and which we ascribe to the *trans* =C−H deformation of the vinylene double bond. As expected, the carbonyl peak has disappeared. It must be stressed that, as with **3**,[13] compound **11** is also expected to be formed as a mixture of different isomers (*cis-cis*, *cis-trans*, *trans-trans*) in the Wittig reaction. Because of aggregation phenomena, the NMR spectra are difficult to interpret. Nevertheless, all signals found in the ^1H and ^{13}C NMR spectra are consistent with the proposed structure. Although binuclear phthalocyanines linked by alkene bridges[20] are known, as are oligo(phenylenevinylene)-bridged porphyrins,[21] compound **11**



Scheme 4. Synthesis of the Pc dimer **11** by a Wittig reaction

represents the first example of an oligo(phenylenevinylene)-bridged bisphthalocyanine.

The UV/Vis spectra of the two dimers **3** and **11** (in CH_2Cl_2 solution) are displayed in Figure 3.

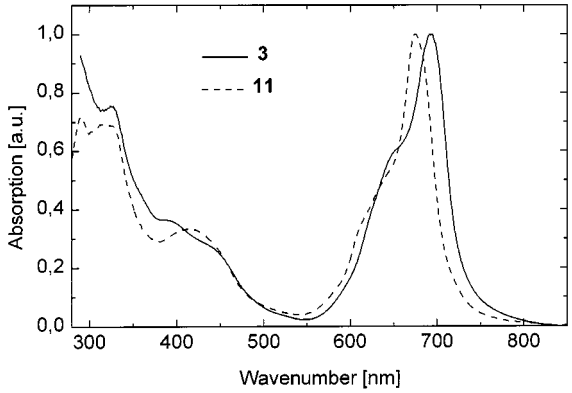


Figure 3. UV/Vis spectra of the dimers **3** and **11** (in CH_2Cl_2 solution)

The absorption bands are broad and show no vibronic fine structure, indicating considerable intermolecular interactions. The Q-band maximum of **3** (693 nm) is bathochromically shifted by 18 nm compared to that of **11** (675 nm). This is reasonable, since the larger conjugated π-system of the TBNP dimer **3** should decrease the HOMO−LUMO gap. A remarkable feature is the increased absorption in the range at around 400 nm, which is especially distinct for the Pc dimer **11**. Absorptions at approximately 380−420 nm are typical for bisstyrylbenzene systems.[22] Therefore, we assume that these bands, observed in the electronic spectra of **3** and **11**, are due to bridging ligand absorptions.

In conclusion, we found the statistical cyclocondensation of two different phthalonitriles to be a suitable and convenient method for the synthesis of unsymmetrical phthalocyanine aldehydes. The phthalonitriles **6** and **8** were successfully combined with **7** to yield the new unsymmetrical phthalocyanines **9a** and **9b**, substituted with a masked aldehyde group in the β- or α-position, respectively. The corresponding free Pc aldehydes **10a** and **10b** could be obtained by cleavage with hydrochloric acid and the first bisvinylene-phenylene-bridged Pc dimer **11** by a Wittig reaction of **10a** with the bis(triphenylphosphonium salt) **2**. A comparison of the Pc derivatives **10a**, **10b** and **11** with their TBNP counterparts **1** and **3** revealed a bathochromic shift of the UV/Vis maxima for the latter due to their more extended conjugated π-system. The phthalocyanine monoaldehydes **10a** and **10b**, as the first examples of this class of compounds, represent useful building blocks for introducing Pc units into various molecules.

Experimental Section

General: Chemicals received from commercial sources (Aldrich and Fluka) were used without further purification. All solvents were dried according to standard procedures. All reactions were performed under dry nitrogen. The melting points are uncorrected. − IR: Bruker IFS 48, KBr pellets. − UV/Vis: Perkin−Elmer Lamda 2, in CH_2Cl_2. − NMR: Bruker AC 250 at 250 MHz (^1H) and 62.9 MHz (^{13}C) in $CDCl_3$ and internally referenced to $CHCl_3$ (^1H: δ = 7.24, ^{13}C: δ = 77.00). For assignments, the labelling is given in Scheme 4. − Elemental analyses were carried out on a VarioEL V. Carbon analyses of some Pcs are somewhat low, but this is not unusual for this class of compounds.

3,4-Dibromobenzaldehyde Ethylene Acetal (5): A mixture of 3,4-dibromobenzaldehyde (**4**)[15] (30.0 g, 0.11 mol), ethylene glycol (7.5 mL, 0.14 mol) and a catalytic amount of *p*-toluenesulfonic acid in toluene (250 mL) was stirred under reflux until the Dean−Stark water separation was complete. After cooling, the solution was washed repeatedly with water. The organic phase was separated, dried with $CaCl_2$, and the solvent was evaporated in vacuo. Purification by column chromatography (silica gel, acetone/*n*-hexane 1:1) and recrystallization from *n*-hexane afforded 30.9 g (88%) of **5** as colorless crystals, m.p. 59−60 °C. − IR (KBr): $\tilde{\nu}$ = 3092 cm^{-1}, 2957, 2880, 1468, 1435, 1414, 1385, 1354, 1267, 1215, 1111, 1092 (COC), 1013, 982, 968, 959, 943, 878, 862, 824 (CBr), 729. − ^1H NMR ([D$_6$]acetone): δ = 3.94−4.13 (m, 4 H, OCH_2 dioxolane), 5.74 (s, 1 H, C*H* dioxolane), 7.38 (dd, *J* = 8.27 Hz, *J* = 2.04 Hz, 1 H, 6-H), 7.74 (d, *J* = 8.38 Hz, 1 H, 5-H), 7.77 (d, *J* = 1.93 Hz, 1 H, 2-H). − ^{13}C NMR ([D$_6$]acetone): δ = 66.0 (O*C*H$_2$ dioxolane), 102.6 (*C*H dioxolane), 124.8 (C-3), 125.4 (C-4), 128.2 (C-6), 132.6 (C-2), 134.6 (C-5), 141.3 (C-1). − MS (EI, 70 eV): *m*/*z* (%) = 306.7 (88) [M^+, isotopic pattern], 262.7 (31) [$M^+ - OC_2H_4$], 228.8 (52) [M^+ − Br], 184.9 (19) [$M^+ - Br - OC_2H_4$]. − $C_9H_8Br_2O_2$ (308.0): calcd. C 35.10, H 2.62, Br 51.89; found C 35.23, H 2.58, Br 51.98.

3,4-Dicyanobenzaldehyde Ethylene Acetal (6): A mixture of **5** (9.46 g, 31 mmol) and copper cyanide (8.25 g, 93 mmol) in dry DMF (100 mL) was stirred for 2−4 h at 150 °C under nitrogen until the reaction was complete (TLC monitoring). The green reaction mixture was then cooled to room temp., poured into concentrated aqueous ammonia (800 mL), and air was bubbled through overnight. The precipitate was filtered, washed thoroughly with water, dried in vacuo and extracted with methanol in a Soxhlet apparatus for 24 h. Column chromatography (silica gel, CH_2Cl_2) and recrystallization from *n*-hexane gave 1.84 g (30%) of **6** as colorless needles, m.p. 100−101 °C. − IR (KBr): $\tilde{\nu}$ = 3113 cm^{-1}, 3082, 3069, 3045, 2966, 2893, 2853, 2241 (CN), 2232 (CN), 1435, 1369, 1298, 1286, 1204, 1171, 1115 (COC), 1086, 1020, 989, 964, 949,

914, 851, 777, 733. − ^{1}H NMR ([D$_6$]acetone): δ = 4.01−4.16 (m, 4 H, OC*H*$_2$ dioxolane), 5.92 (s, 1 H, C*H* dioxolane), 7.98 (dd, *J* = 8.11 Hz, *J* = 1.70 Hz, 1 H, 6-H), 8.09 (dt, *J* = 1.70 Hz, 1 H, 2-H), 8.09 (d, *J* = 7.75 Hz, 1 H, 5-H). − ^{13}C NMR ([D$_6$]acetone): δ = 66.3 (O*C*H$_2$ dioxolane), 102.1 (*C*H dioxolane), 116.3, 116.3, 116.4, 116.5 (C-3, C-4, *C*N), 132.5 (C-2, C-5), 134.9 (C-6), 146.0 (C-1). − MS (EI, 70 eV): *m*/*z* (%) = 199.1 (100) [M$^+$], 169.1 (30), 155.1 (53) [M$^+$ − OC$_2$H$_4$], 140.0 (19), 128.2 (25) [M$^+$ − CN − OC$_2$H$_4$]. − C$_{11}$H$_8$N$_2$O$_2$ (200.2): calcd. C 65.99, H 4.03, N 13.99; found C 65.67, H 4.09, N 13.84.

PcNi β-Acetal (9a): A mixture of **6** (782 mg, 3.9 mmol), 4,5-bis(2′-ethylhexyloxy)benzene-1,2-dinitrile (**7**)[18] (3.0 g, 7.8 mmol), nickel(II) acetate tetrahydrate (875 mg, 3.5 mmol) and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in pentanol (25 mL) was stirred under nitrogen at 140 °C for 48 h. After cooling, the crude product was precipitated in methanol and separated by column chromatography (silica gel, toluene) to yield the monoacetal as the second fraction. After extraction with hot methanol for further purification, drying in vacuo furnished 830 mg of **9a** as a dark-green solid. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (CH$_3$), 2928 (CH$_2$), 2874 (CH$_3$), 2860 (CH$_2$), 1607, 1531, 1460, 1431, 1387, 1362, 1277, 1217, 1157, 1107, 1065, 1034, 895, 852, 750, 741. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 670 nm, 604, 388, 309, 289. − ^{1}H NMR (CDCl$_3$): δ = 1.01−1.28 (m, 36 H, C*H*$_3$), 1.49−1.73 (m, 48 H, C*H*$_2$), 1.96 (br, 6 H, C*H*), 4.21, 4.31, 4.38, 4.41 (br, 16 H, OC*H*$_2$), 6.42 (s, 1 H, C*H* dioxolane), 7.93 (br, 2 H, 15-H, 18-H), 8.03 (br, 2 H, 10-H, 23-H), 8.27 (br, 3 H, 7-H, 26-H, 32-H), 8.79 (br, 1 H, 31-H), 9.00 (br, 1 H, 2-H). − ^{13}C NMR (CDCl$_3$): δ = 11.5, 11.5, 11.6, 14.2, 14.2, 14.2, 14.3 (*C*H$_3$), 23.2, 23.2, 23.3, 23.3, 24.1, 29.3, 29.5, 29.7, 30.8 (*C*H$_2$), 39.8, 39.9 (*C*H), 65.5 (O*C*H$_2$ dioxolane), 71.8 (O*C*H$_2$), 103.0, 103.3, 103.7 (C-7, C-10, C-15, C-18, C-23, C-26), 104.3 (*C*H dioxolane), 119.6 (C-31), 121.5 (C-2), 126.3 (C-32), 128.8, 129.7, 130.2, 130.6 (C-6, C-11, C-14, C-19, C-22, C-27), 136.1, 136.8 (C-3, C-30), 138.2 (C-1), 144.1, 144.6, 145.3, 145.4, 145.5 (C-4, C-5, C-12, C-13, C-20, C-21, C-28, C-29), 151.9 (C-8, C-9, C-16, C-17, C-24, C-25). − MS (FD): *m*/*z* (%) = 1410.4 (100) [M$^+$]. − C$_{83}$H$_{116}$N$_8$NiO$_8$ (1413): calcd. C 70.57, H 8.28, N 7.93; found 69.54, H 8.48, N 8.00.

PcNi α-Hydrazone (9b): A mixture of 2,3-dicyanobenzaldehyde *N*,*N*-dimethylhydrazone (**8**)[17] (200 mg, 1.0 mmol), 4,5-bis(2′-ethylhexyloxy)benzene-1,2-dinitrile (**7**)[18] (1.16 g, 3.0 mmol), nickel(II) acetate tetrahydrate (300 mg, 1.2 mmol) and a catalytic amount of DBU in pentanol (10 mL) was stirred under nitrogen at 135 °C for 48 h. After cooling, the raw product was precipitated in methanol and separated by column chromatography (silica gel, toluene/cyclohexane 2:1) to yield the mono-*N*,*N*-dimethylhydrazone as the second fraction. After extraction with hot methanol for further purification, drying in vacuo furnished 320 mg of **9b** as a dark-green solid. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (CH$_3$), 2928 (CH$_2$), 2874 (CH$_3$), 2860 (CH$_2$), 1607, 1531, 1460, 1433, 1391, 1362, 1279, 1204, 1180, 1171, 1109, 1067, 1049, 1036, 976, 916, 895, 852, 802, 748. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 682 nm, 617, 390, 309, 302, 293. − ^{1}H NMR (CDCl$_3$): δ = 0.87−1.32 (m, 36 H, C*H*$_3$), 1.57−1.88 (m, 48 H, C*H*$_2$), 2.15−2.17 (m, 6 H, C*H*), 3.02 (s, 6 H, NC*H*$_3$ hydrazone), 3.40, 3.94, 4.31, 4.42, 4.52 (br, 12 H, OC*H*$_2$), 6.31 (br, 1 H, C*H* hydrazone), 7.15 (br, 1 H, 18-H), 7.41 (t, *J* = 6.55 Hz, 1 H, 32-H), 8.00 (br, 1 H, 15-H), 8.03 (br, 1 H, 23-H), 8.09 (d, *J* = 5.80 Hz, 1 H, 1-H), 8.29 (br, 2 H, 10-H, 26-H), 8.39 (br, 2 H, 7-H, 31-H). − ^{13}C NMR (CDCl$_3$): δ = 11.4, 11.6, 11.6, 11.6, 14.1, 14.2, 14.3 (*C*H$_3$), 23.1, 23.2, 23.4, 23.6, 24.0, 24.3, 29.3, 29.4, 29.5, 29.5, 30.4, 30.8, 30.9, 31.0, 31.1, 31.1 (*C*H$_2$), 39.5, 39.7, 39.9, 40.0, 40.0, 40.1 (*C*H), 42.8 (N*C*H$_3$ hydrazone), 70.8, 71.4, 71.8, 72.0 (O*C*H$_2$), 100.9, 102.2, 103.7, 104.1 (C-7, C-10, C-15, C-18, C-23, C-26), 119.2 (C-32), 123.3 (C-1), 127.0 (C-31), 128.5 (*C*H hydrazone), 129.4, 129.9, 130.4, 130.6 (C-6, C-11, C-14, C-19, C-22, C-27), 132.2 (C-30), 136.4 (C-3), 142.0, 142.8, 143.8, 144.8 (C-4, C-5, C-12, C-13, C-20, C-21, C-28, C-29), 150.3, 150.5, 151.9 (C-8, C-9, C-16, C-17, C-24, C-25), 151.6 (C-2). − MS (FD): *m*/*z* (%) = 1408.3 (56) [M$^+$], 1376.3 (41) [M$^+$ − 2 CH$_3$], 1365.3 (100) [M$^+$ − N(CH$_3$)$_2$]. − C$_{83}$H$_{118}$N$_{10}$NiO$_6$ (1411): calcd. C 70.67, H 8.43, N 9.93; found C 69.74, H 8.30, N 9.17.

PcNi β-Aldehyde (10a): Compound **9a** (270 mg, 0.2 mmol) was dissolved in THF (20 mL), and 2 N HCl (10 mL) was added dropwise. After stirring for 5 min. at room temp., the solution was quenched with CH$_2$Cl$_2$ (200 mL). The organic layer was separated, washed with water, dried with sodium sulfate, and the solvent was removed in vacuo. The raw product was purified by flash chromatography (silica gel, toluene) to yield the aldehyde as the first fraction. After extraction with hot methanol for further purification, drying in vacuo furnished 210 mg (80%) of **10a** as a green solid. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (CH$_3$), 2928 (CH$_2$), 2874 (CH$_3$), 1693 (CO), 1614, 1516, 1468, 1435, 1393, 1366, 1283, 1265, 1217, 1173, 1159, 1109, 1096, 1063, 1049, 895, 852, 837, 750. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 689 nm, 664, 633 (sh), 605 (sh), 394, 313, 289. − ^{1}H NMR (CDCl$_3$): δ = 0.85−1.29 (m, 36 H, C*H*$_3$), 1.54−1.85 (m, 48 H, C*H*$_2$), 1.98−2.16 (m, 6 H, C*H*), 3.99, 4.21, 4.42, 4.44 (br, 12 H, OC*H*$_2$), 7.24 (br, 2 H, 15-H, 18-H), 7.73 (br, 3 H, 10-H, 23-H, 32-H), 7.95 (br, 1 H, 31-H), 8.14 (br, 2 H, 7-H, 26-H), 8.26 (br, 1 H, 2-H), 10.05 (s, 1 H, C*H*O). − ^{13}C NMR (CDCl$_3$): δ = 11.6, 11.6, 14.3, 14.3 (*C*H$_3$), 23.3, 24.0, 24.1, 24.2, 29.4, 29.5, 29.7, 30.7, 30.9, 31.0 (*C*H$_2$), 39.7, 39.8, 40.0 (*C*H), 71.6, 71.8, 72.1 (O*C*H$_2$), 102.7 (C-15, C-18), 103.5 (C-10, C-23), 104.6 (C-7, C-26), 120.6 (C-31), 123.2 (C-2), 126.8 (C-32), 128.0, 128.2, 129.0, 129.4, 129.8, 130.6 (C-6, C-11, C-14, C-19, C-22, C-27), 132.9, 133.4 (C-3, C-30), 134.7 (C-1), 138.0, 141.2, 142.5 (C-5, C-12, C-13, C-20, C-21, C-28), 145.6 (C-4, C-29), 151.3, 151.7, 152.1 (C-8, C-9, C-16, C-17, C-24, C-25), 191.9 (*C*HO). − MS (FD): *m*/*z* (%) = 2736.0 (24) [M$^+$, dimer], 2052.2 (11) [M$^+$/M^{2+} dimer], 1368.1 (100) [M$^+$], 1338.0 (9) [M$^+$ − CO], 1255.2 (4) [M$^+$ − C$_8$H$_{17}$]. − C$_{81}$H$_{112}$N$_8$NiO$_7$ (1369): calcd. C 71.09, H 8.25, N 8.19; found C 70.54, H 8.39, N 8.12.

PcNi α-Aldehyde (10b): Compound **9b** (40 mg, 0.03 mmol) was dissolved in THF (15 mL), and 2 N HCl (5 mL) was added dropwise. After stirring for 15 min. at room temp., the solution was quenched with CH$_2$Cl$_2$ (200 mL). The organic layer was separated, washed with water, dried with sodium sulfate, and the solvent was removed in vacuo. The raw product was purified by flash chromatography (silica gel, toluene) to yield the aldehyde as the first fraction. After extraction with hot methanol for further purification, drying in vacuo furnished 26 mg (67%) of **10b** as a green solid. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (CH$_3$), 2930 (CH$_2$), 2874 (CH$_3$), 2860 (CH$_2$), 1682 (CO), 1607, 1529, 1462, 1433, 1379, 1364, 1281, 1229, 1205, 1111, 1065, 1051, 1034, 895, 852, 800, 748. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 675 nm, 610, 412, 386, 312, 293. − ^{1}H NMR (CDCl$_3$): δ = 1.03−1.28 (m, 36 H, C*H*$_3$), 1.55−1.79 (m, 48 H, C*H*$_2$), 2.03−2.15 (m, 6 H, C*H*), 4.02, 4.08, 4.24, 4.31, 4.44, 4.46 (br, 12 H, OC*H*$_2$), 7.08 (br, 1 H, 18-H), 7.40 (t, *J* = 6.88 Hz, 1 H, 32-H), 7.43 (br, 1 H, 15-H), 7.73 (br, 1 H, 23-H), 7.89 (br, 1 H, 10-H), 8.03 (br, 1 H, 26-H), 8.10 (d, *J* = 7.38 Hz, 1 H, 1-H), 8.19 (br, 2 H, 7-H, 31-H), 11.68 (s, 1 H, C*H*O). − ^{13}C NMR (CDCl$_3$): δ = 11.4, 11.6, 11.6, 14.2, 14.3, 14.3 (*C*H$_3$), 23.1, 23.3, 24.1, 24.2, 29.2, 29.4, 29.5, 30.8, 30.9, 31.0 (*C*H$_2$), 39.5, 39.7, 39.9, 39.9, 40.0 (*C*H), 71.4, 71.6, 71.8, 71.9, 72.0 (O*C*H$_2$), 102.6 (C-18), 102.9 (C-15), 103.3 (C-23), 103.7 (C-10), 104.1 (C-26), 104.3 (C-7), 125.5 (C-31), 126.3 (C-1, C-32), 129.0, 129.7, 129.9, 130.4, 130.5, 130.9 (C-6, C-11, C-14, C-19, C-

22, C-27), 133.2 (C-30), 135.6 (C-3), 140.4, 140.9, 142.1, 143.2, 144.4, 145.2, 145.3, 145.7 (C-4, C-5, C-12, C-13, C-20, C-21, C-28, C-29), 151.4, 151.5, 151.6, 151.7, 151.9 (C-8, C-9, C-16, C-17, C-24, C-25), 152.0 (C-2), 192.1 (*C*HO). − MS (FD): *m*/*z* (%) = 1366.4 (100) [M^+]. − $C_{81}H_{112}N_8NiO_7$ (1369): calcd. C 71.09, H 8.25, N 8.19; found C 69.98, H 8.65, N 8.33.

PcNi Dimer (11): Compound **10a** (200 mg, 0.15 mmol) and *p*-xylylene-bis(triphenylphosphonium bromide) (**2**)[14] (54 mg, 0.08 mmol) were dissolved in dry THF (10 mL) under nitrogen. A solution of potassium *tert*-butoxide (22 mg, 0.20 mmol) in dry THF (3 mL) was added dropwise, and the mixture was stirred at room temp. for 24 h. The solvent was evaporated and the raw product purified by flash chromatography (silica gel, CH_2Cl_2/*n*-hexane 2:1). After extraction with hot methanol for further purification, drying in vacuo furnished 57 mg (27%) of **11** as a dark-green solid. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (CH_3), 2928 (CH_2), 2872 (CH_3), 2858 (CH_2), 1607, 1531, 1460, 1431, 1418, 1391, 1362, 1277, 1205, 1157, 1105, 1065, 1034, 960, 897, 854, 750. − UV/Vis (CH_2Cl_2): λ_{max} = 675 nm, 414, 313, 290. − ^{1}H NMR ($CDCl_3$): δ = 1.01, 1.17, 1.25 (br, 72 H, CH_3), 1.50, 1.70 (br, 96 H, CH_2), 1.99 (br, 12 H, C*H*), 4.32 (br, 24 H, OCH_2), 6.82, 7.12 (br, aromatic H), 7.36−8.34 (br, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 11.5, 14.2 (*C*H_3), 23.2, 24.1, 29.4, 30.8 (*C*H_2), 39.8 (*C*H), 71.9 (O*C*H_2), 103.3, 103.6, 103.8, 104.1, 104.1, 104.4 (C-7, C-10, C-15, C-18, C-23, C-26), 121.6 (C-33, C-34), 126.8 (C-36), 127.4 (C-33, C-34), 129.3, 129.5, 130.0, 130.1, 130.4, 131.1 (C-2, C-6, C-11, C-14, C-19, C-22, C-27, C-31, C-32), 134.6 (C-3, C-30), 137.0 (C-1, C-35), 144.0, 144.7, 145.0, 145.4 (C-4, C-5, C-12, C-13, C-20, C-21, C-28, C-29), 151.9 (C-8, C-9, C-16, C-17, C-24, C-25). − MS (FAB): *m*/*z* (%) = 2804.7 (35) [M^+], 2690.1 (24) [$M^+ - C_8H_{17}$], 1734.5 (35), 1456.1 (89). − $C_{170}H_{228}N_{16}Ni_2O_{12}$ (2805): calcd. C 72.79, H 8.19, N 7.99; found C 70.60, H 8.54, N 7.57.

Acknowledgments

We thank the Fonds der Deutschen Forschungsgemeinschaft for financial support.

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Received January 20, 2000
[O00024]