Synthesis and Diels–Alder Reactions of Some New (Phthalocyanine)nickel Complexes

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The octasubstituted (phthalocyanine)nickel complexes **4a**,**b**, soluble in common organic solvents, bearing four dienophilic functionalities were synthesized from the corresponding phthalodinitriles **3a**,**b** and nickel(II) acetate. Reaction of **4a** with tetracyclone **5** led to the phthalocyanine–tetracyclone adduct **6** which is a precursor for an intermediate phthalocyanine **7** containing four isobenzofuran moieties. The capability of **7** to react as tetrakis(diene) was demonstrated by its reaction with naphthoquinone. Furthermore, the unsymmetrical phthalocyanines **13** and **16a**,**b**,**c** containing one dienophilic functionality were synthesized using a statistical approach. Their tetracyclone adducts **17**, **18a**,**b**,**c** can be used for the synthesis of ladder-type phthalocyanine dimers. The dimer **22** was synthesized from **18c** and *p*-benzoquinone via the isobenzofuran intermediate **19** and the benzoquinone adduct **21**. For dehydration experiments the naphthoquinone monoadduct **23** was synthesized from **18c**. Dehydration of **22** and **23** was carried out successfully with *p*-toluenesulfonic acid. The Diels–Alder reactions are discussed with respect to the occurring *exo*/*endo* ratio.

Introduction

We are involved in the synthesis of ladder-type oligomers and polymers consisting of metallomacrocycles (e. g. metallohemiporphyrazines and metallophthalocyanines) as repeating units.[1] Especially conjugated ladder polymers with phthalocyanine (Pc) subunits are expected to show − besides a high thermal and chemical resistance − remarkable properties like nonlinear optical behaviour and low band gaps.[2]

We already reported on the successful synthesis of ladder-type oligomers and polymers starting from hemiporphyrazine (Hp) building blocks,[3] whereby a Diels−Alder strategy[4] was used. Hp intermediates with isobenzofuran moieties (**2**) were generated from convenient precursors (**1**, compare Scheme 1) and used as bis(dienes) in repetitive Diels−Alder (DA) reactions.[3b,5] These diene moieties gave the best results regarding yields and the suppression of side reactions. In this paper, similar Pc intermediates are described.

Results and Discussion

In a previous work, we already reported the synthesis of unsubstituted PcM complexes bearing four diene or dienophilic functionalities (M = H_2, Ni, Zn).[6] Due to the poor solubility of these compounds, DA reactions with e.g. 2,3-dimethylbutadiene proceeded with unsatisfactory conversion rates. Therefore, we now attempted the synthesis of the tetrakis(dienophilic), octaalkoxy-substituted PcNi complexes **4a**,**b** (Scheme 2) showing an enhanced solubility in organic solvents. The reaction of the phthalodinitriles **3a,b**[7] in the presence of nickel(II) acetate and a catalytic amount of DBU in 1-butanol (**3a**) or *n*-hexanol (**3b**) at elevated temperatures furnished the PcNi complexes **4a**,**b** after several hours (24−36 h, the nucleophilic alkoxide ions generated from an *n*-alcohol and DBU may attack the phthalodinitriles **3a**,**b** and replace the alkoxy substituents; therefore, we chose the solvents in a way that the replacement led to identical molecules). Chromatographic work up on silica gel gave pure, deep green compounds in isolated yields of ca. 30%. **4a**,**b** proved to be well soluble in e.g. toluene or $CHCl_3$.

Attempts to synthesize similar octaalkyl-substituted PcNi (instead of octaalkoxy-substituted compounds) from 5,8-dialkyl-6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalenes failed, probably due to the bigger steric interactions of the alkyl groups.

PcNi **4a,b** are unequivocally characterized by their NMR and FD-MS spectra (see Experimental Section). In the ^{1}H-NMR spectra of both compounds, only two slightly broadened singlets (at $\delta \approx 6.4$ and 7.3) appear besides the resonances of the aliphatic protons. These singlets are assigned to the two different kinds of protons on the oxo-brigded ring [**4a**: δ = 6.38 (2-H), 7.33 (1-H), **4b**: δ = 6.37 (2-H), 7.32 (1-H)].

Due to the relative orientations of the epoxy bridges, the molecules **4a,b** can exist in four isomeric forms (C_{4v}, C_s, C_{2h}, D_{2d}). The NMR spectra do not allow the distinction between the single isomers. The separation of the mixture (e.g. by HPLC) was not furthermore pursued. Therefore, the relative amounts of the isomers in the mixture are not known.

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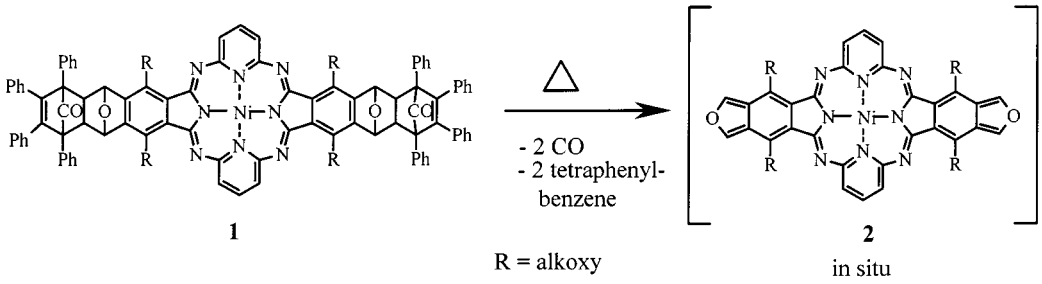
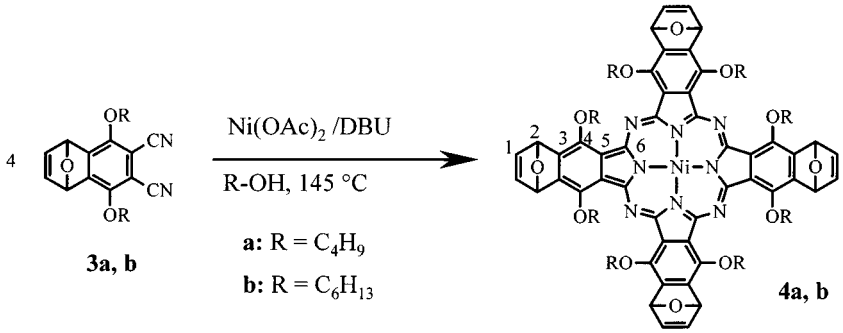


Scheme 1. Generation of the reactive isobenzofuran intermediate



Scheme 2. Synthesis of **4a,b** bearing four dienophilic groups

The UV/Vis spectra of the compounds **4a,b** (recorded from $CHCl_3$ solutions) do not show a remarkable influence of the side-chain length on the wavelength values of the electronic transitions. The $Q_{0\text{-}0}$ bands appear at 713 (**4a**) and 714 nm (**4b**), respectively. The $Q_{0\text{-}0}$ transition of the corresponding unsubstituted compound, namely [2,5,11,14,20,23,29,32-octahydro-2,5:11,14:20,23:29,32-tetraepoxynaphthalocyaninato]nickel(II) is found at 668 nm.[6] As expected, the introduction of eight auxochromic alkoxy substituents leads to a bathochromic shift of the Q band of ca. 45 nm. The comparison of the values of **4a,b** with the $Q_{0\text{-}0}$ transitions found for [1,4,8,11,15,18,22,25-octaalkoxyphthalocyaninato]nickel(II) complexes (which contain the same π-conjugated system as **4a,b**) shows a significant hypsochromic shift of ca. 30 nm [compare the $Q_{0\text{-}0}$ transition of the 1,4-substituted $(PentO)_8PcNi$ appearing at 742 nm[8]]. This shift seems to be caused by the electronic influence of the four epoxybenzo units attached to the phthalocyanine core.

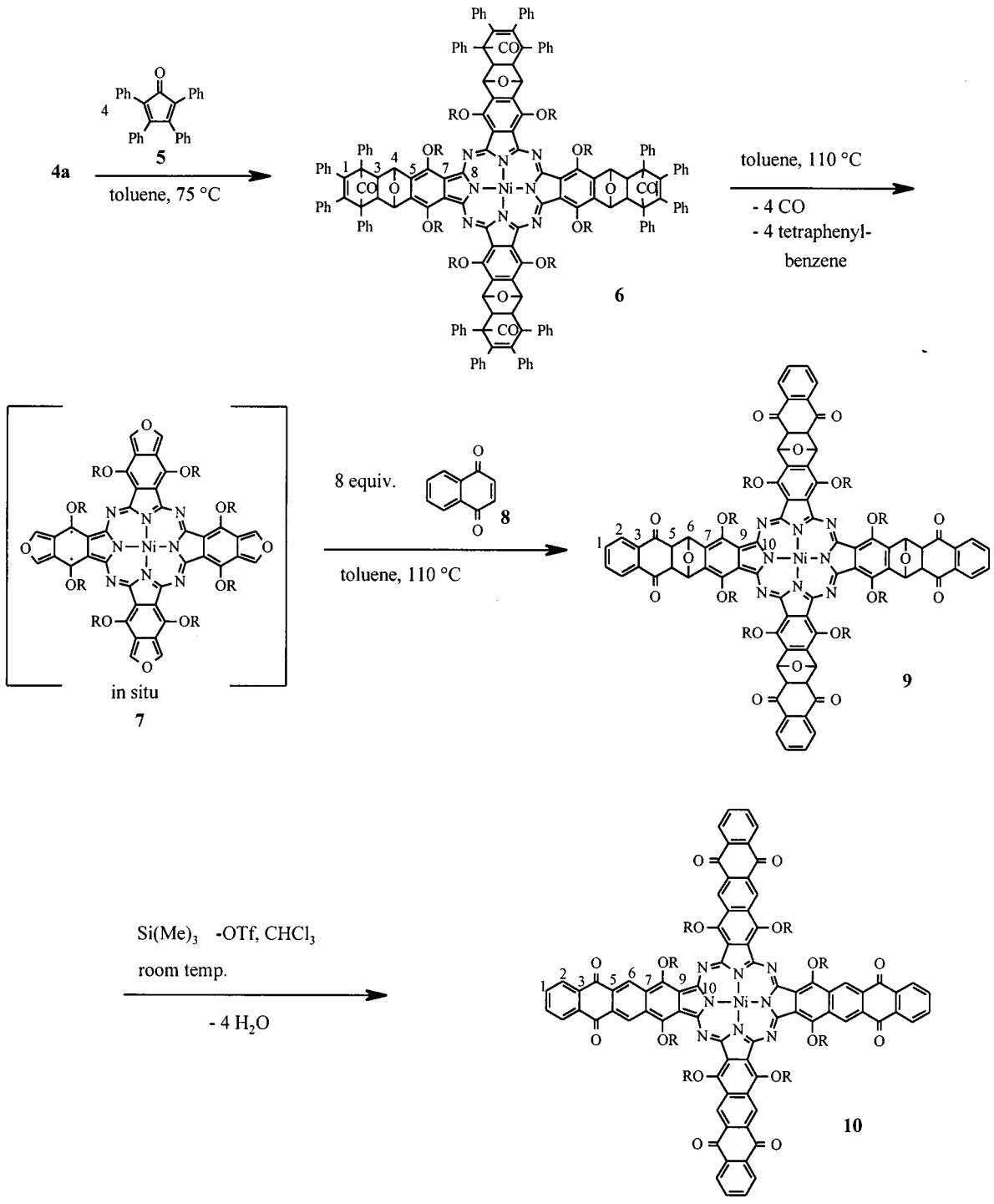
As already mentioned, the unsubstituted [2,5,11,14,20,23,29,32-octahydro-2,5:11,14:20,23:29,32-tetraepoxynaphthalocyaninato]nickel(II) complex underwent a DA reaction when heated with an excess of 2,3-dimethylbutadiene in toluene for several days.[6] However, this reaction proceeded with unsatisfactory conversion rates. The well-soluble compounds **4a,b** should give much better conversions when allowed to react with dienes.

In the next synthetic step, we therefore envisaged the addition of four molecules of 1,2,3,4-tetraphenylcyclopentadienone (tetracyclone, **5**) to the tetrafunctional PcNi **4a** (Scheme 3).[9] This was accomplished in a single reaction by stirring **4a** with a fourfold excess of **5** in toluene at 75°C over 48 h. Chromatographic workup (silica gel; *n*-hexane/ethyl acetate, 6:1) afforded the deep green compound **6** in 66% isolated yield. PcNi **6** is the precursor of the intermediate **7** exhibiting four isobenzofuran moieties.

The ability of **7** to react as a tetrafunctional diene was tested with excess naphthoquinone (**8**) as trapping dienophile (Scheme 3) in the following procedure: The precursor **6** and naphthoquinone (8 equiv.) were stirred in refluxing toluene for 24 h. Subsequent flash chromatography (*n*-hexane/ethyl acetate, 3:2) allowed the separation of 1,2,3,4-tetraphenylbenzene and of unreacted quinone as the first and second fraction. The third, deep green fraction proved to be the desired compound **9**. The PcNi **9** was obtained in a yield of 70%.

In previous work, exclusive *exo* orientation was observed during the DA addition of tetracyclone to 1,4-epoxynaphthalenes.[5a,b] Since the isomeric mixture of **4a** (vide infra) was used as starting material to prepare **6**, the tetracyclone adduct **6** is present as a mixture of at least four isomers. The NMR spectra of **6** are in agreement with exclusive *exo* addition, since two clearly separated resonances should appear for e.g. 3-H in the case of *endo* and *exo* addition. The resonances of 3-H and 4-H appear as signal groups of alleged singlets at $\delta = 3.49-3.66$ and at $6.44-6.50$. The appearance of several singlets arises from the magnetic non-equivalence of 3-H and 4-H even in a single all-*exo* isomer of **6** (with exception of the C_{4v} isomer). This non-equivalence and the presence of at least four isomers also complicates the ^{13}C-NMR spectrum (see Experimental Section).

The completeness of the tetracyclone addition is clearly demonstrated by the integration values obtained from the ^1H-NMR spectrum of **6** which are in excellent agreement with the expected values. Moreover, in the DEPT-135 spectrum of **6**, no signal is found downfield from $\delta = 131$. A



Scheme 3. Synthesis of the dehydrated naphthoquinone adduct **10**

remaining vinylic carbon signal (C-1 in structure **4a**) should appear at $\delta \approx 143$.

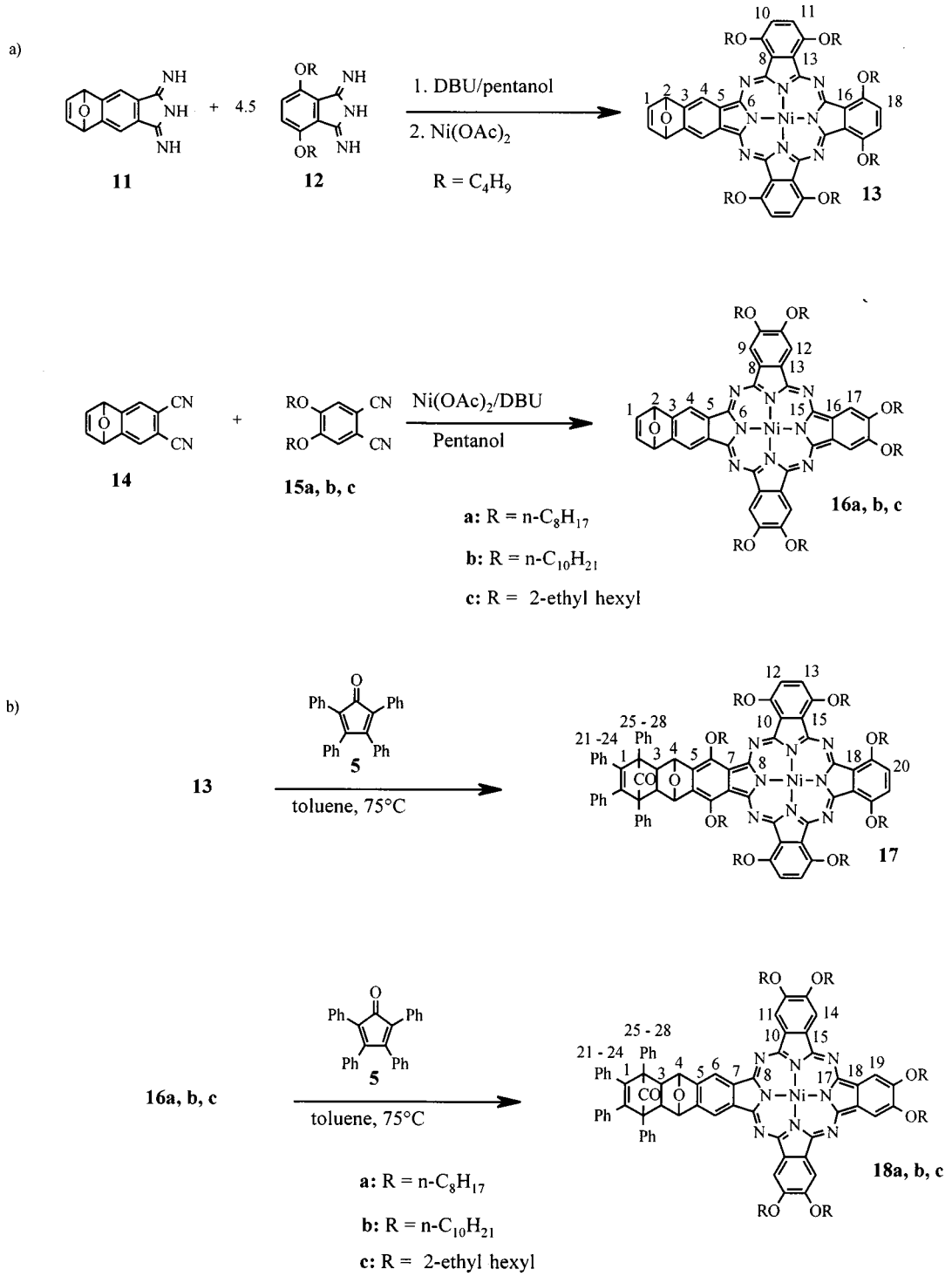
The Q-band transitions in the electronic spectrum of **6** ($CHCl_3$ solution) are bathochromically shifted compared to the "parent" compound **4a**. The $Q_{0\text{-}0}$ transition appears at 724 nm (**4a**: 713 nm, vide infra), thus indicating that the electronic influence of the epoxybenzo units on the Pc core decreases during the DA addition to the dienophilic double bonds in **4a**.

exo and *endo* attack was expected for the DA addition of naphthoquinone (**8**) to the isobenzofuran moieties of **7**.[3c,10] The fact that both orientations are present in compound **9** is reflected by two clearly separated broad signals for 5-H at $\delta = 3.51$ (*exo*) and 4.09 (*endo*) in the corresponding ^{1}H-NMR spectrum. The *exo*/*endo* assignments given in the Experimental Section are in agreement with the chemical shifts and with an additionally performed H,C-COSY experiment. Comparison of the integrals of the mentioned

5-H signals allowed the determination of the overall *exo*/*endo* ratio (*exo*/*endo* ≈ 2.5:1). Similar reactions of mono- and bifunctional hemiporphyrazine intermediates with *p*-benzoquinone proceeded with the same ratio.[3c]

The $Q_{0\text{-}0}$ transition in the electronic spectrum of compound **9** is found at 728 nm. In comparison to the "parent" molecule **4a**, the same tendency (bathochromic shift) as found for the above described DA adduct **6** occurs.

Full dehydration and therefore planarization of PcNi **9** was attempted next to obtain first informations about the behaviour of phthalocyanine–quinone adducts against dehydrating agents. Treatment with *p*-toluenesulfonic acid (toluene, reflux, 1 h) led to complete decomposition of **9**. The use of the Lewis acid trimethylsilyl triflate was more successful. When **9** was allowed to react with $SiMe_3OTf$ in dry $CHCl_3$ (room temp., 36 h), the reddish-brown naphtha-



Scheme 4. Synthesis of the unsymmetrical Pcs **13**, **16a–c** and their tetracyclone adducts **17**, **18a–c**

locyanine (Nc) **10** was formed (Scheme 3). **10** was isolated after quenching of the reaction and chromatographic workup (silica gel, toluene/ethyl acetate 8:1) in 12% yield. The low yield is due to partial decomposition of **10** during the reaction. The acid stability of substituted Ncs is generally lower than the one of Pcs. Overall 1,4-substitution on the Pc core additionally raises the lability to hydrolysing agents by causing a slight deviation from the perfect planarity of the macrocyclic plane. In air, compound **10** slowly decomposes over days.

Complete dehydration is clearly demonstrated by the absence of any residual signals from the starting compound **9** in the ^{1}H-NMR spectrum of **10**. A strongly downfield-shifted broad singlet at $\delta = 9.95$ is observed for 6-H. Characteristic of 1,6,10,15,19,24,28,33-octaalkoxy-substituted NcNi complexes, the $Q_{0\text{-}0}$ transition appears in the near IR region at 855 nm.

As described above, the overall substitution in the 1,4-positions on a Pc core decreases its hydrolytic stability. Therefore, the target molecules **13** and **16a,b,c** (having one DA functionality and a lower number of or even no 1,4-substituents) were chosen next to test DA building blocks with an increased hydrolytic stability (Scheme 4a). The synthesis of such AAAB-Pcs, composed of three subunits A and one subunit B, is possible by a statistical condensation of two differently substituted phthalodinitriles or diiminoisoindolines A and B,[11] whereby the desired compounds are formed besides other combinations. In order to obtain a relatively large amount of the AAAB-Pc, an excess of the starting compound A is generally used.

The 1,4-substituted PcNi **13** was obtained by the reaction of 1 equiv. of 5,8-dihydro-1,3-diimino-5,8-epoxybenz[*f*]isoindoline (**11**)[6] with 4.5 equiv. of 4,7-dibutoxy-1,3-diiminoisoindoline (**12**)[8][12] in refluxing *n*-pentanol and in the presence of catalytic amounts of DBU (72 h). Metallation was achieved by adding 1.2 equiv. of nickel(II) acetate to the reaction mixture and refluxing for further 6 h. The desired product **13** was separated from other Pcs formed by flash chromatography, whereby two subsequent separations with different eluents were performed (first column: $CHCl_3$/ethyl acetate, 2:1, **13** is contained in the 1st fraction; second column: toluene/ethyl acetate, 10:1, the pure blue-green compound **13** is eluted as the 2nd fraction in a yield of 9%).

The preparation of the 2,3-substituted PcNi **16a,b,c** was realized by the condensation reaction of 1 equiv. of 6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalene (**14**)[6] with 8 equiv. of 1,2-dicyano-4,5-dioctyloxybenzene (**15a**), 1,2-dicyano-4,5-didecyloxybenzene (**15b**) and 1,2-dicyano-4,5-bis(2-ethylhexyloxy)benzene (**15c**),[13] respectively in *n*-pentanol at 145°C (18 h, catalytic amounts of DBU). To minimize the separation problems arising from the strong aggregation in a statistical mixture of 2,3-substituted PcNi molecules, we chose an 8-fold excess of the phthalodinitriles **15a,b,c** in order to obtain a product mixture mainly consisting of the AAAA-Pc besides the AAAB-Pcs **16a,b,c**. The blue-green compound **16a,b,c** was separated from other Pcs formed by flash chromatography starting with CH_2Cl_2 and later using CH_2Cl_2/ethyl acetate, 4:1 as the mobile phase (see Experimental Section). We obtained **16a,b** and **c** in average yields of 14%.

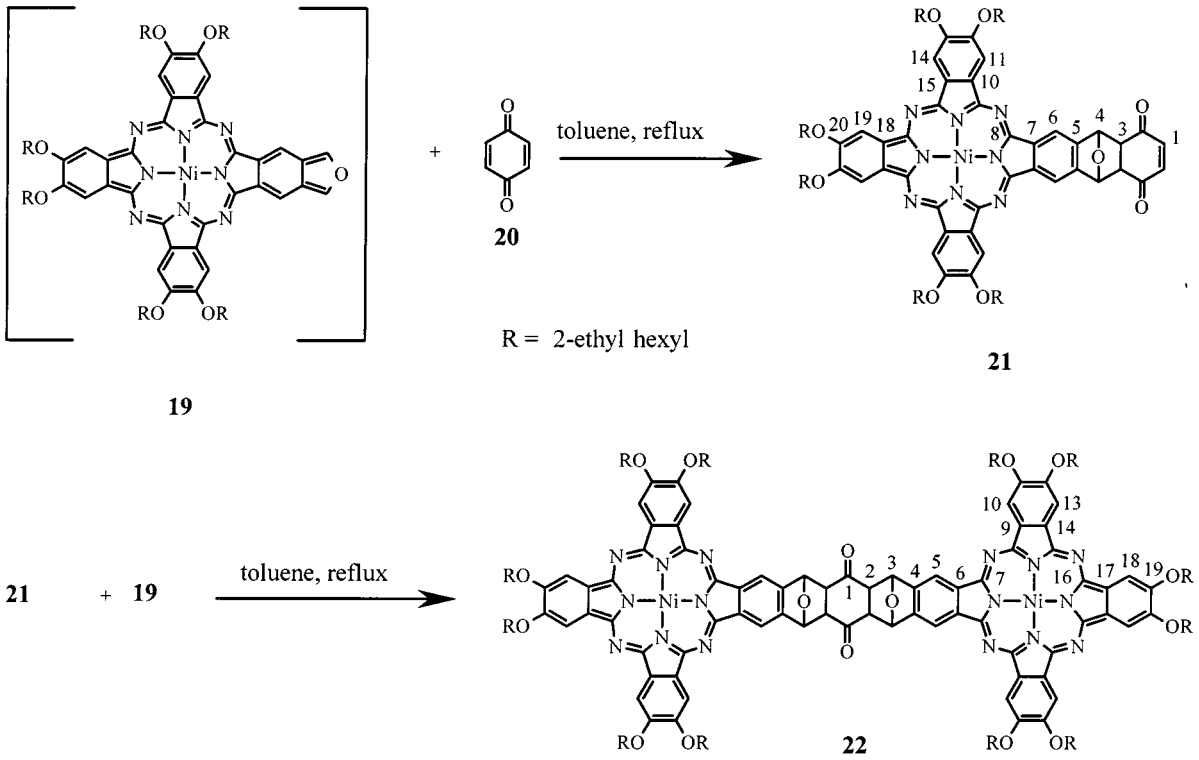
The hydrolytic stability of the PcNi dienophiles **13** and **16a** was tested by treating them with *p*-toluenesulfonic acid (200-fold excess) over a period of 1 h in a toluene solution (room temp.). **13** partially decomposed while **16a** showed no reaction at all (TLC control). The epoxy bridge in **13** and **16a** was not affected under these conditions.

The compounds **13** and **16a,b,c** could be converted to the corresponding PcNi–tetracyclone adducts **17**, **18a,b,c** in moderate to good yields (Scheme 4b). In a typical procedure, the corresponding PcNi (**13**, **16a,b,c**) was stirred with 1 equiv. of tetracyclone in toluene at 75°C (several days). In contrast to a similar addition reaction starting from hemiporphyrazines,[3b,14] the reaction could not be driven to completion within 7 days for **13** and **16a,b**. The isolated yields were 69% (**17**) and 55% (**18a,b**), respectively, whereas the reaction with HpNi complexes proceeded almost quantitatively within 24 h and gave isolated yields of ca. 90%.[3b,14] The hindered reactivity of the PcNi dienophiles **13** and **16a,b** during this DA addition may be due to aggregation phenomena in the corresponding reaction mixture. One possibility to suppress aggregation is the introduction of bulky or branched substituents on the Pc core.[15] Therefore, **16c** was expected to give better yields under identical reaction conditions. As expected, the reaction proceeded almost quantitatively and yields of 90% were obtained.

The purified compounds **13**, **16a,b,c**, **17** and **18a,b,c** were identified on the basis of their NMR and FD- or FAB-MS spectra (see Experimental Section). Characteristic for the epoxybenzo units in **13** and **16a,b,c** are three singlets in the ^{1}H-NMR spectra arising from 1-H, 2-H, and 4-H. In the case of compound **13**, these signals are sharp and appear at $\delta = 6.13$ (2-H), 7.24 (1-H) and 8.93 (4-H), while the stronger aggregation in $CDCl_3$ solutions of **16a,b,c** leads to broadened resonances. For **16a** these resonances appear at $\delta = 6.14$ (2-H), 7.23 (1-H) and 8.20 (4-H). All other NMR data are in agreement with the proposed structures.

By the addition of tetracyclone to the isolated double bonds in **13**, **16a,b,c**, the signals of the vinylic protons 1-H disappear and singlets for the methine protons 3-H are found at $\delta = 3.44$ (**17**) and 3.24 (**18a**), respectively. The appearance of singlets for 3-H, 4-H is in agreement with the expected *exo* orientation of the tetracyclone addition (vide infra). The *exo* orientation causes a dihedral angle between the two mentioned protons which is close to 90°. Therefore, a small coupling constant results.

The DA reaction of the isobenzofuran intermediate **19** (generated from **18c**) with *p*-benzoquinone **20** furnished the benzoquinone monoadduct **21** which (after removal of unreacted **20** by sublimation) was treated (without further purification) with a second equiv. of **19** to form the ladder-type phthalocyanine dimer **22** in a yield of 55%. **18a** was also treated with *p*-benzoquinone according to the same sequence, but the formed dimer could not be identified by spectroscopic means due to heavy aggregation (see below).



Scheme 5. Synthesis of Pc dimer **22**

A small amount of the benzoquinone adduct **21** was isolated and purified by flash chromatography (silica gel; CH_2Cl_2/ethyl acetate, 8:1). As described for compound **9**, *exo* and *endo* orientation is present in compound **21**. The ^{1}H-NMR spectrum shows two clearly separated broad signals for 3-H at δ = 3.24 (*exo*) and 3.88 (*endo*). The *exo*/*endo* assignments given in the Experimental Section are in agreement with the chemical shifts and comparison of the integrals of the mentioned 3-H signals allowed the determination of the overall *exo*/*endo* ratio (*exo*/*endo* ≈ 1:2).

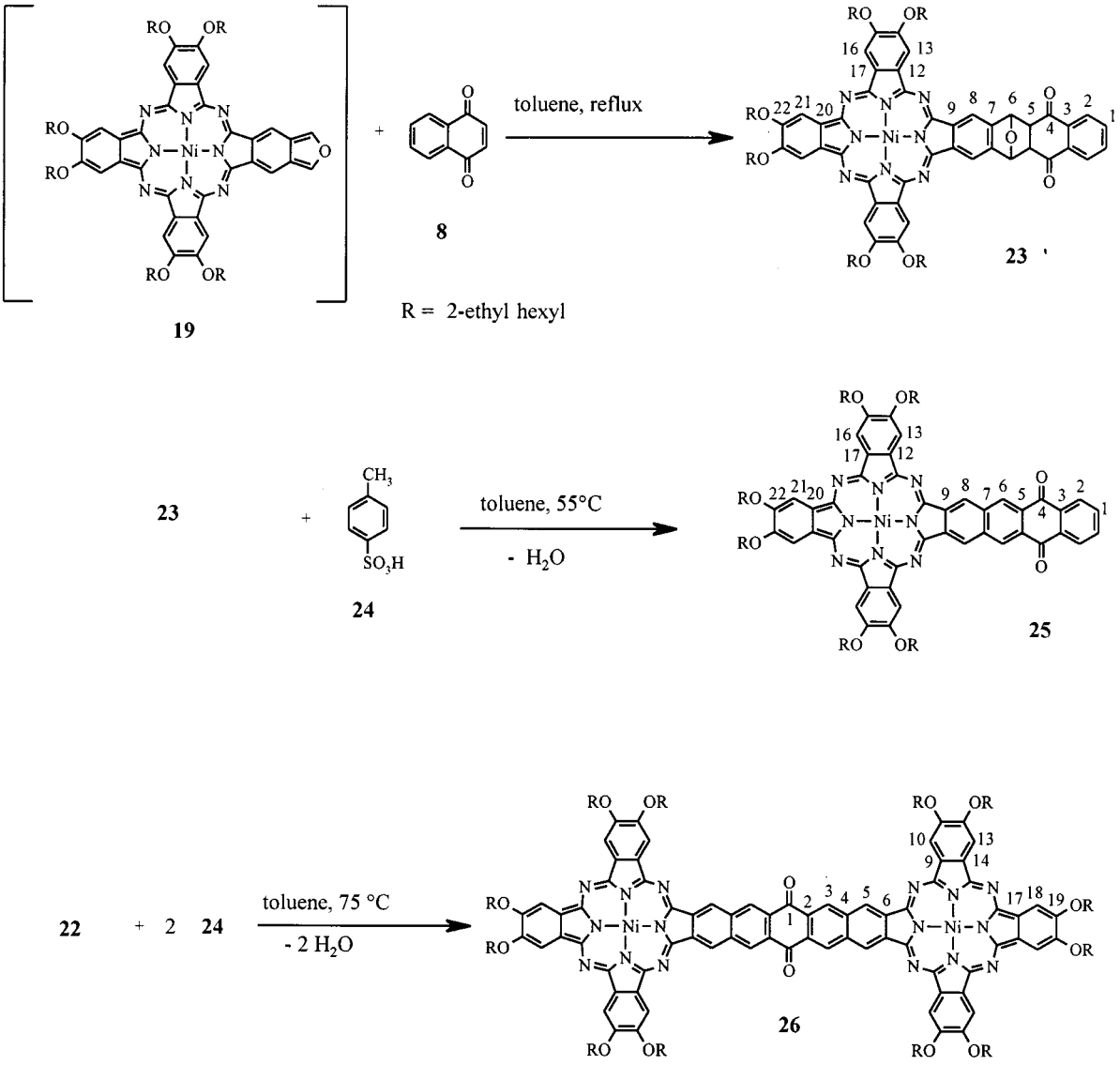
Due to aggregation phenomena and the fact that six isomers can be formed, the full spectroscopic characterization of the ladder-type PcNi dimer **22** was difficult. The resolution of the NMR spectra is only moderate, therefore a discussion of the *exo*/*endo* ratio is not possible. Yet all the signals found in the ^{1}H-NMR and the ^{13}C-NMR spectrum verify the proposed structure. The ^{1}H-NMR spectrum shows broad resonances for the methine proton 2-H at δ = 2.93, 3.48, and 3.74 and at δ = 6.11, 6.36, and 6.58 for 3-H. The corresponding carbon signals appear at δ = 53.7, 55.1, 55.3 (C-2) and at δ = 84.1, 85.1 (C-3), respectively. The IR spectrum shows the carbonyl band at 1701 cm^{-1}. If the DA addition of a second equiv. of isobenzofuran **19** had failed, the carbonyl band should still appear at 1676 cm^{-1} (**21**). The shift to higher wavelengths also indicates that the two carbonyl groups in the molecule are no longer conjugated.

In order to prepare a model compound for dehydration experiments we treated **18c** with a 7-equiv. excess of naphthoquinone (**8**, toluene, 110°C, 24 h,). The naphthoquinone monoadduct **23** was obtained in a yield of 70%. Again, the NMR spectra indicate *exo* and *endo* orientation. Two signals appear for 5-H at δ = 3.42 (*exo*), 4.14 (*endo*) and 6-H at 6.30 (*exo*), 6.38 (*endo*) The *exo* and *endo* isomers are formed in a ratio of 1:2.5 and can be separated by preparative TLC with CH_2Cl_2 as eluent. For further dehydration reactions the isomers were not separated because both isomers form the same product during the dehydration reaction.

Since **16a** proved to be stable against strong proton acids, **23** was expected to undergo acid-promoted dehydration easily to give the corresponding planarized and fully unsaturated naphthoquinone adduct **25** without decomposition.

By treating **23** with a 4-fold excess of *p*-toluenesulfonic acid (**24**) dehydration was carried out successfully and **25** was obtained in a yield of 85% after isolation by flash chromatography with CH_2Cl_2 as eluent. During the whole reaction time no decomposition was observed. Complete dehydration is clearly demonstrated by the absence of any residual signals from the methine proton 5-H in its ^{1}H-NMR spectrum.

A downfield-shifted singlet at δ = 8.17 is observed for 6-H. All NMR data are in agreement with the proposed structure and with an additionally performed H,C-COSY experiment. In the IR spectrum the carbonyl band has been shifted from 1680 cm^{-1} (**23**) to 1672 cm^{-1} in **25**. This shows an increased conjugation of the two carbonyl functions in the molecule. As expected the Q-band transitions in the electronic spectrum of **25** are bathochromically shifted compared to the precursor molecule **23**. The $Q_{0\text{-}0}$ transition appears at 708.5 nm (**23**: 668 nm).



Scheme 6. Synthesis of the dehydrated naphthoquinone adduct **25** and the fully unsaturated Pc dimer **26**

By an identical treatment of **22** with a 6-fold excess of toluenesulfonic acid (**24**) in toluene at 75°C the completely unsaturated dimer **26** was obtained in a yield of 68% after purification by flash chromatography with CH_2Cl_2 as eluent. Compared to the dehydration of **21** slightly higher reaction temperatures and longer reaction times were necessary to obtain optimized yields. During the reaction also the monodehydrated dimer was observed during TLC control. A small amount was isolated and identified by ^{1}H NMR. Further identification was not pursued.

The NMR spectra of **26** show that dehydration was successful although **26** has a strong tendency to form aggregates and the resolution of the ^{1}H-NMR spectrum is only moderate. The methine proton signals of **22** (2-H) have completely vanished and the 3-H signal now appears at δ = 8.1. Moreover, in the DEPT-135 spectrum no signal is found between δ = 40 and 60. A remaining methine carbon signal should appear at $\delta \approx 55$. In the IR spectrum the carbonyl band has been shifted to lower wavelengths (1695 cm^{-1}) compared with **23**. The Q transitions in the electronic spectrum of **26** are bathochromically shifted (730, 681 nm) compared to **22** (659, 628 nm).

Experimental Section

The following compounds were prepared as described in the literature: 5,8-dibutoxy-6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalene (**3a**),[7] 6,7-dicyano-5,8-dihexyloxy-1,4-dihydro-1,4-epoxynaphthalene (**3b**),[7] 5,8-dihydro-1,3-diimino-5,8-epoxybenz[*f*]isoindoline (**11**),[6] 4,7-dibutoxy-1,3-diiminoisoindoline (**12**),[8][12] 6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalene (**14**),[6] 1,2-dicyano-4,5-dioctyloxybenzene (**15a**), 1,2-dicyano-4,5-didecyloxybenzene (**15b**), 1,2-dicyano-4,5-bis(2-ethylhexyloxy)benzene (**15c**).[13] – FT IR: Bruker IFS 48. – UV/Vis: Shimadzu UV-2102 PC. – NMR: Bruker AC 250, Bruker ARX 250 (^{1}H: 250.1 MHz, ^{13}C: 62.9 MHz). – MS: Finnigan ISQ 70; Varian MAT 711A (modified by AMD Intectra). – Elemental analyses were performed with Carlo Erba Elemental Analyzer 1104, 1106. All chemical shifts are referenced to the signals of $CDCl_3$ (except for **16c**). All chromatographic sep-

arations (column chromatography or TLC) with "$CHCl_3$" as eluent or as part of the eluent were performed with $CHCl_3$ containing 1% of EtOH.

General Procedure for the Preparation of the PcNi 4a,b: The corresponding phthalodinitrile (**3a,b**), 1.2 equiv. of $Ni(OAc)_2 \cdot 4\ H_2O$ and a catalytic amount of DBU were suspended in the convenient *n*-alcohol (**3a**: *n*-butanol, **3b**: *n*-hexanol) under nitrogen. The mixture was then heated for several hours (**3a**: reflux, 36 h; **3b**: 145°C, 24 h). After cooling, the solvent was stripped from the butanol solution in a rotatory evaporator. The crude product was purified by column chromatography on silica gel. The hexanol solution was cooled down and poured into a mixture of $MeOH/H_2O$, 2:1. The precipitate was collected by centrifugation and washed several times with MeOH. The crude product was then dried and purified by column chromatography (silica gel). Both deep green solids were furthermore extracted with MeOH and dried in vacuo.

1,6,10,15,19,24,28,33-Octabutoxy-2,5,11,14,20,23,29,32-octahydro-2,5:11,14:20,23:29,32-tetraepoxynaphthalocyaninato]nickel(II) (4a): 550 mg (1.62 mmol) of **3a** and 121 mg (0.49 mmol) of $Ni(OAc)_2 \cdot 4\ H_2O$ were allowed to react in 30 ml of *n*-butanol according to the general procedure (36 h). Column chromatography was performed using *n*-hexane/ethyl acetate, 2:1 as eluent and afforded 172 mg (30%) of **4a**. R_f (SiO_2; toluene/ethyl acetate, 10:1) = 0.50. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2928, 2858, 1591, 1518, 1493, 1466, 1362, 1288, 1246, 1178, 1124, 1111, 1076, 988, 870, 710. − UV/Vis ($CHCl_3$): λ_{max} = 713 nm, 642, 383, 338, 311. − ^1H NMR ($CDCl_3$): δ = 1.01 (t, *J* = 7.3 Hz, 24 H, CH_3), 1.51−1.66 (m, 16 H, CH_2), 1.89−2.02 (m, 16 H, CH_2), 4.72−5.03 (m, 16 H, OCH_2), 6.38 (s, 8 H, 2-H), 7.33 (s, 8 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 19.4 (CH_2), 32.6 (CH_2), 75.4 (OCH_2), 81.3 (C-2), 130.0 (C-5), 143.0 (C-1), 143.1, 144.9, 145.6 (C-3, C-4, C-6). − MS (FD); *m/z* (%): 1412.6 (100) [M^+]. − $C_{80}H_{88}N_8NiO_{12}$ (1412.3): calcd. C 68.04, H 6.28, N 7.93; found C 67.55, H 6.68, N 7.59.

[1,6,10,15,19,24,28,33-Octahexyloxy-2,5,11,14,20,23,29,32-octahydro-2,5:11,14:20,23:29,32-tetraepoxynaphthalocyaninato]-nickel(II) (4b): 107 mg (260 μmol) of **3b** and 20 mg (80 μmol) of $Ni(OAc)_2 \cdot 4\ H_2O$ were allowed to react for 24 h in 20 ml of *n*-hexanol according to the general procedure. Column chromatography was carried out with *n*-hexane/ethyl acetate, 4:1 as the mobile phase. R_f (SiO_2; toluene/ethyl acetate, 10:1) = 0.61. Yield: 34 mg (32%) of **4b**. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2928, 2858, 1591, 1518, 1493, 1466, 1362, 1288, 1246, 1178, 1124, 1111, 1076, 988, 870, 710. − UV/Vis ($CHCl_3$): λ_{max} = 714 nm, 643, 385, 336, 313. − ^1H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 24 H, CH_3), 1.31−1.44 (m, 32 H, 2 × CH_2), 1.48−1.60 (m, 16 H, CH_2), 1.91−2.04 (m, 16 H, CH_2), 4.69−5.00 (m, 16 H, OCH_2), 6.37 (s, 8 H, 2-H), 7.32 (s, 8 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7 (CH_2), 25.8 (CH_2), 30.4 (CH_2), 31.9 (CH_2), 75.7 (OCH_2), 81.3 (C-2), 130.0 (C-5), 143.0 (C-1), 143.1, 144.9, 145.6 (C-3, C-4, C-6). − MS (FD); *m/z* (%): 1636.1 (100) [M^+]. − $C_{96}H_{120}N_8NiO_{12}$ (1636.7): calcd. C 70.45, H 7.39, N 6.85; found C 71.75, H 7.41, N 7.50.

Tetrakis(tetracyclone) Adduct PcNi 6: 117 mg (82.8 μmol) of **4a** and 128 mg (332.9 μmol) of tetracyclone **5** were dissolved in 30 ml of toluene under nitrogen and stirred for 48 h at 75°C. After cooling and evaporation of the solvent, the raw product was purified using column chromatography (silica gel) with *n*-hexane/ethyl acetate, 6:1 (1st fraction: tetracyclone; 2nd fraction: **6**; 3rd fraction: incompletely converted products). After evaporating the solvent from the 2nd fraction, it was extracted several times with *n*-hexane to remove remaining traces of **5**. Drying in vacuo gave 162 mg (66%) of **6** as a deep green powder. R_f (SiO_2; *n*-hexane/ethyl acetate, 3:1) = 0.44. − IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1}, 3028, 2957, 2932, 2872, 1778 (C=O), 1605, 1587, 1497, 1447, 1356, 1340, 1298, 1250, 1223, 1198, 1115, 1074, 1026, 982, 949, 897, 820, 752, 698. − UV/Vis ($CHCl_3$): λ_{max} = 724 nm, 651, 422 (sh), 360, 339, 306. − ^1H NMR ($CDCl_3$): δ = 0.96−1.11 (m, 24 H, CH_3), 1.59−1.88 (m, 16 H, CH_2), 2.05−2.44 (m, 16 H, CH_2), 3.49−3.66 (m, 8 H, 3-H), 4.57−5.57 (m, 16 H, OCH_2), 6.44−6.50 (m, 8 H, 4-H), 7.07 (br., 40 H, 10-H, 11-H, 12-H), 7.37−7.75 (m, 40 H, 14-H, 15-H, 16-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.2 (CH_3), 19.4, 19.5 (CH_2), 32.5, 32.6 (CH_2), 46.9, 47.2 (C-3), 64.6 (C-2), 75.9 (OCH_2), 80.4 (C-4), 126.9, 127.7, 128.4, 129.74, 129.83, 129.95, 130.02 (C-10-12, C-14-16), 130.5 (C-7), 135.2, 135.27, 135.33, 135.6 (C-9, C-13), 138.8, 138.87, 138.90, 139.0 (C-1), 142.1, 142.2, 142.3, 142.5, 144.30, 144.34, 144.46, 144.52, 144.65, 144.74, 145.01, 145.07 (C-5, C-6, C-8), 196.6 (CO). − MS (FAB); *m/z* (%): 2949.0 (18) [M^+], 2538.7 (5) [M^+ − CO − $C_{30}H_{22}$], 2127.5 (5) [M^+ − 2 × CO − 2 × $C_{30}H_{22}$], 1717.9 (12) [M^+ − 3 × CO − 3 × $C_{30}H_{22}$], 1305.9 (90) [M^+ − 4 × CO − 4 × $C_{30}H_{22}$ − 1]. − $C_{196}H_{168}N_8NiO_{16}$ (2950.2): calcd. C 79.80, H 5.74, N 3.80; found C 79.10, H 5.92, N 4.07.

Tetrakis(naphthoquinone) Adduct PcNi 9: 155 mg (52.5 μmol) of **6** and 266 mg (1.68 mmol) of 1,4-naphthoquinone (**8**) were dissolved in 30 ml of toluene (under nitrogen) and heated under reflux for 24 h. The solvent was removed and the residue was separated by flash chromatography (*n*-hexane/ethyl acetate, 3:2), whereby 1,2,3,4-tetraphenylbenzene and unreacted naphthoquinone were eluted in front of the green fraction containing **9**. Drying in vacuo furnished 71 mg (70%) of **9** as a deep-green solid. R_f (SiO_2; *n*-hexane/ethyl acetate, 1:1) = 0.50. − IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1}, 2959, 2934, 2872, 1682 (C=O), 1593, 1495, 1358, 1294, 1267, 1223, 1153, 1113, 989, 949, 750. − UV/Vis ($CHCl_3$): λ_{max} = 728 nm, 655, 425 (sh), 360, 308. − ^1H NMR ($CDCl_3$): δ = 1.02−1.13 [m, *exo*], 1.16−1.29 [m, *endo*] (24 H, CH_3), 1.58−1.95 (m, 16 H, CH_2), 2.07−2.25 (m, 16 H, CH_2), 3.46−3.56 [m, *exo*], 4.09 [br., *endo*] (8 H, 5-H), 4.30−5.50 (m, 16 H, OCH_2), 6.49 (m, 8 H, 6-H), 7.50−7.81 [m, *endo*, 1-H, 2-H], 7.85−7.89 [m, *exo*, 1-H], 8.26−8.30 [m, *exo*, 2-H] (16 H). − ^{13}C NMR ($CDCl_3$): δ = 14.2 (CH_3), 19.5 (CH_2), 32.3, 32.8 (CH_2), 50.8 [*endo*], 52.1 [*exo*] (C-5), 75.4, 75.8 (OCH_2), 82.4 [*endo*], 84.3 [*exo*] (C-6), 125.9 [br., *endo*], 127.5 [*exo*] (C-2), 129.8 [br.] (C-9), 132.6 [br., *endo*], 134.7 [*exo*] (C-1), 134.3, 135.7 (C-3), 139.1, 139.5 [br.] (C-7), 144.8 [br.], 145.0 [br.] (C-8, C-10), 193.4, 194.7 (CO). − MS (FAB); *m/z* (%): 1939.4 (55) [M^+], 1781.5 (35) [M^+ − $C_{10}H_6O_2$], 1623.3 (20) [M^+ − 2 × $C_{10}H_6O_2$], 1464.0 (30) [M^+ − 3 × $C_{10}H_6O_2$ − 1], 1307.4 (70) [M^+ − 4 × $C_{10}H_6O_2$]. − $C_{112}H_{104}N_8NiO_{20}$ (1940.7): calcd. C 69.31, H 5.40, N 5.77; found C 69.62, H 5.53, N 5.84.

Dehydrated Tetrakis(naphthoquinone) Adduct PcNi 10: 62 mg (31.9 μmol) of **9** was dissolved in 10 ml of freshly distilled, dry $CHCl_3$ in a nitrogen-purged vessel. 2 ml (11.1 mmol) of trimethylsilyl triflate was added by means of a syringe. The mixture, which turned immediately to a deep purple colour, was stirred for 36 h at room temp. Then 2 ml of NEt_3 was added before quenching the mixture dropwise with water. The organic layer was separated, washed two times with water, dried with $MgSO_4$ and the solvent was evaporated. Subsequent column chromatography (SiO_2; toluene/ethyl acetate, 8:1; R_f = 0.70) gave after drying in vacuo 7 mg (12%) of **10** as a reddish-brown powder. − IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2932, 2872, 1671 (C=O), 1591, 1433, 1379, 1321, 1275, 1231, 1177, 1117, 978, 719. − UV/Vis (toluene): λ_{max} = 855 nm, 758, 484, 327. − ^1H NMR ($CDCl_3$): δ = 1.05 (t, 24 H, CH_3), 1.65−1.77 (m, 16 H, CH_2), 2.16−2.32 (m, 16 H, CH_2), 5.16 (t, J = 7.0 Hz, 16 H, OCH_2), 7.88−7.92 (m, 8 H, 1-H), 8.51−8.55 (m, 8 H, 2-H), 9.96 (s, br., 8 H, 6-H). − ^{13}C NMR, DEPT-135 ($CDCl_3$): δ = 14.1 (CH_3), 19.5 (CH_2), 32.6 (CH_2), 77.6 (OCH_2), 126.9, 127.7 (C-2, C-6), 134.3 (C-1). − MS (FD); *m/z* (%): 1868.0 (15) [M^+]. − $C_{112}H_{96}N_8NiO_{16}$

(1868.7): calcd. C 71.99, H 5.18, N 6.00; found C 68.08, H 5.27, N 5.58.

[1,4,8,11,15,18-Hexabutoxytribenzo[*b*,*g*,*l*]-23,26-dihydro-23,26-epoxynaphtho[*q*]porphyrazinato]nickel(II) (13): 300 mg (1.42 mmol) of the diiminoisoindoline **11** and 1.85 g (6.39 mmol) of the diiminoisoindoline **12** were suspended in 50 ml of *n*-pentanol (under nitrogen) and a catalytic amount of DBU was added. The mixture was kept under reflux for 72 h. 582 mg (2.34 mmol) of $Ni(OAc)_2 \cdot 4\ H_2O$ was added to the hot reaction mixture and it was heated for further 6 h. The mixture was allowed to cool down and poured into 200 ml of MeOH/H_2O, 3:1, whereby a green solid precipitated. This was collected by centrifugation and washed several times with MeOH. The crude statistical mixture was dried and separated using flash chromatography by doing two subsequent separations. The first column was performed with $CHCl_3$/ethyl acetate, 2:1 as the mobile phase. The desired PcNi **13** was contained in the 1st fraction. The second column was eluted with toluene/ethyl acetate, 10:1, whereby **13** was contained in the second blue-green fraction. After evaporation of the solvent, the residue was extracted several times with MeOH and dried in vacuo. Yield: 189 mg (9%) of **13**. R_f (SiO_2; $CHCl_3$/ethyl acetate, 3:2) = 0.63. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2932, 2870, 1607, 1522, 1502, 1466, 1385, 1312, 1275, 1254, 1232, 1198, 1178, 1107, 1074, 926, 870, 852, 793, 760. − UV/Vis ($CHCl_3$): λ_{max} = 725 nm, 651, 448, 332, 305. − ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, *J* = 7.4 Hz, 12 H, 4 CH_3), 1.30 (t, *J* = 7.3 Hz, 6 H, 2 CH_3), 1.54−1.70 (m, 8 H, 4 CH_2), 2.02−2.22 (m, 12 H, 6 CH_2), 2.29−2.40 (m, 4 H, 2 CH_2), 4.50−4.59 (m, 4 H, 2 OCH_2), 4.69−4.78 (m, 8 H, 4 OCH_2), 6.13 (s, 2 H, 2-H), 7.24 (s, 2 H, 1-H), 7.34 (m [AB], 4 H, 10-H, 11-H), 7.49 (s, 2 H, 18-H), 8.93 (s, 2 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.4 (CH_3), 19.4, 20.0 (CH_2), 31.5, 31.6, 32.4 (CH_2), 69.3, 71.2, 71.4 (OCH_2), 82.7 (C-2), 113.6 (C-4), 116.5, 117.0 (C-10, C-11, C-18), 125.8, 127.0, 127.5 (C-8, C-13, C-16), 136.1 (C-5), 143.0 (C-1), 145.37, 145.44, 145.9, 146.3 (C-3, C-9, C-12, C-17), 149.8, 150.0, 150.2, 150.5 (C-6, C-7, C-14, C-15). − MS (FD); *m*/*z* (%): 1068.3 (100) [M^+]. − $C_{60}H_{66}N_8NiO_7$ (1069.9): calcd. C 67.36, H 6.22, N 10.47; found C 68.51, H 6.60, N 10.66.

General Procedure for the Preparation of the PcNi 16a,b,c: 4.40 mmol of the corresponding phthalodinitrile **15a,b,c** (A), 0.55 mmol of the phthalodinitrile **14** and 1.49 mmol of $Ni(OAc)_2 \cdot 4\ H_2O$ were suspended in 50 ml of *n*-pentanol and a catalytic amount of DBU was added (under nitrogen). The mixture was heated to 145°C and stirred for 18 h. It was allowed to cool down and poured into 200 ml of MeOH. The formed precipitate was isolated using centrifugation and washed several times with MeOH. The raw mixture of PcNi complexes was separated by flash chromatography starting with CH_2Cl_2 as the mobile phase. After complete elution of the 1st fraction (AAAA-PcNi) a mixture of CH_2Cl_2/ethyl acetate, 4:1 was used as eluent to obtain **16a,b,c** as the 2nd fraction. The solvent was removed and the blue-green solid was extracted several times with acetone to achieve further purification. Drying in vacuo furnished average yields of 14% of **16a,b,c**.

[2,3,9,10,16,17-Hexaoctyloxytribenzo[*b*,*g*,*l*]-23,26-dihydro-23,26-epoxynaphtho[*q*]porphyrazinato]nickel(II) (16a): IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2924, 2854, 1609, 1533, 1481, 1466, 1429, 1393, 1362, 1281, 1217, 1109, 849, 748. − UV/Vis ($CHCl_3$): λ_{max} = 671 nm, 604, 400, 328 (sh), 310, 288. − ^{1}H NMR ($CDCl_3$): δ = 1.00 (br., 18 H, CH_3), 1.30 (br., 12 H, 6 CH_2), 1.46 [br.], 1.56 [br.] (36 H, 18 CH_2), 1.81 (br., 12 H, 6 CH_2), 2.17 (br., 12 H, 6 CH_2), 4.37 [br.], 4.49 [br.] (12 H, OCH_2), 6.14 (s, br., 2 H, 2-H), 7.23 (s, br., 2 H, 1-H), 7.57, 7.67, 7.76 (3 s, br., 6 H, 9-H, 12-H, 17-H), 8.20 (s, br., 2 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.2 (CH_3), 22.9 (CH_2), 26.6 (CH_2), 29.6, 30.0 (3 × CH_2), 32.1 (CH_2), 69.3, 69.4 (OCH_2), 82.7 (C-2), 103.7, 103.8, 104.0 (C-9, C-12, C-17), 112.9 (C-4), 129.5, 129.7, 130.1 (C-8, C-13, C-16), 134.2 (C-5), 143.1 [br.], 144.0 [br.] (C-1, C-3, C-7, C-14, C-15), 148.3 (C-6), 150.9, 151.0, 151.1 (C-10, C-11, C-18). − MS (FD); *m*/*z* (%): 1404.1 (50) [M^+], 1291.9 (95) [$M^+ - C_8H_{16}$], 1180.0 (100) [$M^+ - 2 \times C_8H_{16}$]. − $C_{84}H_{114}N_8NiO_7$ (1406.6): calcd. C 71.73, H 8.17, N 7.97; found C 71.42, H 8.35, N 7.39.

[2,3,9,10,16,17-Hexadecyloxytribenzo[*b*,*g*,*l*]-23,26-dihydro-23,26-epoxynaphtho[*q*]porphyrazinato]nickel(II) (16b): IR (KBr) $\tilde{\nu}$ = 2924 cm^{-1}, 2853, 1647, 1607, 1531, 1481, 1466, 1429, 1389, 1360, 1279, 1215, 1140, 1108, 1070, 1059, 847, 750. − UV/Vis (CH_2Cl_2): λ_{max} = 667.5 nm, 611, 394. − ^{1}H NMR ($CDCl_3$): δ = 0.90, 1.29 (br., 36 H, CH_3), 1.43, 1.55 (br., 48 H, CH_2), 2.06 (m, 6 H, CH), 4.09 (br., 12 H, OCH_2), 6.14 (s, br., 2 H, 2-H), 7.16 (s, br., 2 H, 1-H), 7.32 (3 s, br., 6 H, 9-H, 12-H, 17-H), 8.16 (s, br., 2 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 14.11, 14.18 (CH_3), 19.77, 22.69, 22.80, 23.43, 26.00, 26.61, 28.16, 29.37, 29.60, 29.93, 30.02, 31.64, 31.92, 32.09, 34.20 (CH_2), 68.91, 69.34, 69.49 (OCH_2), 82.64 (C-2), 103.75, 103.94, 106.44 (C-9, C-12, C-17), 112.98 (C-4), 129.71, 131.12, 132.53 (C-8, C-13, C-16), 134.35 (C-5), 143.14, 143.44, 144.23 (C-1, C-3, C-7, C-14, C-15), 148.0 (C-6), 150.70, 150.99 (br., C-10, C-11, C-18). − MS (FD); *m*/*z* (%): 1574.4 (100) [M^+], 1433 (65) [$M^+ - C_{10}H_{21}$]. − $C_{96}H_{138}N_8NiO_7$ (1574.9): calcd. C 73.15, H 8.83, N 7.11; found C 70.25, H 8.04, N 6.61.

[2,3,9,10,16,17-Hexakis(2-ethylhexyloxy)tribenzo[*b*,*g*,*l*]-23,26-dihydro-23,26-epoxynaphtho[*q*]porphyrazinato]nickel(II) (16c): IR (KBr) $\tilde{\nu}$ = 2958 cm^{-1}, 2926, 2872, 2858, 1607, 1531, 1460, 1427, 1381, 1360, 1277, 1217, 1197, 1105, 1068, 1058, 852, 750. − UV/Vis (CH_2Cl_2), λ_{max} = 665 nm, 601, 401, 309. − ^{1}H NMR (CD_2Cl_2): δ = 1.05, 1.18 (br., 36 H, CH_3), 1.52, 1.79 (br., 48 H, CH_2), 2.08 (br., 6 H, CH), 4.36 (br., 12 H, OCH_2), 6.24 (s, 2 H, 2-H), 7.36 (s, 2 H, 1-H), 8.23 (3 s, br., 6 H, 9-H, 12-H, 17-H), 8.80 (s, 2 H, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 11.33, 11.54, 14.13, 14.25 (CH_3), 21.55, 23.10, 23.24, 23.94, 24.17, 29.24, 29.40, 29.45, 30.30, 30.68, 30.86 (CH_2), 39.68, 39.86 (CH), 71.79 (OCH_2), 82.69 (C-2), 103.84, 104.26, 104.50 (C-9, C-12, C-17), 113.44 (C-4), 130.48, 130.90 (br., C-8, C13, C-16), 135.06 (C-5), 143.22, 143.58, 144.73, 146.03 (C-1, C-3, C-7, C-14, C-15), 149.30 (C-6), 151.89, 152.11, 152.63 (C-10, C-11, C-18). − MS (FD); *m*/*z* (%): 1405.1 (100), [M^+], 1389 (10), 1293.0 (30) [$M^+ - C_8H_{16}$]. − $C_{84}H_{114}N_8NiO_7$ (1406.6): calcd. C 71.73, H 8.17, N 7.97; found C 70.40, H 7.96, N 7.68.

Mono(tetracyclone) Adduct PcNi 17: 62 mg (57.9 μmol) of **13** and 23 mg (59.8 μmol) of **5** were dissolved in 20 ml of toluene under nitrogen and stirred at 70−75°C (3−6 d; TLC control: SiO_2; CH_2Cl_2/ethyl acetate, 6:1). After cooling and evaporation of the solvent, the mixture was worked up by column chromatography on silica gel (toluene/ethyl acetate, 8:1; 1st fraction: tetracyclone; 2nd fraction: **17**). The solvent was removed from the second fraction, the residue extracted several times with *n*-hexane and then dried in vacuo. Yield: 58 mg (69%) of **17** as a blue-green solid. − R_f (SiO_2; toluene/ethyl acetate, 5:1): 0.71. − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 2955, 2932, 2870, 1778 (C=O), 1605, 1501, 1466, 1447, 1385, 1310, 1273, 1223, 1200, 1090, 1072, 926, 760, 746, 697. − UV/Vis ($CHCl_3$): λ_{max} = 728 nm, 653, 452, 331, 304. − ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, *J* = 7.3 Hz, 12 H, 4 CH_3), 1.36 (t, *J* = 7.4 Hz, 6 H, 2 CH_3), 1.57−1.71 (m, 8 H, 4 CH_2), 2.06−2.32 (m, 12 H, 6 CH_2), 2.44−2.55 (m, 4 H, 2 CH_2), 3.44 (s, 2 H, 3-H), 4.65−4.81 (m, 12 H, OCH_2), 6.25 (s, 2 H, 4-H), 7.06 (br., 10 H, 22-H, 23-H, 24-H), 7.32−7.61 (m, 16 H, 12-H, 13-H, 20-H, 26-H, 27-H, 28-H), 9.24 (s, 2 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.4 (CH_3), 19.4, 19.8 (CH_2), 31.5, 32.2 (CH_2), 47.2 (C-3), 64.6 (C-2), 69.2, 71.3 (OCH_2), 81.8 (C-4), 112.4 (C-6), 114.0, 116.8, 117.1 (C-12, C-13,

C-20), 125.9, 127.1, 127.5 (C-10, C-15, C-18), 126.9, 127.4, 127.6, 128.3, 129.7, 130.1 (C-22-24, C-26-28), 135.3, 135.5 (C-21, C-25), 137.3 (C-7), 138.9 (C-1), 145.2, 145.6, 146.2, 146.6, 147.7 (C-5, C-8, C-11, C-14, C-19), 150.2, 150.3, 150.5 (C-9, C-16, C-17), 196.4 (CO). − MS; *m/z* (%): FD: 1453.3 (100) [M^+]; FAB: 1043.3 (100) [$M^+ - C_{30}H_{22} - CO$]. − $C_{89}H_{86}N_8NiO_8$ (1454.4): calcd. C 73.50, H 5.96, N 7.70; found C 73.28, H 6.13, N 7.83.

General Procedure for the Preparation of the Mono(tetracyclone) Adducts 18a,b,c: 100 μmol of **16a,b,c** and 102 μmol of **5** were dissolved in 30 ml of toluene and stirred at 70−75°C (5−7 d; TLC control: SiO_2, $CHCl_3$). The solvent was evaporated and the residue was separated by flash chromatography (CH_2Cl_2; 1st fraction: tetracyclone; 2nd fraction: **18a,b,c**). Evaporation of the solvent and drying in vacuo gave average yields of 55% of **18a,b** and 90% of **18c** as a blue-green solid.

PcNi 18a: IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2924, 2854, 1780 (C=O), 1607, 1531, 1481, 1464, 1429, 1393, 1362, 1279, 1236, 1202, 1109, 1092, 1065, 851, 750, 694. − UV/Vis ($CHCl_3$): λ_{max} = 672 nm, 605, 393, 327 (sh), 309, 289. − ^{1}H NMR ($CDCl_3$): δ = 0.96 (br., 18 H, CH_3), 1.41 (br., 24 H, 12 CH_2), 1.53 (br., 24 H, 12 CH_2), 1.78 (br., 12 H, 6 CH_2), 2.18 (br., 12 H, 6 CH_2), 3.24 (s, br., 2 H, 3-H), 4.46 [br.], 4.65 (br., 12 H, OCH_2), 6.20 (s, br., 2 H, 4-H), 7.13 (br., 10 H, 22-H, 23-H, 24-H), 7.33−7.60 (m, 10 H, 26-H, 27-H, 28-H), 8.08, 8.22, 8.27 (3 s, br., 6 H, 11-H, 14-H, 19-H), 8.75 (s, br., 2 H, 6-H). − ^{13}C NMR ($CDCl_3$): δ = 14.20, 14.22 (CH_3), 22.82, 22.85 (CH_2), 26.55, 26.59, 26.66 (CH_2), 29.57, 29.63, 29.66, 29.9, 30.0 (3 × CH_2), 32.06, 32.11 (CH_2), 46.9 (C-3), 64.5 (C-2), 69.3, 69.6 (OCH_2), 81.3 (C-4), 104.1, 104.3, 104.5 (C-11, C-14, C-19), 111.4 (C-6), 126.9, 127.4, 127.7, 128.3, 129.7, 130.1, 130.3, 130.5 (C-10, C-15, C-18, C-22-24, C-26-28), 135.36, 135.43 (C-21, C-25), 138.8 (C-1), 142.7, 143.9, 144.9, 145.2, 146.2 (C-5, C-6, C-8, C-9, C-16, C-17), 151.4, 151.6, 151.7 (C-12, C-13, C-20), 196.4 (CO). − MS (FAB); *m/z* (%): 1380.3 (15) [$M^+ - C_{30}H_{22} - CO$]. − $C_{113}H_{134}N_8NiO_8$ (1791.1): calcd. C 75.78, H 7.54, N 6.26; found C 75.67, H 8.04, N 6.39.

PcNi 18b: IR (KBr) $\tilde{\nu}$ = 2963 cm^{-1}, 2853, 1778 (ν_{CO}), 1607, 1481, 1464, 1429, 1391, 1360, 1263, 1213, 1199, 1103, 1022, 851, 800, 748, 694. − UV/Vis (CH_2Cl_2): λ_{max} = 669.5 nm, 605.5,388.5. − ^{1}H NMR ($CDCl_3$) δ = 0.91, 1.22 (br., 36 H, CH_3), 1.34, 1.54, 1.77 (br., 48 H, CH_2), 2.15 (br., 6 H, CH_2), 3.23(s, br., 2 H, 3-H), 4.48 (br., 12 H, OCH_2), 6.20 (s, 2 H, 4-H), 7.22 (br., 10 H, 22-H, 23-H, 24-H), 7.33−7.70 (br., 10 H, 26-H, 27-H, 28-H), 8.05, 8.15, 8.20 (3 s, br., 6 H, 11-H, 14-H, 19-H), 8.71 (s, br., 2 H, 6-H). − ^{13}C NMR ($CDCl_3$) δ = 14.24, 14.36 (CH_3), 22.88, 22.98, 23.75, 26.56, 26.61, 28.92, 29.54, 29.57, 29.69, 29.88, 29.90, 29.95, 30.37, 32.06 (CH_2), 46.96 (C-3), 64.59 (C-2), 68.16, 69.62 (OCH_2), 104.08, 104.35 (br., C-11,C-14, C-19), 111.80 (C-6), 126.92, 127.44, 127.73, 128.40, 129.78, 130.14, 130.54, 130.75 (C-10, C-15, C-18, C-22-24, C-26-28), 135.39, 135.46 (C-21, C-25), 138.82 (C-1), 145.13 (br., C-5, C-6, C-8, C-9, C-16, C-17), 151.43, 151,60, 151.70 (C-12, C-13, C-20), 196.50 (CO). − MS (FD); *m/z* (%): 1548.9 (100) [$M^+ - C_{30}H_{22} - CO$]. − $C_{125}H_{158}N_8NiO_8$ (1959.3): calcd. C 76.61, H 8.13, N 6.26; found C73.89, H7.42, N 4.37.

PcNi 18c: IR (KBr) $\tilde{\nu}$ = 2959 cm^{-1}, 2926, 2856, 1778 (ν_{CO}), 1605, 1481, 1462, 1427, 1391, 1358, 1275, 1263, 1234, 1215, 1202, 1105, 1061, 1026, 852, 802, 750, 696. − UV/Vis (CH_2Cl_2): $\lambda_{max\ =\ 6}$70 nm, 603, 391. − ^{1}H NMR (CD_2Cl_2) δ = 1.00 (br., 18 H, CH_3), 1.05 (br., 18 H, CH_3), 1.18 [br.],1.27 [br.], 1.52 [br.], 1.79 (48 H, CH_2), 2.06 (br., 6 H, CH), 3.39 (s, 2 H, 3-H), 4.35 (br., 12 H OCH_2), 6.33 (s, 2 H, 4-H), 7.20 (br., 10 H, 22-H, 23-H, 24-H), 7.40−7.68 (br., 10 H, 26-H, 27-H, 28-H), 8.07, 8.25, 8.41 (3 s, br., 6 H, 11-H, 14-H, 19-H), 9.12 (s, 2 H, 6-H). − ^{13}C NMR ($CDCl_3$) δ = 11.34, 11.52, 14.10, 14.25 (CH_3), 23.06, 23.24, 23.93, 29.16, 29.38, 30.68, 30.85 (CH_2), 39.63, 39.84 (CH), 47.10 (C-3), 64.61 (C-2), 68.16, 71.72 (OCH_2), 81.56 (C-4), 104.50, 104.57, 104.61 (C-11, C-14, C-19), 112.20 (C-6), 126.87, 127.51, 127.96, 128.01, 128.48, 129.31, 129.79, 130.10, 130.75(C-10, C-15, C-18, C-22-24, C-26-28), 135.37, 135.43,(C-21, C-25), 152.38, 154.47 [br.] (C-12, C-13, C-20), 196.63 (CO). − MS (FAB); *m/z* (%): 1790.5 (10) [M^+], 1380.0 (100) [$M^+ - C_{30}H_{22} - CO$]. − $C_{113}H_{134}N_8NiO_8$ (1791.1): calcd. C 75.78, H 7.54, N 6.26; found C 73.49, H 7.18, N 5.19.

PcNi 22 (Dimer): 90 mg (50.2 μmol) of **18c** and 23 mg (213 μmol) of *p*-benzoquinone (**20**) were dissolved in 30 ml of toluene (under nitrogen) and heated under reflux for 24 h. The solvent was evaporated and unreacted **20** was removed by sublimation (TLC control, CH_2Cl_2). Again 30 ml of toluene and 100 mg (55.2 μmol) of **18c** were added to the crude product **21** and the mixture was heated under reflux for 24 h. The solvent was removed and the residue was separated by flash chromatography starting with CH_2Cl_2 as eluent, whereby 1,2,3,4-tetraphenylbenzene was eluted in front of a green fraction containing unreacted **18c**. After complete elution of the 2nd fraction, CH_2Cl_2/ethyl acetate, 4:1 was used as eluent to obtain **22** as the 3rd fraction. The solvent was removed and the blue-green solid was extracted several times with acetone to achieve further purification. Drying in vacuo furnished 102 mg (55%) of **22**. − IR (KBr) $\tilde{\nu}$ = 2957 cm^{-1}, 2928, 1701, 1653, 1607, 1539, 1522, 1458, 1429, 1389, 1279, 1234, 1205, 1155, 1061, 1030, 1024, 972, 890, 845, 745. − UV/Vis (CH_2Cl_2): λ_{max} = 660 nm, 629, 440 (sh), 392, 288. − ^{1}H NMR ($CDCl_3$) δ = 0.96 (br., 36 H, CH_3), 1.13 (br., 36 H, CH_3), 1.20, 1.28, 1.38, 1.70 (br., 96 H, CH_2), 2.20 (br., 12 H, CH), 2.93, 3.48, 378 (br., 4 H, 2-H), 4.24, 4.32, 4.56, 4.75 (br., 24 H, OCH_2), 6.11, 6.36, 6.58 (br., 4 H, 3-H), 7.63, 7.96, 8.15, 8.24 (br., 12 H, 10-H, 13-H, 18-H), 8.78, 9.31 (br., 4 H, 5-H). − ^{13}C NMR ($CDCl_3$) δ = 10.6, 10.71, 14.2, 14.3, 14.9 (CH_3), 23.2, 24.0, 24.9, 29.4, 29.7, 30.8 (CH_2), 38.4, 38.8, 39.7, 40.4 (CH), 53.7, 55.1, 55.3 (C-2), 70.6, 71.0, 72.0 (OCH_2), 84.1, 85.1 (C-3), 102.5, 103.5, 103.7 103.9, 104.3 (C-10, C13, C-18), 112.3, 112.9 (C-5), 127.7, 129.7, 130.4 (C-6, C-9, C-14, C-17), 136.0, 141.6, 143.3, 143.7, 144.3, 145.0, 145.2, 145.8, (C-4, C-7, C-8, C-15, C-16), 150.6, 151.0 (C-11, C-12, C-19), 205.0 (C-1). − MS (FD); *m/z* (%): 1516.6 (20), 1380.3 (100) [M^+ (**19**)], 1271 (50). − $C_{170}H_{228}N_{16}Ni_2O_{16}$ (2869.1): calcd. C 71.17, H 8.01, N 7.80; found C 68.73, H 7.21, N 7.13.

Mono(*p*-benzoquinone) Adduct PcNi 21: IR (KBr) $\tilde{\nu}$ = 2957 cm^{-1}, 2926, 2856, 1734, 1676, 1653, 1607, 1533, 1481, 1387, 1277, 1221, 1200, 1105, 1061, 898, 857, 750. − UV/Vis (CH_2Cl_2): λ_{max} = 666 nm, 603, 390, 309, 288. − ^{1}H NMR ($CDCl_3$) δ = 0.97, 1.04, 1.11, 1.17 (br., 36 H, CH_3), 1.23, 1.50, 1.80, (br., 48 H, CH_2), 2.03, 2.06 (br., 6 H, CH), 3.24 [br., *exo*], 3.88 [d, br., *endo*] (2 H, 3-H), 4.43 (br., 12 H, OCH_2), 5.84 [br., *endo*], 6.98 [*exo*] (2 H, 1-H), 6.17 [*exo*], 6.28 [*endo*] (2 H, 4-H), 8.40, 8.51, 8.67, (br., 6 H, 11-H, 14-H, 19-H), 8.88, 9.07 (br., 2 H 6-H). − ^{13}C NMR ($CDCl_3$) δ = 11.5, 11.8, 14.2, 14.3 (CH_3), 23.2, 23.3, 24.1, 29.4, 29.7, 30.8, 31.0 (CH_2), 39.8, 40.0 (CH), 49.6 [*endo*], 51.6 [*exo*] (C-3), 71.9 ([br.] OCH_2), 82.9 [*endo*], 85.1 [*exo*] (C-4), 103.8, 104.7 ([br.] C-11, C-14, C-19), 112.2 [*exo*], 113.8 [*endo*] (C-6), 130.2, 131.0 (C-10, C-15, C-18), 135.8 (C-7), 139.4 (C-1), 141.9, 144.2, 145.9, 146.2 (C-5, C-8, C-16, C-17), 151.9, 152.1, 152.3 (12, 13, 20), 196.3 (C-2). − MS (FAB); *m/z* (%): 1488.7 (10) [M^+], 1380.7 (100) [$M^+ - C_6H_4O_2$], 1267.5 (60) [$M^+ - C_6H_4O_2 - C_8H_{17}$]. $C_{88}H_{116}N_8NiO_9$ (1488.6): calcd. C 71.0, H 7.85, N 7.52; found C 68.40, H 7.07, N 6.76.

Mono(naphthoquinone) Adduct PcNi 23: 395 mg (220 μmol) of **18c** and 300 mg (1.9 mmol) of 1,4-naphthoquinone (**8**) were dissolved in 50 ml of toluene (under nitrogen) and heated under reflux for 24 h. The solvent was removed and the residue was separated by

flash chromatography starting with CH_2Cl_2 as the mobile phase. After complete elution of the first two fractions (1,2,3,4-tetraphenylbenzene and unreacted naphthoquinone), a mixture of CH_2Cl_2/ethyl acetate, 4:1 was used as eluent to obtain **23** as the 3rd fraction. Drying in vacuo furnished 260 mg (76%) of **23** as a deep green solid. − IR (KBr) $\tilde{\nu}$ = 2957 cm^{-1}, 2926, 1680, 1605, 1531, 1481, 1460, 1429, 1389, 1381, 1360, 1294, 1277, 1103, 1061, 950, 900, 855, 755. − UV/Vis (CH_2Cl_2): λ_{max} = 668 nm, 603, 390.5, 309.5, 288.5. − ^{1}H NMR ($CDCl_3$) δ = 0.96, 1.06, 1.19, 1.22 (br., 36 H, CH_3), 1.52, 1.68, 1.78 (br., 48 H, CH_2), 2.09 (br., 6 H, CH), 3.42 [br., *exo*], 4.14 [br., *endo*] (2 H, 5-H), 4.39, 4.43, 4.49 (br., 12 H, OCH_2), 6.30 [br., *exo*], 6.38 [br., *endo*] (2 H, 6-H), 6.89 [br., *endo*] (1-H), 7.60 [br., *endo*] (2-H), 7.84 [br., *exo*] (1-H), 8.26 [br., *exo*] (2-H), 8.51, 8.61, 8.68 [br., *exo*] (13-H, 16-H, 21-H), 8.57, 8.65, 8.72 [br., *endo*] (13-H, 16-H, 21-H), 8.90 [br., *endo*] (8-H), 9.17 [br., *exo*] (8-H). − ^{13}C NMR ($CDCl_3$) δ = 11.3, 11.5, 11.6, 11.8, 14.1, 14.2, 14.3 (CH_3), 23.1, 23.2, 23.3, 24.0, 24.2, 29.2, 29.3, 29.7, 30.8, 31.0 (CH_2), 39.8, 40.1 (CH), 50.5 [*endo*], 52.4 [*exo*] (C-5), 68.5, 71.7, 72.0 (OCH_2), 83.3 [*endo*], 85.7 [*exo*] (C-6), 103.7, 104.0, 104.1, 104.6 (C-13, C-16, C-21), 111.31 [*exo*], 114.0 [*endo*] (C-8), 126.2, [*endo*], 127.3 [*exo*] (C-2), 130.1, 130.2, 130.3, 130.6, 130.8, 131.0 (C-9, C-12, C-17, C-20), 133.7 [*endo*], 134.4 [*exo*] (C-1),135.5 [*exo*], 135.7 [*endo*] (C-3), 142.4,142.5, 144.1 144.2, 144.8, 145.6, 145.7, 145.9 (C-7, C-10, C-11, C-18, C-19) 151.7, 151.9, 152.0, 152.3 (C-14, C-15, C-22)194.6 [*endo*], 195.1 [*exo*] (C-4). − MS (FD); *m/z* (%): 1380.5 (100) [$M^+ - C_{10}H_6O_2$]. − $C_{92}H_{118}N_8NiO_9$ (1538.6): calcd. C 71.82, H 7.73, N 7.28; found C 72.84, H 7.49, N 7.36.

Dehydrated Mono(naphthoquinone) Adduct PcNi 25: 42 mg (27.3 μmol) of **23** was dissolved in 40 ml of freshly distilled, dry toluene in a nitrogen-purged vessel and 17 mg (86 μmol) of *p*-toluenesulfonic acid (**24**) was added. The mixture was stirred for 1.5 h at 60°C. Then 1 ml of NEt_3 was added. After 15 min, the solvent was evaporated. Subsequent flash chromatography (SiO_2, CH_2Cl_2) gave after drying in vacuo 37 mg (87%) of **25** as an olive-green powder. − IR (KBr) $\tilde{\nu}$ = 2957 cm^{-1}, 2926, 1672, 1661, 1497, 1458, 1429, 1384, 1364, 1317, 1283, 1211, 1101, 1061, 1028, 966, 860, 756. − UV/Vis (CH_2Cl_2): λ_{max} = 708.5 nm, 680 (sh), 422, 329. − ^{1}H NMR ($CDCl_3$) δ = 1.02, 1.06, 1.08, 1.13, 1.20, 1.24 (br., 36 H, CH_3), 1.54, 1.61, 1.76, 1.88 (br., 48 H, CH_2), 2.06 (br., 6 H, CH), 4.03, 4.28, 4.41 (br., 12 H, OCH_2), 6.97 (br., 2 H, 1-H), 7.43 (br., 2 H, 2-H), 7.49 (s, 2 H, 13-H), 7.86 (s, 2 H, 8-H), 8.17, 8.21, 8.28 (br., 6 H, 6-H, 16-H, 21-H). − ^{13}C NMR ($CDCl_3$) δ = 11.5, 11.6, 14.2, 14.3, 14.4 (CH_3), 23.2, 23.3, 23.4, 23.9, 24.0, 29.3, 29.4, 30.6, 30.8 (CH_2), 39.5, 39.7, 39.9 (CH), 71.9 (OCH_2), 103.5, 103.8, 104.0 (C-13, C-16, C-21), 120.9 (C-8), 125.8 (C-2), 127.3 (C-9), 129.9 (C-6), 130.2 [br.] (C-12, C-17, C-20), 131.7 (C-1), 132.9 (C-3), 133.4 (C-5), 142.0 (C-7), 144.3, 144.7, 145.0 [br.] (C-10, C-11, C-18, C-19), 151.5, 151.7 [br.] (C-14, C-15, C-22), 180.4 (C-4). − MS (FAB); *m/z* (%): 1518.9 (100) [M^+], 1406.9 (40) [$M^+ - C_8H_{17}$]. − $C_{92}H_{116}N_8NiO_8$ (1520.6): calcd. C 72.68, H 7.69, N 7.37; found C 69.07, H 6.69, N 7.29.

Dehydrated Dimer PcNi 26: 32 mg (10.46 μmol) of **22** was dissolved in 30 ml of freshly distilled, dry toluene in a nitrogen-purged vessel and 25 mg (125 μmol) of *p*-toluenesulfonic acid (**24**) was added. The mixture was stirred for 4 h at 65°C. Then 1 ml of NEt_3 was added. After 15 min, the solvent was evaporated. Subsequent flash chromatography (SiO_2, CH_2Cl_2) gave after drying in vacuo 22 mg (68%) of **25** as an olive-green powder. − IR (KBr) $\tilde{\nu}$ = 2957 cm^{-1}, 2928, 1695, 1684, 1653, 1616, 1497, 1458, 1427, 1362, 1273, 1204, 1155. 1097, 1061, 991, 854, 750, 737. − UV/Vis (CH_2Cl_2): λ_{max} = 730 nm (sh), 681, 333, 287. − ^{1}H NMR ($CDCl_3$) δ = 0.91, 1.05, 1.15 (br., 72 H, CH_3), 1.40−2.0 (br., 96 H, CH_2), 2.0−2.3 (br., 12 H, CH), 4.54 (br., 24 H, OCH_2), 8.10, 8.50, 8.71, 8.92 (br., 20 H, 3-H, 5-H, 10-H, 13-H, 18-H). − ^{13}C NMR ($CDCl_3$) δ = 10.9, 11.4, 13.8, 14.1 (CH_3), 20.5, 22.7, 23.1, 23.6, 28.8, 29.3, 29.5, 30.2, 30.8 (CH_2), 39.0, 39.8 (CH), 71.7, 72.0 (OCH_2), 104.6 [br.] (C-10, C-13, C-18), 122.0 [br.] (C-5), 129.5−131.2 [br.] (C-2, C-3, C-9, C-14, C-17), 144.5−145.2 [br.] (C-4, C-6, C-7, C-8, C-15, C-16), 152.0, 152.7 (C-11, C-12, C-19), 199.3 (C-1). − MS (FAB); *m/z* (%): 2682.0 (10), 2412.1 (20), 2057.7 (10). − $C_{170}H_{224}N_{16}Ni_2O_{14}$ (2833.1): calcd. C 72.07, H 7.97, N 7.91; found C 69.42, H 7.28, N 7.36.

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[1] B. Hauschel, P. Stihler, M. Hanack, *Trends Polym. Sci.* **1996**, *4*, 348−354.
[2] P. Gomez-Romero, Y.-S. Lee, M. Kertesz, *Inorg. Chem.* **1988**, *27*, 3672−3675.
[3] [3a] M. Rack, M. Hanack, *Angew. Chem.* **1994**, *106*, 1712−1715; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1646−1648. − [3b] B. Hauschel, D. Ruff, M. Hanack, *J. Chem. Soc., Chem. Commun.* **1995**, 2449−2451. − [3c] B. Hauschel, P. Stihler, M. Hanack, *Synth. Met.* **1997**, *84*, 439−440.
[4] [4a] A.-D. Schlüter, *Adv. Mater.* **1991**, *3*, 282−291. − [4b] S. Wegener, K. Müllen, *Macromolecules* **1993**, *26*, 3037−3040.
[5] [5a] L. F. Fieser, M. J. Haddadin, *Can. J. Chem.* **1965**, *43*, 1599−1606. − [5b] J. Luo, H. Hart, *J. Org. Chem.* **1988**, *53*, 1341−1343. − [5c] B. Schlicke, H. Schirmer, A.-D. Schlüter, *Adv. Mater.* **1995**, *7*, 544−546.
[6] C. Feucht, T. Linßen, M. Hanack, *Chem. Ber.* **1994**, *127*, 113−117.
[7] M. Rack, B. Hauschel, M. Hanack, *Chem. Ber.* **1996**, *129*, 237−242.
[8] M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson, K. J. Harrison, *J. Chem. Soc., Perkin Trans. 1* **1988**, 2453−2458.
[9] M. Hanack, B. Hauschel, P. Stihler, M. Rack, T. Linßen, *Mat. Res. Soc. Symp. Proc.* **1996**, *413*, 465−470.
[10] K. Blatter, A.-D. Schlüter, *Chem. Ber.* **1989**, *122*, 1351−1356.
[11] [11a] N. B. McKeown, I. Chambrier, M. J. Cook, *J. Chem. Soc., Perkin Trans. 1* **1990**, 1169−1177. − [11b] T. G. Linssen, K. Dürr, M. Hanack, A. Hirsch, *J. Chem. Soc, Chem. Commun.* **1995**, 103−104. − [11c] T. G. Linßen, M. Hanack, *Chem. Ber.* **1994**, *127*, 2051−2057. − [11d] G. Schmid, M. Sommerauer, M. Geyer, M. Hanack in *Phthalocyanines: Properties and Applications*, vol. 4 (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, New York, **1996**, p. 5.
[12] M. Rack, Ph. D. Thesis, Eberhard-Karls-Universität Tübingen, **1994**.
[13] M. Hanack, A. Gül, A. Hirsch, B. K. Mandal, L. R. Subramanian, E. Witke, *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 365−382.
[14] P. Stihler, B. Hauschel, M. Hanack, *Chem. Ber.* **1997**, *130*, 801−806.
[15] S. Rodriguez-Morgade, M. Hanack, *Chem. Eur. J.* **1997**, *3*, 1042−1051.

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