Synthesis of Ladder-Type Oligomers Incorporating Phthalocyanine Units

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The condensation of substituted diiminoisoindolines with alkyl-substituted 1,3,3-trichloroisoindolines results in the formation of the highly soluble metal-free phthalocyanines **9**, **15**. By the same methodology, metal-containing phthalocyanines such as **16**, **18** are accessible from suitable metal salts. The precursors **24** and **26** were obtained from the phthalocyanine **9** and tetracyclone. The generation of the phthalocyanines **23** and **25** possessing isobenzofuran moieties as diene subunits was accomplished; in the presence of excess **28**, the tetracyclone-bisadducts **22** and **24** were transformed into the model compounds **29** and **30,** while an excess of **20** or **9** leads to the appropriate trimer-oligomers **31** and **32**.

Introduction

According to MO-calculations, ladder polymers with macrocyclic subunits containing extended areas of π-electron conjugation can be intrinsic conductors.[1] In addition, this type of ladder polymer should exhibit high thermal and chemical stability as well as non-linear optical properties.[2] A general route to structurally well-defined, planar double-stranded polymers is the repetitive Diels−Alder reaction.[3] Suitable macrocyclic monomers that allow the stepwise synthesis of defined oligomers by Diels−Alder reaction are e.g. hemiporphyrazines (Hp′s) and phthalocyanines (Pc′s).[4] However, these macrocycles have to fulfil three important requirements: they must (i) possess Diels−Alder functionalities, (ii) exhibit "ABAB"-symmetry (see Scheme 1) for the formation of ladder type oligomers (opposite-faced), and (iii) have a conjugated π-electron system.

A hemiporphyrazine macrocycle with ABAB-symmetry is more accessible than the corresponding Pc system[4][5] because the starting compounds (2,6-diaminopyridine and a substituted diiminoisoindoline) afford a hemiporphyrazine with ABAB-symmetry suitable for the formation of ladder type polymers.[6] However, in contrast to phthalocyanines, hemiporphyrazines are chemically not very stable, especially towards acids. Phthalocyanines (condensation products of four phthalonitrile or diiminoisoindoline units,[7] respectively) are therefore of greater interest as subunits in conjugated ladder polymers. The combination of two different substituted phthalonitriles or diiminoisoindolenines A with a diene or dienophilic functionality and B (nonfunctional) results in the formation of six phthalocyanines viz AAAA (self condensation of A), AAAB, AABB, ABAB, ABBB and BBBB (self condensation of B).[8] For the formation of ladder oligomers by a Diels−Alder reaction the phthalocyanines used must exhibit the ABAB form (D_{2h} symmetry). This methodology involves a very tedious separation of the six different phthalocyanines which are always formed in the above described statistical synthesis, e.g. by column chromatography or preparative HPLC, to isolate the pure ABAB form.[8a,9] Recently we described a direct synthesis of a bisdienophilic phthalocyanine with ABAB-symmetry suitable for repetitive Diels−Alder reactions, avoiding the chromatographic separation of the different structural isomers. This was achieved by condensation of 1,3,3-trichloro-6/7-nitroisoindolenine (**1**) and the dienophilic diiminoisoindoline **8**.[10][11] The ability of the bisdienophilic phthalocyanine formed to undergo Diels−Alder reactions was investigated by reaction with tetracyclone.[11]

As a continuation of the experiments reported in ref.[11] and to demonstrate the general use of the described synthetic pathway (apart from the preparation of ladder-type polymers), a hexa-substituted phthalocyanine **4** was synthesized by the condensation of 6/7-nitro-1,3,3-trichloroisoindolenine **(1)** (A) with diiminoisoindoline **3** (B), which was prepared by reacting the dinitrile **2** with ammonia in methanol (Scheme 1). In contrast to the observations made in ref.[10], a mixture containing two phthalocyanines **4** (ABAB, 90%) and **5** (ABBB, 10%) was obtained. Separation of **4** and **5** was easily performed by a combination of column chromatography and preparative TLC. Compound **4** exists in two isomeric forms (not separated) due to symmetry (C_{2v}: *syn*; C_{2h}: *anti*).

The ^{1}H NMR spectra of **4** and **5** exhibit clear differences. In particular the signals of the CH_2^g-protons of **4** appear as two broad multiplets at δ = 2.77−3.44 and 3.54−4.02. The spectrum of **5** shows three multiplets centered at δ = 3.23, 3.59 and 4.13 due to the two as well as three different environments of the heptyl side chains with respect to the nitro group. The different coupling pattern of the aromatic protons also support this conclusion. The UV/Vis spectrum of **4** exhibits a split Q-band (Q_x: 744.5 nm and Q_y: 701.5 nm), while a sharp Q-band at 708 nm is observed for **5**.

For the direct synthesis of a pure ABAB-type bisdienophilic phthalocyanine without nitro groups in the macrocycle, alkyl substituents were introduced into 1,3,3-trichloro-

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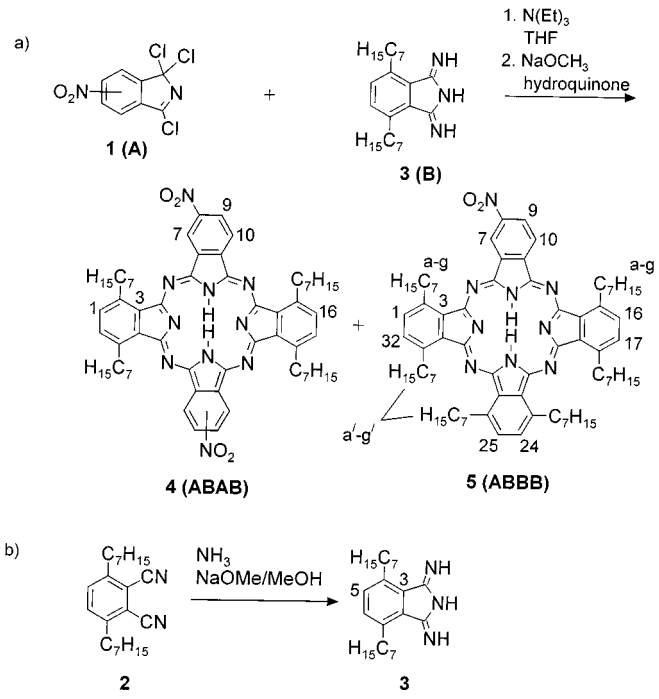
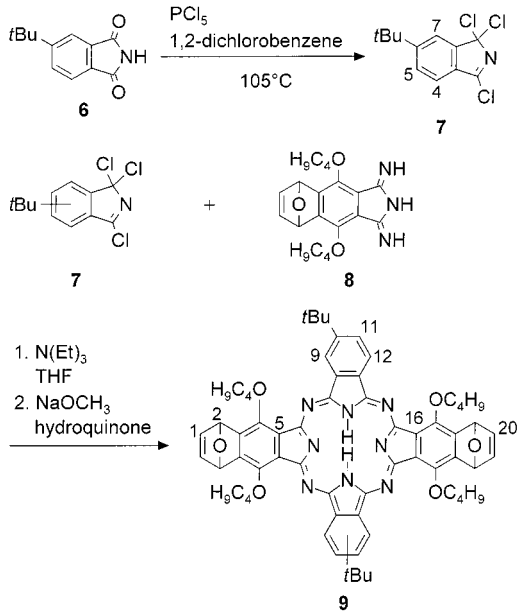


Scheme 1. Synthesis of the hexasubstituted phthalocyanine **4**

isoindoline. This was accomplished by the preparation of the *tert*-butyl-substituted **7**, which should also lead to an increased solubility of the resulting bisdienophilic phthalocyanines. Compound **7** was prepared by treating *tert*-butylphthalimide **6**[12b] with freshly sublimed PCl_5 in anhydrous 1,2-dichlorobenzene at 105°C. Fractional vacuum distillation gave **7** as a viscous, light yellow oil which decomposes in air within a few minutes. Compound **7** was briefly mentioned in ref.[13] without any spectroscopic characterization or method of synthesis.

As expected the ^{1}H NMR spectrum of **7** confirms the formation of an isomeric mixture as indicated by two *tert*-butyl signals at δ = 1.24 and 1.25. Furthermore, the typical coupling pattern of the aromatic protons was observed.

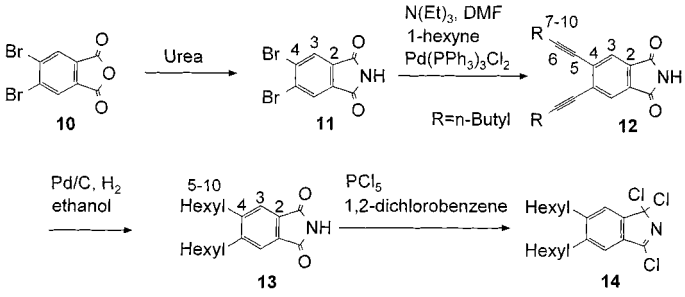
The synthesis of the ABAB-type Pc **9** was carried out by condensation of diiminoisoindoline **8**[6b] with an excess of the freshly distilled 6/7-*tert*-butyl-1,3,3-trichloroisoindolenine **7** (Scheme 2). The ABAB phthalocyanine **9**, which exists as a mixture of four isomers (*syn*/*anti* with regard to the relative positions of the *t*-butyl groups and the epoxy-bridges), was obtained exclusively. As expected phthalocyanine **9** exhibits high solubility in organic solvents such as toluene, chloroform, ethyl acetate and acetone. It was possible to separate the mixture of isomers into two components **9a** and **9b**, present in a 1:1 ratio, by preparative HPLC. These are probably the *syn*/*anti*-isomers, since only the differently positioned *t*-butyl group will lead to different polarities. The ^{1}H NMR spectra of the two isomers differ only in the coupling pattern of the OCH_2-protons at δ = 4.87−4.98 and 5.15−5.25, respectively. The resonances of the OCH_2-protons form a multiplet due to their diastereotopy and the existence of structural isomers. The sharp singlets of the NH-, the double-bond protons H-1/H-



Scheme 2. Preparation of the alkyl-substituted phthalocyanine **9**

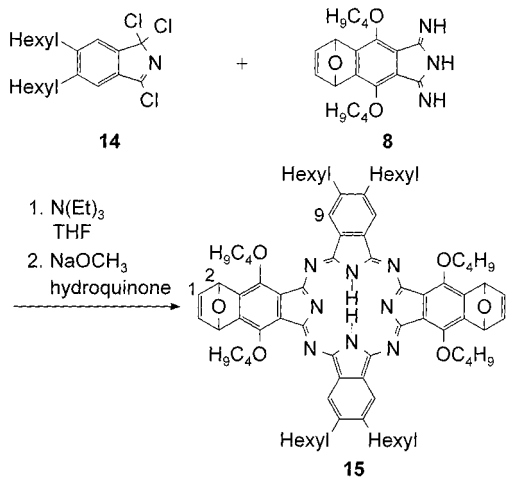
20 and the epoxy-bridge protons H-2/H-19 appear at δ = −0.51, 7.32 and 6.44, respectively. In addition, the typical *o*-, *m*- and *p*-coupling pattern of the aromatic protons H-9, H-11 and H-12 was observed. The UV/Vis spectrum of **9** shows, as expected, a split Q-band at 723 nm (Q_X: 744.5, Q_y: 701.5 nm) due to its ABAB-symmetry.

To reduce the number of isomers in the substituted dienophilic phthalocyanines without loss of solubility in organic solvents, *n*-hexyl groups were introduced into the 1,3,3-trichloroisoindolenine molecule (Scheme 3). Di-*n*-hexyltrichloroisoindolenine **14**, was prepared from the anhydride **10**,[14a−c] which was transformed first to the phthalimide **11** by heating with urea at 170°C.[14d] Coupling of the dibromophthalimide **11** with an excess of the terminal hexyne-1 in a Heck-type reaction gave the 4,5-dihexynylphthalimide **(12)** in 70% yield. Catalytic hydrogenation of **12** in the presence of Pd/C led to 4,5-dihexylphthalimide **(13)**. Chlorination of **13** with freshly sublimed PCl_5 in anhydrous 1,2-dichlorobenzene gave **14**, which could not be distilled due to decomposition. Since **14** decomposes within a few minutes after isolation even under argon atmosphere, we are unable to comment on the yield of **14** compared to **7** during the chlorination reaction.



Scheme 3. Synthesis of di-*n*-hexyltrichloroisoindolenine **14**

After removal of the solvent, $POCl_3$ and unchanged PCl_5, the residue containing compound **14** was directly reacted with isoindolenine **8**[6b] in anhydrous THF to afford the ABAB-type phthalocyanine **15** in a yield of 1.1% (Scheme 4). We believe that the poor yield is due to the low stability of **14** and the fact that compound **14** was obtained as a distillation residue and not as a completely pure product. Nevertheless, the use of 4,5-disubstituted trichloroisoindolines makes the interpretation of spectroscopic data easier and also increases the solubility of oligomers and polymers prepared from these precursors. Attempts to improve the yields of this reaction are presently underway.



Scheme 4. Preparation of the *n*-hexyl-substituted phthalocyanine **15**

The ^1H NMR spectrum of **15** exhibits the expected resonances of the hexyl- and butoxy protons at δ = 0.97−5.13, the singlet due to H-9 is observed at δ = 9.02. The protons H-1 and H-2 appear due to their small coupling constant as broad signals. The *syn*/*anti*-isomers[6a] with respect to the epoxy-bridges lead to a doubling of the H-1 signal (δ = 7.30 and 7.32). The ^{13}C NMR DEPT 135 spectrum confirms the formation of **15**; the carbon atoms each appear as single signals. The signals of C-1 (δ = 142.99) and C-9 (δ = 123.25) are very significant. As expected, the UV/Vis spectrum of **15** exhibits an analogous pattern as described for **9**. The split Q-band is centered at 726 nm while Q_x and Q_y are located at 746.0 nm and 706.5 nm, respectively.

In order to increase the stability of phthalocyanine ladder polymers, it is advantageous to use metal phthalocyanines as subunits.[11] Moreover, their electrical and optical properties make metal phthalocyanines more promising candidates as subunits for ladder polymers.[1][2]

We therefore developed a method for the direct metallation of our ABAB-type phthalocyanines during their preparation as described above. The metal phthalocyanines **16** and **18** were synthesized by condensation of **1** and **8** in THF following our earlier procedure described in ref. 11 with $Ni(py)_4Cl_2$ for **16** and $ZnCl_2$ for **18**, respectively, both in presence of $(n\text{-}C_4H_9)_4NBr$. The choice of $Ni(py)_4Cl_2$ is due to the fact that nickel salts such as $Ni(acac)_2$, $NiCl_2$ and $Ni(OAc)_2$ are insoluble in anhydrous THF, whilst $Ni(py)_4Cl_2$ is appreciably soluble in THF under phase transfer conditions.

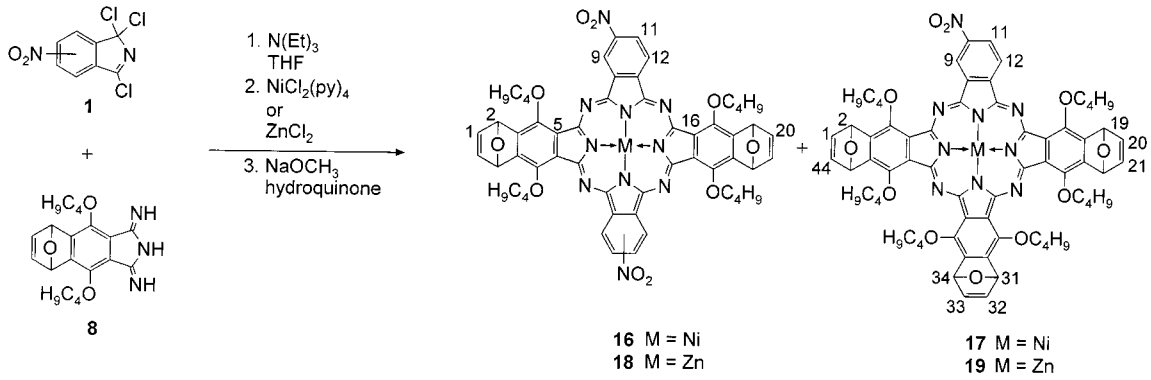
As a great variety of differently colored fractions (from yellow, orange to violet) is formed, the chromatographic workup of metal phthalocyanines **16** and **18** is more difficult compared to the metal-free phthalocyanines (e.g. **9** or **15**). As observed for the metal-free phthalocyanine **4**, the ABBB-phthalocyanine side products (**17**, **19**) were formed in about 10% yield. The phthalocyanines **16**−**19** were isolated by preparative TLC (see experimental part). In contrast to the equivalent metal-free phthalocyanine **20** (compare Scheme 6), the ^1H-NMR spectra of **16** and **17** exhibit broad and poorly resolved resonances caused by aggregation while those of **18** show the characteristic coupling pattern of the aromatic protons H-9, H-11 and H-12. The ^{13}C NMR-DEPT 135 spectra show the different symmetries of **16** and **17**. The OCH_2-carbons of **16** (ABAB) appear as a single signal at δ = 74.10 while **23** (ABBB) exhibits signals at δ = 73.53, 73.87 and 75.96. Phthalocyanine **19** was isolated in trace amounts only and characterized on the basis of its mass spectrum. The broadened Q-Band of **16** is split into Q_x at 694 nm and Q_y at 658 nm. In contrast the Q-band of **17** at 708.5 nm exhibits a bathochromic shift due to the different substitution pattern.

Up to this point we have described a direct method for the preparation of soluble bisdienophilic phthalocyanines (**9**, **15**, **16**, and **18**) with ABAB-symmetry. However, in order to synthesize complementary bisdienes needed for the repetitive Diels−Alder reactions, we returned to our earlier reported isobenzofuran route.[11]

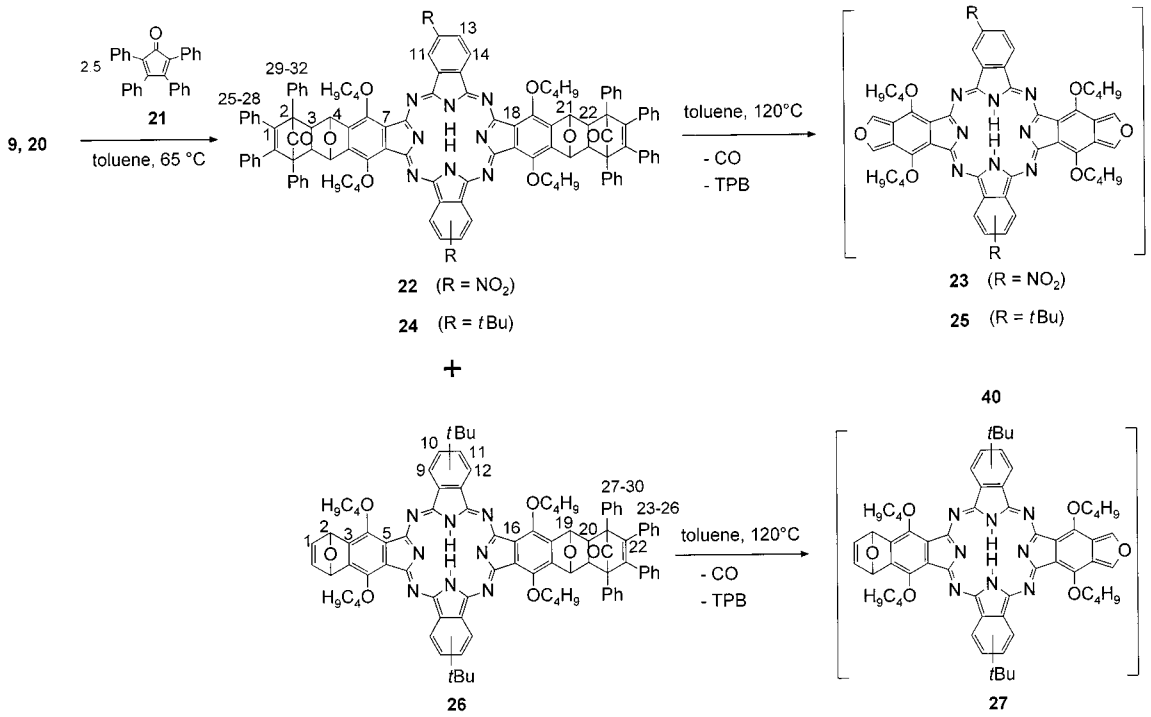
As noted above, metal free phthalocyanines showed better resolved spectra (esp. NMR-Spectra), these were consequently used for the preparation of further model compounds in order to achieve good characterization. However, for the future preparation of conjugated ladder polymers, metal phthalocyanines with their higher stabilities will require to be used.

The bisdienophilic phthalocyanines **9** and **20** on treatment with tetracyclone **21** gave the precursors **22** and **24** which were thermally decomposed to afford the reactive bisdienes **23** and **25** (see Scheme 6).

The advantage of this method is the use of the same starting compound **9**/**20** as bisdienophile and **22**/**24** as bisdiene. During the preparation of the *tert*-butyl-substituted precursor **24**, which leads to **25** (see Scheme 6), a small amount of the tetracyclone-monoadduct **26** was also obtained. Separation of **24** and **26** was easily achieved by preparative TLC. The ^1H NMR of **24** exhibits well resolved signals in both the aliphatic and aromatic regions. The *t*-butyl protons appear as two separate singlets at δ = 1.81 and 1.82. The resonances of H-3/22 at δ = 3.47−3.55 confirm the successful addition of tetracyclone. In contrast to **9**, H-4/21 appear together at δ = 6.46−6.48. Due to the *exo*-addition, the resulting angle between H-4/22 and H-4/21 should reach 90°. Therefore, the appearance of multiple signals for H-3/22 and H-4/21 result from different *syn*/*anti*-isomers (with



Scheme 5. Preparation of metal phthalocyanines **16**–**19**

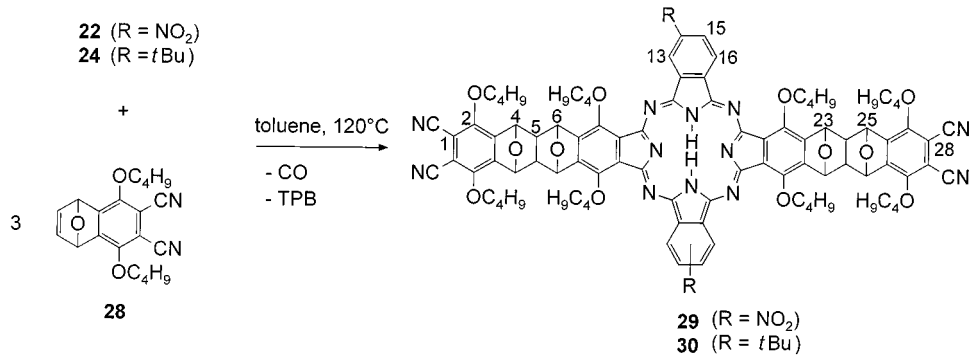


Scheme 6. Generation of reactive intermediates **23**, **25**, **27**

respect to epoxy and/or *t*-butyl group). The aromatic resonances of the phenyl groups are observed at δ = 7.07–7.85, while the signals of H-11, H-13 and H-14 form two multiplets at δ = 8.32–8.42 and 9.32–9.58. The ^{13}C NMR also shows the signals due to tetracyclone addition at δ = 46.95 and 47.06. Additionally, the CO signal appears, as expected, at very low field (δ = 196.47). The difference between **24** and **26** can be readily observed by comparison of their NMR spectra. Compound **26** exhibits two singlets at δ = 1.77 and 1.79 for the *t*-butyl protons due to the different adjacent fragments (tetracyclone-adduct and the dienophilic part). The different *syn*-/*anti*-orientations of the *t*-butyl-groups also affect the multiplicity of H-20; two resonances at δ = 3.53 and 3.58 were observed. The characteristic signal for H-1 is obscured by the phenyl protons. The linkage between tetracyclone and **9** is indicated by the signal of C-20 at δ = 46.97 in a DEPT 135 experiment. Tetracyclone addition also leads to a shift of epoxy-bridge carbon C-19 to δ = 80.32, while C-2 appears at δ = 81.41 (compare **9**: 81.39). As in the case of **9**, the vinylic carbon C-1 of **26** appears at δ = 142.98.

The Diels–Alder reaction of the phthalocyanines **22** and **24** with a 3 fold excess of dinitrile **28**[6b] (see Scheme 7) was then studied as a model reaction for preparing ladder-type polymers.

Thermolysis of precursors **22** and **24** at 120°C leads to the loss of CO and 1,2,3,4-tetraphenylbenzene (TPB) with *in situ* generation of the reactive intermediates **23** and **25** (Schemes 5 and 6) and the formation of bisadducts **29** and **30**, respectively. Compounds **29** and **30** can be further condensed with suitable nitriles to give ladder-type oligomers. Moreover, **29** and **30** serve as model compounds for the spectroscopic characterization of oligomers and polymers prepared. This turned out to be necessary, since the trimers had unsatisfactory solubilities or strong aggregation tendencies (see below).

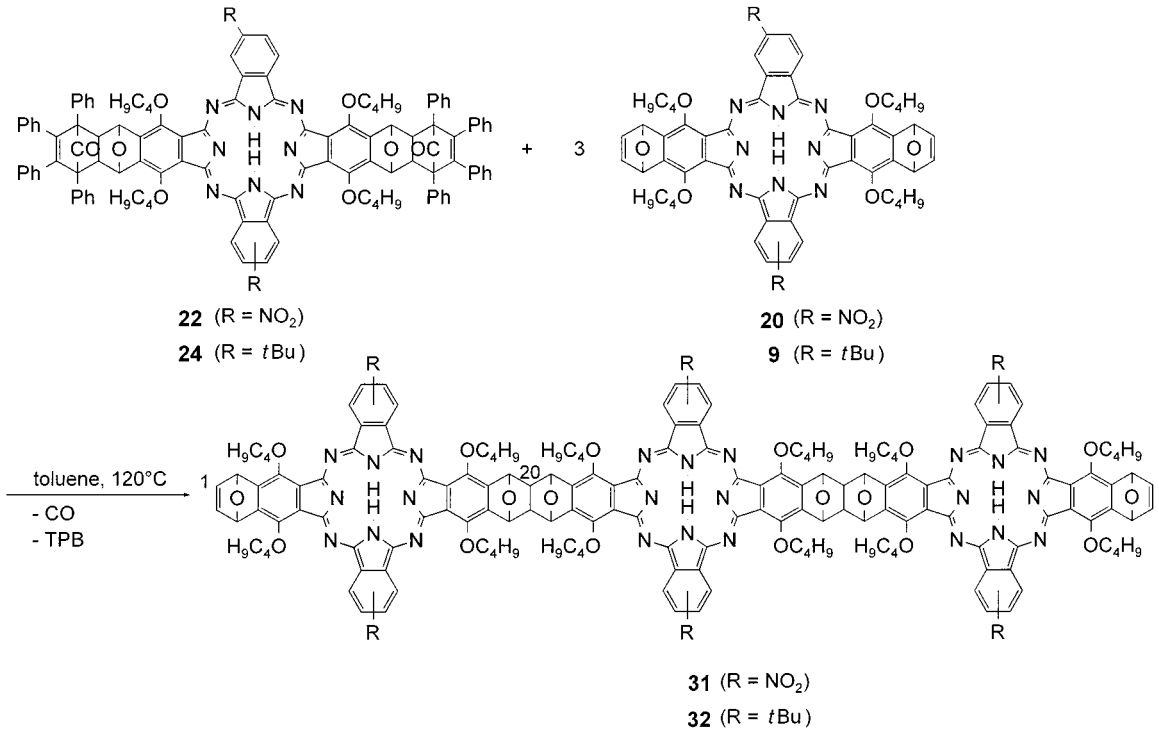


Scheme 7. Synthesis of nitrile-adducts **29** and **30**

In earlier work, only *exo*-addition was observed in the Diels–alder reaction of isobenzofurans with 1,4-epoxynaphthalenes.[6c,16] Consequently, the arrangement of adjacent oxygen bridges in **29** and **30** should be either *exo*/*exo* or *exo*/*endo*. The ^{13}C NMR data of **29** and **30** are consistent with these two possible arrangements. The nonequivalence of the butoxy side chains of the dinitrile-fragment and the phthalocyanine-fragment can be observed. Since the butoxy side chains are part of the dinitrile-fragments, their resonances are shifted to higher fields relative to those of the phthalocyanine-fragment. As expected, the *exo*/*endo*- and the *exo*/*exo*-arrangements of **29** are clearly evident at δ = 76.59 and 79.11 (H-4/25) and at δ = 80.28, respectively. For **30** the pertinent signals appear at δ = 76.28, 78.9 and δ = 80.02. However, it did not prove possible to determine the ratio of the *exo*/*exo*- and *exo*/*endo*-arrangements by ^1H NMR. The linkage between the phthalocyanine- and the dinitrile-fragment is characterized by two resonances for C-5/24 at δ = 50.13 and 50.77 in **29** and at δ = 50.07 and 50.52 in **30**. Evidence for a successful Diels–Alder reaction was provided by the signal for H-5/24 at δ = 3.19 (**29**) and δ = 3.15 (**30**), respectively.

The formation of ladder-type oligomers, e.g. trimers **31** and **32** occurs by generation of the intermediates **23** and **25** in the presence of the macrocyclic bisdienophiles **20** and **9,** respectively (Scheme 8).

These trimers contain directly linked macrocyclic units of **20** or **9**, which are isomeric mixtures. The less soluble trimer **31** precipitated from the reaction mixture and was extracted with a suitable organic solvent. The structure assigned to **31** was established mainly by ^{13}C CP/MAS spectroscopy. The characteristic signal resulting from the Diels–Alder addition is found at δ = 51.00 (C-20), whilst other signals are in agreement with the ^{13}C NMR data of the monomer **20**[11] and the signals of **29**.



Scheme 8. Preparation of trimers **31**, **32**

MALDI-TOF mass spectra of **31** showed the most intense peak at *m/z* 1011.7, which is in accord with 1/3 the mass of the six-fold deuterated **31** (in CF_3CO_2D) where all phthalocyanine units are twice deuterated.

In contrast to **31**, the trimer **32** is soluble in chloroform and ethyl acetate. The purification of **32** was accomplished by extraction of the monomer **9** and the TPB with CCl_4. Purification by column chromatography on silica gel, Al_2O_3 or reversed phase silica gel was not possible due to very strong interactions. The structure of **32** was established mainly by ^1H NMR and ^{13}C NMR DEPT 135. The characteristic resonance of the linkage between the macrocycles appears at δ = 3.12 and 3.65 (H-20) and δ = 51.14 (C-20), respectively. The ^1H NMR exhibits very broad signals due to aggregation; in particular the resonances of the NH-protons appear as scarcely visible flat broad signals. The ^{13}C NMR DEPT 135 results in very weak but significant resonances which are in agreement with the ^{13}C NMR data of monomer **9** and model compound **30**. All attempts to obtain mass spectroscopic data for **32** failed. The UV/VIS spectrum is dominated by aggregation effects which result in a broadened split Q-band (Q_X: 750, Q_y: 704 nm).

Experimental Section

General: All solvents were dried and distilled prior to use. PCl_5 was freshly sublimed before use and stored under argon. The synthesis of all phthalocyanines and 1,3,3-trichloroisoindolenines were carried out under argon. − FT-IR: Bruker IFS 48. − UV/VIS: Shimadzu UV-2101 PC, Shimadzu UV-365. − ^1H NMR: Bruker AC 250, Bruker ARX 250 (250 MHz). − ^{13}C NMR: Bruker AC 250, Bruker ARX 250 (62.9 MHz). − ^{13}C-CP/MAS: Bruker ASX 300 (75.5 MHz). Glycin as external standard (δ_{CO} = 176.03). − EI-MS: Finnigan ISQ 70 (70 eV). − FD-MS: Varian MAT 711 A. − FAB-MS: Finnigan ISQ 70, Varian MAT 711 A. − Ionspray-MS: Perkin−Elmer Sciex API III TAGA 6000E (solvent: CF_5COOD). − Elemental Analysis: C, H, N: Carlo Erba Elemental Analyzer 1104 and 1106. Preparative TLC was carried out using 20 × 20 cm plates with concentration zone 4 × 20 cm, thickness 1 mm, silica gel 60 F_{254}, (Merck).

4,7-Diheptyldiiminoisoindoline (3): Sodium (0.1 g, 4.3 mmol) was dissolved in anhydrous methanol (20 mL) at room temperature and a stream of dry ammonia bubbled through the mixture for 1 h. Compound **2**[17] (4.8 g, 14.8 mmol) was added and the mixture stirred at 60°C for 7 d with constant passage of ammonia. After cooling to room temperature the product was filtered, washed with cold methanol and dried in vacuo at 70°C. Yield of **3** 4.16 g (12.2 mmol), m.p. 79−81°C. − IR (KBr): $\tilde{\nu}$ = 3445 cm^{-1}, 3209, 2955, 2926, 2856, 1678, 1622, 1610, 1537, 1443, 1339, 1315, 1169, 1136, 1065, 822. − ^1H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 6 H, CH_3), 1.22−1.61 (m, 16 H, CH_2), 1.65−1.89 (m, 4 H, CH_2), 3.03 (br, 4 H, CH_2), 7.28 (s, H-5). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 29.1, 29.5, 30.2, 31.8, 32.0 (CH_2), 131.8 (C-3), 132.8 (C-5), 137.8 (C-4), 166.3 (C-2). − EI-MS; *m/z* (%): 341 (49) [M^+], 270 (100) [$M^+ - C_5H_{11}^+$]. − $C_{22}H_{35}N_3$ (341.3): calcd. C 77.37, H 10.33, N 12.30; found C 75.94, H 9.63, N 10.98.

Phthalocyanines 4 and 5: Anhydrous TEA (0.6 mL, 4.08 mmol) was added to a solution of **3** (0.46 g, 1.36 mmol) in anhydrous THF (40 mL) under argon. The mixture was cooled to approximately 0°C in an ice/salt bath and a solution of freshly distilled **1**[10] (0.36 g, 1.36 mmol) in anhydrous THF (10 mL) was added dropwise over a period of 15 min. The mixture was stirred for 1 h at 0°C, allowed to warm slowly to room temperature overnight and filtered to remove triethylamine hydrochloride. The filtrate was returned to the reaction vessel, hydroquinone (0.15 g, 1.36 mmol) and sodium methoxide (0.2 g, 4.00 mmol) were added and the resulting mixture heated at 65°C under argon for 6 h. After cooling to room temperature, the solvent was removed from the filtrate. The green fraction was separated from the residue by column chromatography on silica gel using chloroform as eluent. The purified two green fractions consisting of **4** and **5** were separated by PTLC (silica gel, hexane/chloroform 10:4) to give 14 mg (9.59%) **5** (fraction 1), 132 mg (90.4%) **4** (fraction 2). R_f (SiO_2, hexane/$CHCl_3$ 10:4): 0.1 (**4**), 0.45 (**5**).

1,4,15,18-Tetraheptyl-9,23/24-dinitrophthalocyanine (4): IR (KBr): $\tilde{\nu}$ = 3281 cm^{-1} (NH), 3093, 2956, 2925, 2856, 1728, 1529, 1464, 1339, 1134, 1107, 1022, 840, 734. − UV/Vis ($CHCl_3$): λ_{max} = 720 nm, 690.5, 654, 333. − ^1H NMR ($CDCl_3$): δ = −6.50, −6.38, −6.09, −5.42 (4s, br, 2 H, NH), 0.85−1.05 (m, 12 H, CH_3^a), 1.20−2.27 (m, br, 40 H, CH_2^{b-f}), 2.77−3.44, 3.54−4.02 (m, br, 8 H, CH_2^g), 7.13−8.47 (m, 10 H, H-1, H-7, H-9, H-10, H-16). − ^{13}C NMR ($CDCl_3$): δ = 14.2, 14.3 (CH_3^a), 22.8, 22.9, 22.9 (CH_2^b), 29.3, 29.7 (CH_2^c), 30.0, 30.5, 30.6 (CH_2^{d-e}), 31.9, 32.0, 32.2, 32.9, 33.2 (CH_2^{f-g}), 115.9 (C-7), 120.5 (C-10), 122.2 (C-9). − FD-MS; *m/z* (%): 996 (100) [M^+].

1,4,8,11,15,18-Hexaheptyl-23-nitrophthalocyanine (5): IR (KBr): $\tilde{\nu}$ 3282 cm^{-1} (NH), 3055, 2953, 2924, 2853, 1529, 1464, 1339, 1261, 1140, 1096, 1022, 802, 760. − UV/Vis ($CHCl_3$): λ_{max} = 708 nm, 639, 359, 322. − ^1H NMR ($CDCl_3$): δ = −3.11 (s, 2 H, NH), 0.78−0.95 (m, 18 H, $CH_3^{a,a'}$), 1.20−2.27 (m, 60 H, $CH_2^{b-f,\,b'-f''}$), 3.23, 3.59 (m, br, 4 H, CH_2^g), 4.13 (m, br, 8 H, $CH_2^{g'}$), 7.46, 7.54, 7.62, 7.67 (4 d, *J* = 7.4 Hz, 4 H, H-16−17, H-32−1), 7.73 (s, 2 H, H-24−25), 7.86 (d, *J* = 8.02 Hz, 1 H, H-10), 8.09 (d, *J* = 8.32 Hz, 1 H, H-9), 8.79 (s, 1 H, H-7). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.1, 14.2 ($CH_3^{a,a'}$), 22.7, 22.8, 22.9 ($CH_2^{b,b'}$), 29.5, 29.6, 29.7, 29.9, 30.0, 30.1, 30.3, 30.5, 31.9, 32.0, 32.1, 32.2, 32.3, 33.2, 33.9 ($CH_2^{c-g,\,c'-g'}$), 116.3 (C-7), 120.4 (C-10), 122.1 (C-9), 129.2, 129.6, 129.9, 130.6, 131.1, 136.2, 136.7, 138.1, 138.4, 138.4, 138.5, 139.0, 140.1, 140.3, 140.4, 141.0, 143.1, 143.5, 146.6 (C-1−6, C-8, C-11−32). − FD-MS; *m/z* (%): 1147 (100) [M^+]. − $C_{74}H_{101}N_9O_2$ (1147.3): calcd. C 77.38, H 8.86, N 10.97; found C 75.94, H 8.61, N 10.77.

6/7-*tert*-Butyl-1,3,3-trichloroisoindolenine (7): Compound **6**[12b] (4 g, 19.7 mmol) and freshly sublimed PCl_5 (8.6 g, 41.4 mmol) were added to anhydrous 1,2-dichlorobenzene (20 mL) under argon and stirred for 7 d at 105°C. The mixture was cooled to room temperature and stirred vigorously while aspirator vacuum was slowly applied to remove volatiles. When full aspirator vacuum had been applied and the frothing subsided, all remaining $POCl_3$ (reaction by-product) and 1,2-dichlorobenzene were removed at 120°C. Fractional vacuum distillation (b.p. 160°C at p = 5×10^{-2} mbar) gave **7** as a light yellow oil which decomposed in air to yield the corresponding phthalimide. Yield 2.5 g (46%). − IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 2966, 2907, 2877, 1774, 1753, 1609, 1539, 1479, 1466, 1367, 1327, 1238, 1084, 947, 748. − ^1H NMR ($CDCl_3$): δ = 1.24, 1.25 [2s, 9 H, $C(CH_3)_3$], 7.39 (dd, 1 H, H-5), 7.61 (dd, 1 H, H-4), 7.92 (dd, 1 H, H-7). − FD-MS (70 eV); *m/z* (%): 275 (7) [M^+], 240 (100) [M^+ − Cl], 205 (34) [M^+ − 2Cl], 168 (9) [M^+ − 3Cl]. The calculated isotopic pattern was in accord with the observed pattern.

1,6,17,22-Tetrabutoxy-11,27/28-di-*tert*-butyldibenzo[*g,q*]-2,5,18,21-tetrahydro-2,5,18,21-diepoxynaphtho[*b,l*]-porphyrazine (9): Compound 9 was prepared in an analogous manner to 4. A mixture of

8 (0.48 g, 1.35 mmol) and a fourfold excess of freshly distilled 7 were allowed to react at 0°C in anhydrous THF (40 mL) and TEA (0.9 mL, 6.12 mmol) for 24 h under argon. After filtration, hydroquinone (0.11 g, 1.02 mmol) and sodium methoxide (0.17 g, 3.06 mmol) were added to the filtrate and the mixture stirred at 65°C for 6 h. After cooling to room temperature the solvent was removed from the filtrate and the green fraction separated from the residue by column chromatography on silica gel with a mixture of chloroform/ethyl acetate (3:1) as eluent. Yield 125.1 mg (35.2%) of isomer mixture. − IR (KBr): $\tilde{\nu}$ = 3274 cm^{-1}(NH), 3081, 3034, 2956, 2932, 2870, 1610, 1581, 1493, 1466, 1393, 1360, 1315, 1288, 1128, 1002, 870, 760. − UV/Vis ($CHCl_3$): λ_{max} = 744.5 nm, 701.5, 652.5, 600.5, 346. − ^{1}H NMR ($CDCl_3$): δ = −0.51 (s, 2 H, NH), 1.14−1.23 (m, 12 H, CH_3), 1.75 [s, 18 H, $C(CH_3)_3$], 1.83−1.95 (m, 8 H, CH_2), 2.30−2.52 (m, 8 H, CH_2), 4.87−4.98 (m, 4 H, OCH_2), 5.15−5.25 (m, 4 H, OCH_2), 6.44 (s, 4 H, H-2, H-19), 7.32 (s, 4 H, H-1, H-20), 8.23−8.27 (d, ^3J = 8.1 Hz, 2 H, H-11), 9.26 (d, ^3J = 8.3 Hz, 2 H, H-12), 9.43 (d, ^5J = 0.6 Hz, 2 H, H-9). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.2 (CH_3), 19.69 (CH_2), 32.0 [$C(CH_3)_3$], 33.0, 33.1 (CH_2), 36.0 [$C(CH_3)_3$], 74.8, 74.9 (OCH_2), 81.4 (C-2, C-19), 119.4 (C-9), 122.6 (C-12), 128.0 (C-11), 128.4 (C-5, C-16), 135.6, 135.7, 135.8 (C-8, C-13), 138.1 (C-7, C-14), 143.0 (C-1, C-20), 143.1, 143.2, 145.7 (C-3, C-4, C-6, C-15, C-17, C-18), 154.0 (C-10). − FD-MS; *m/z* (%): 1046 (100) [M^+]. − $C_{64}H_{70}N_8O_6$ (1046.5): calcd. C 73.4, H 6.74, N 10.70; found C 73.4, H 6.78, N 10.38.

4,5-Dibromophthalimide (11): A mixture of **10**[14] (17 g, 55.6 mmol) and urea (3.4 g, 55.6 mmol) was finely powdered in a mortar and then heated to 180°C. The reaction was complete when no further gas evolution was observed (2 h). After cooling to room temperature the reaction mixture was poured into water and stirred for 1 h. The precipitate was filtered and dried in vacuo to yield a white powder (16 g, 96%), m.p. 247−250°C. − IR (KBr): $\tilde{\nu}$ = 3456 cm^{-1}, 3364, 3275, 3204, 3082, 1774 (CO), 1730, 1713 (CO), 1579, 1371, 1337, 1277, 1232, 1157, 1144, 1084, 1051, 874, 766, 744, 677. − ^{1}H NMR ([D$_6$]DMSO): δ = 8.12 (s, 2 H, H-3), 11.56 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]DMSO): δ = 127.9 (C-3), 130.3 (C-4), 133.8 (C-2), 167.4 (C-1). − EI-MS (70 eV); *m/z* (%): 305 (100) [M^+], 262 (37) [M^+ − CO − NH], 234 (32) [M^+ − 2CO − NH], 153 (38) [M^+ − 2CO − NH − Br], 74 (73) [M^+ − 2CO − NH − 2Br]. − $C_8H_3Br_2NO_2$ (304.93): calcd. C 31.59, H 0.99, N 4.59, Br 52.41; found C 31.41, H 1.08, N 5.07, Br 52.10.

4,5-Dihexynylphthalimide (12): A solution of **11** (4 g, 13 mmol) in anhydrous TEA (150 mL) and DMF (30 mL) under nitrogen was treated with 1-hexyne (7.5 mL, 65 mmol) and $PdCl_2(PPh_3)_2$ (5 mol.%). The mixture was heated to 65°C and stirred for two days. After cooling to room temperature the reaction was filtered, evaporated and dried in vacuo. Purification by column chromatography on silica gel using $CHCl_3$ as eluent gave yellow-orange crystals (2.7g, 67.6%), m.p. 139−142°C. − IR (KBr): $\tilde{\nu}$ = 3209 cm^{-1}(NH), 3067, 2961, 2934, 2864, 2220 (C≡C), 1778 (CO), 1728 (CO), 1618, 1358, 1290, 1034, 905, 743. − ^{1}H NMR ([D$_6$]acetone): δ = 0.96 (t, J = 7.3 Hz, 6 H, CH_3), 1.46−1.69 (m, 8 H, H-8−9), 2.54 (t, J = 6.71 Hz, 4 H, H-7), 7.72 (s, 2 H, H-3), 10.22 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]acetone): δ = 13.9 (C-10), 19.8 (C-7), 22.6 (C-9), 31.4 (C-8), 79.7 (C-5), 99.8 (C-6), 126.7 (C-3), 132.4 (C-4), 132.8 (C-2), 168.3 (C-1). − EI-MS (70 eV); *m/z* (%): 307 (80) [M^+], 250 (62) [M^+ − C_4H_9], 193 (100) [M^+ − 2C_4H_9]. − $C_{20}H_{21}NO_2$ (307.39): calcd. C 78.15, H 6.89, N 4.56; found C 75.10, H 6.79, N 4.19.

4,5-Dihexylphthalimide (13): A solution of **12** (2.5 g, 8.13 mmol) in absolute ethanol (80 mL) containing Pd/C catalyst (1 g) was stirred for seven days under a hydrogen atmosphere (1 bar) at room temperature. After the reaction was complete, the catalyst was removed by filtration, the solvent evaporated and the residue purified by column chromatography on silica gel with a mixture of hexane and ethyl acetate (8:1) as eluent to afford the title compound (2.2 g, 85%), m.p. 115−117°C. − IR (KBr): $\tilde{\nu}$ = 3213 cm^{-1}(NH), 3067, 2955, 2928, 2858, 1776 (CO), 1715 (CO), 1622, 1377, 1313, 1111, 748. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, J = 6.7 Hz, 6 H, H-10), 1.22−1.39 (m, 12 H, H-7−9), 1.52−1.64 (m, 4 H, H-6), 2.69 (t, J = 7.5 Hz, 4 H, H-5), 7.60 (s, 2 H, H-3), 8.09 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]acetone): δ = 14.0 (C-10), 22.5 (C-9), 29.2 (C-7), 30.7 (C-8), 31.6 (C-6), 33.1 (C-5), 124.1 (C-3), 130.3 (C-2), 148.1 (C-4), 168.8 (C-1). − EI-MS (70 eV); *m/z* (%): 315 (55) [M^+], 245 (44) [M^+ − C_5H_{11}], 230 (27) [M^+ − C_6H_{13}], 174 (100) [M^+ − 2C_5H_{11}]. − $C_{20}H_{29}NO_2$ (315.22): calcd. C 76.15, H 9.27, N 4.44; found C 75.18, H 9.16, N 4.29.

1,3,3-Trichloro-6,7-dihexylisoindoline (14): Compound **14** was prepared as described above for **7** by reaction of **13** (1.7 g, 5.39 mmol) with PCl_5 (2.36 g, 11.32 mmol) in 1,2-dichlorobenzene under an argon atmosphere. Volatiles, $POCl_3$ and solvent were removed by vacuum distillation and the distillation residue used without further purification.

1,6,17,22-Tetrabutoxy-9,10,23,24-tetrahexyldibenzo[*g,q*]-2,5,18,21-tetrahydro-2,5,18,21-diepoxynaphtho[*b,l*]-porphyrazine (15): A solution of **8** (0.21 g, 0.59 mmol) in anhydrous THF (40 mL) under argon was treated with anhydrous TEA (0.45 mL, 3.06 mmol) and, after cooling to approximately 0°C in an ice/salt bath, a solution of **14** in anhydrous THF (10 mL) was added dropwise over a 15 min period The mixture was stirred for 1 h at 0°C, and then allowed to warm slowly to room temperature overnight. After filtration, the filtrate was returned to the reaction vessel, hydroquinone (65 mg, 0.59 mmol) and sodium methoxide (0.1 g, 1.77 mmol) added and the resulting mixture heated at 65°C under argon for 6 h. After cooling to room temperature, the solvent was removed from the filtrate and the green fraction separated from the residue by column chromatography on silica gel with a mixture of chloroform/ethyl acetate (26:1) as eluent. Final purification by PTLC (silica gel) with chloroform/ethyl acetate (20:1) gave **15** (4 mg, 1.1%). R_f (silica gel, chloroform/ethyl acetate 20:1): 0.68. − IR (KBr):$\tilde{\nu}$ = 3290 cm^{-1} (NH), 3076, 2959, 2932, 2872, 1609, 1581, 1494, 1463, 1358, 1321, 1288, 1263, 1121, 1105, 1072, 1053, 1016, 955, 870, 757. − UV/Vis ($CHCl_3$): λ_{max} = 746 nm, 706.5, 662.5, 350.5. − ^{1}H NMR ($CDCl_3$): δ = −0.65 (br, 2 H, NH), 0.97−1.19 (m, 24 H, CH_3), 1.50−2.40 (m, 48 H, CH_2), 3.14, 3.60 (m, 8 H, CH_2), 4.91−5.13 (m, 8 H, OCH_2), 6.45 (s, 4 H, H-2), 7.30, 7.32 (2s, 4 H, H-1), 9.02 (s, br, 4 H, H-9). − ^{13}C NMR, DEPT 135 ($CDCl_3$): δ = 14.3 (CH_3), 19.8, 31.9, 33.1 (CH_2), 74.7 (OCH_2), 81.4 (C-2), 123.3 (C-9), 143.0 (C-1).

General Procedure for the Preparation of PcNi 16/17 and PcZn 18/19: The reaction was carried out as described above for **20**,[11] with **8** (0.24 g, 0.68 mmol) and **1** (0.36 g, 1.36 mmol). After filtration, anhydrous $NiCl_2(py)_4$ (0.6 g, 1.36 mmol) was added along with four drops of $(C_4H_9)_4NBr$ as phase transfer catalyst and the mixture stirred 24 h at room temperature during which time the color of the reaction mixture changed from yellow to red-brown. After evaporation of the solvent, the crude product was initially purified by column chromatography on silica gel with chloroform/ethyl acetate (9:2) as eluent and then the isolated green fraction separated into two green fractions by PTLC (silica gel) with chloroform/ethyl acetate (40:1) as eluent. Further purification of the resulting two green fractions **16/17** by PTLC (silica gel) with a mixture of chloroform/ethyl acetate/THF (20:2:1 to 40:1) gave **16** (34.2 mg, 93%) and **17** (2 mg, 1%). R_f (silica gel, chloroform/ethyl acetate 40:1): 0.52 (**17**), 0.24 (**16**).

[1,6,17,22-Tetrabutoxy-11,27/28-dinitrodibenzo[*g,q*]-2,5,18,21-tetrahydro-2,5,18,21-diepoxynaphtho[*b,l*]-porphyrazinato]nickel(II) (16):

IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2959, 2934, 2872, 1603, 1592, 1531, 1335, 1285, 1273, 1161, 1124, 1092, 879, 797, 716. − UV/Vis ($CHCl_3$): λ_{max} = 694 nm, 658, 396, 324. − ^1H NMR (CD_2Cl_2): δ = 1.04−1.40 (br, 12 H, CH_3), 1.63−1.94 (br, 8 H, CH_2), 1.97−2.31 (br, 8 H, CH_2), 4.12−4.62 (br, 8 H, OCH_2), 6.03, 6.18 (2s, br, 4 H, H-2, H-19), 7.09−7.42 (m, br, 4 H, H-1, H-20), 7.89−8.48 (br, 4 H, H-11−12), 8.86−9.25 (br, 2 H, H-9). − ^{13}C NMR ([D_8]THF): δ = 14.5, 14.6, 14.7 (CH_3), 20.5. 20.7 (CH_2), 33.7 (CH_2), 74.1 (br, OCH_2), 81.8, 82.0 (C-2, C-19), 117.5 (C-9), 121.6, 121.7, 121.8 (C-12), 123.7, 123.8, 123.9 (C-11), 126.6, 127.0, 127.2, 127.3, 127.5, 127.6, 127.9, 135.7, 135.8, 138.9, 141.6, 142.0, 142.1, 142.3, 143.1, 143.5, 144.0, 144.6, 144.7 (C-3−8, C-13−18), 143.4 (C-1, C-20), 148.6 (C-10). − FD-MS, *m/z* (%): 1081 (100) [M^+]. − $C_{56}H_{50}N_{10}NiO_{10}$ (1081.7): calcd. C 62.18, H 4.66, N 12.95; found C 62.46, H 5.25, N 10.81. − Electrochemistry: $E_{1/2}$ values vs. SCE (CH_2Cl_2/*n*-Bu_4NPF_6): −1.19, −0.78, −0.61 V.

[1,6,10,15,19,24-Hexabutoxy-29-nitrobenzo[*q*]-2,5,11,14,20,23-hexahydro-2,5,11,14,20,23-triepoxynaphtho[*b,q,l*]-porphyrazinato]-nickel(II) (17): IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3022, 2957, 2932, 2872, 1597, 1526, 1464, 1360, 1335, 1286, 1167, 1097, 1081, 993, 872, 798, 695. − UV/Vis ($CHCl_3$): λ_{max} = 708.5 nm, 639.5, 368.5, 330. − ^1H NMR ([D_8]THF): δ = 0.97−1.29 (m, 18 H, CH_3), 1.78−2.28 (m, br, 24 H, CH_2), 4.25−5.38 (m, br, 12 H, OCH_2), 6.29−6.56 (m, 6 H, H-2, H-19, H-22, H-31, H-34, H-43), 7.27−7.53 (m, 6 H, H-1, H-20−21, H-32−33, H-44), 7.79−8.29 (br, 2 H, H-11−12), 8.59−8.96 (br, 1 H, H-9). − ^{13}C NMR DEPT 135 ([D_8]THF): δ = 13.9, 14.2, 14.3 (CH_3), 20.1 (CH_2), 33.3 (CH_2), 73.5, 73.9, 76.0 (OCH_2), 81.2, 81.8, 82.3, 82.7 (C-2, C-19, C-22, C-31, C-34, C-43), 117.0 (C-9), 121.6 (C-12), 122.5 (C-11), 143.4, 143.6 (C-1, C-20−21, C-32−33, C-44). − FAB-MS; *m/z* (%): 1246 (100) [M^+].

PcZn 18 and 19: The reaction was carried out as described in the general procedure. After filtration freshly calcined $ZnCl_2$ (0.19 g, 1.36 mmol) was added and the mixture stirred for 24 h at room temperature during which time the initial yellow color changed to red-brown. After evaporation, the crude product was purified by column chromatography on silica gel with chloroform/THF (10:1). The resulting green fraction was then purified in two steps by PTLC (silica gel) with chloroform/THF/ethyl acetate (40:4:1) and then with a mixture of hexane/THF (10:8). The yield of **18** was 4 mg (11%). R_f (SiO_2, $CHCl_3$/THF 10:1): 0.75.

[1,6,17,22-Tetrabutyloxy-11,27/28-dinitrodibenzo[*g,q*]-2,5,18,21-tetrahydro-2,5,18,21-diepoxynaphtho[*b,l*]-porphyrazinato]zinc(II) (18): IR (KBr): $\tilde{\nu}$ = 3101 cm^{-1}, 2957, 2934, 2870, 1610, 1593, 1524, 1487, 1339, 1248, 1151, 1124, 1078, 1042, 972, 872, 795, 744, 719. − UV/VIS ($CHCl_3$): λ_{max} = 725 nm, 698, 666.5, 634, 355. − ^1H NMR ([D_8]THF): δ = 1.23−1.41 (br, 12 H, CH_3), 1.93−2.18 (br, 8 H, CH_2), 2.32−2.67 (br, 8 H, CH_2), 4.74−5.28 (m, br, 8 H, OCH_2), 6.38−6.51 (m, 4 H, H-2, H-19), 7.36−7.63 (m, 4 H, H-1, H-20), 8.05 (dd, ^3J = 8.09 Hz, 2 H, H-12), 8.57 (dd, ^4J = 2.02 Hz, 2 H, H-9), 8.62 (dd, ^3J = 8.09 Hz, 2 H, H-11). − ^{13}C NMR DEPT 135 ([D_8]THF): δ = 14.3, 14.4 (CH_3), 20.5, 20.6 (CH_2), 33.9 (CH_2), 74.4, 74.5 (OCH_2), 81.8, 82.0 (C-2, C-19), 118.4, 118.8 (C-9), 123.0, 124.0 (C-12), 124.6 (C-11), 143.5, 143.5, 143.6 (C-1, C-20). − FAB-MS; *m/z* (%): 1086 (26) [M^+].

Phthalocyanine-Tetracyclone Adducts 24 and 26: A solution of **9** (42 mg, 40 μmol) and tetracyclone (38.5 mg, 0.1 mmol) in toluene (20 mL) was stirred at 65° for 24−48 h under nitrogen. After evaporation, the crude material was purified by preparative TLC on silica gel with chloroform in order to remove unchanged **9** and excess of tetracyclone. The resulting green fraction was separated in two green fractions consisting of the tetracyclone-diadduct **24** and the tetracyclone-monoadduct **26** by PTLC (silica gel) with a mixture of chloroform/toluene (40:1). Yield 50.6 mg (70%) **24** and 4.2 mg (7%) **26**. The relative amounts of **24** and **26** were 91:9%. R_f (silica gel, chloroform): 0.76 (**24**), 0.66 (**26**).

PcH_2-Tetracyclone Bisadduct 24: IR (KBr): $\tilde{\nu}$ = 3323 cm^{-1}, 3273 (NH), 3055, 3030, 2956, 2934, 2878, 1778 (CO), 1605, 1582, 1508, 1454, 1333, 1298, 1227, 1103, 1049, 995, 758, 698. − UV/Vis ($CHCl_3$): λ_{max} = 742 nm, 703, 669, 633.5, 336. − ^1H NMR ($CDCl_3$): δ = −0.82, −0.57 (2s, 2 H, NH), 1.19−1.27 (m, 12 H, CH_3), 1.81, 1.82 [2s, 18 H, $C(CH_3)_3$], 1.88−2.08 (m, 8 H, CH_2), 2.34−2.79 (m, 8 H, CH_2), 3.47, 3.50, 3.54, 3.55 (4s, 4 H, H-3, H-22), 4.96−5.49 (m, 8 H, OCH_2), 6.46, 6.47, 6.48 (3s, 4 H, H-4, H-21), 7.07−7.17 (m, 20 H, H-26−28), 7.27−7.85 (m, 20 H, H-30−32), 8.32−8.42 (m, 2 H, H-13), 9.32−9.58 (m, 4 H, H-11, H-14). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.2, 14.3, (CH_3), 19.7, 19.8 (CH_2), 32.0 [$C(CH_3)_3$], 33.2, 33.2, 33.4 (CH_2), 36.2, 36.2 [$C(CH_3)_3$], 47.0, 47.1 (C-3, C-22), 64.5, 64.6 (C-2, C-23), 75.2 (OCH_2), 80.3 (C-4, C-21), 119.5, 119.6 (C-11), 122.8, 123.0 (C-14), 126.9, 127.5, 127.7, 128.3, 128.4, 128.6, 128.7, 129.8, 130.0, 132.7 (C-13, C-26−28, C-30−32), 131.3, 131.4 (C-7, C-18), 133.3, 133.4, 135.2, 135.3, 135.4, 135.6, 135.8, 136.4 (C-10, C-15, C-25, C-29), 138.9, (C-1, C-24), 142.7−143.0, 144.6, 144.7, 146.2−146−7 (C-5, C-6, C-8, C-17, C-19, C-20), 152.6−152.9 (br, C-9, C-16), 154.6, 154.7, 154.8 (C-12), 196.5 (C=O). − FD-MS; *m/z* (%): 994 (100) [M^+ − 2CO − 2TPB]. − $C_{122}H_{110}N_8O_8$ (1816.26): calcd. C 80.68, H 6.10, N 6.17; found C 78.53, H 5.90, N 5.24.

PcH_2-Tetracyclone Monoadduct 26: IR (KBr): $\tilde{\nu}$ = 3317 cm^{-1}, 3280 (NH), 3036, 2957, 2932, 2870, 1778 (CO), 1680, 1620, 1580, 1491, 1360, 1281, 1244, 1128, 1096, 1070, 1047, 760, 696. − UV/Vis ($CHCl_3$): λ_{max} = 743.5 nm, 703, 661, 633, 605.5, 340.5. − ^1H NMR ($CDCl_3$): δ = −0.52, −0.47 (2s, 2 H, NH), 1.15−1.24 (m, 12 H, $CH_3^{a,a'}$), 1.77, 1.79 [(2s, 18 H, $C(CH_3)_3$], 1.83−2.07 (m, 8 H, $CH_2^{b,b'}$), 2.36−2.73 (m, 8 H, $CH_2^{c,c'}$), 3.53, 3.58 (2s, 2 H, H-20), 4.85−5.48 (m, 8 H, $OCH_2^{d,d'}$), 6.43 (s, 2 H, H-2), 6.47, 6.48 (2s, 2 H, H-19), 7.06 (br, 10 H, H-24−26), 7.32−7.69 (m, 12 H, H-1, H-28−30), 8.31−8.34 (m, 2 H, H-11), 9.32−9.39 (m, 2 H, H-12), 9.52 (br, 2 H, H-9). − ^{13}C NMR DEPT 135 ($CDCl_3$): δ = 14.1, 14.3 ($CH_3^{a,a'}$), 19.7, 19.8 ($CH_2^{b,b'}$), 29.7 ($CH_2^{c'}$), 32.0 [$C(CH_3)_3$], 33.0, 33.1, 33.2, 33.4 (CH_2^{c}), 47.0 (C-20), 74.8, 75.3 ($OCH_2^{d,d'}$), 80.3 (C-19), 81.4 (C-2), 119.6 (C-9), 122.8, 122.9 (C-12), 126.9, 127.5, 128.4, 129.8, 130.0 (C-11, C-24−26, C-28−30), 143.0 (C-1). − FAB-MS; *m/z* (%): 1431 (5) [M^+], 1020 (100) [M^+ − CO − TPB].

Synthesis of Phthalocyanine-Dinitrile Adducts 29 and 30. General procedure: To a solution of the tetracyclone-bisadduct **22** or **24**,respectively, in anhydrous toluene (20 mL) was added a 3 fold excess of dinitrile **28.**[6b] The reaction mixture was stirred at 120°C for 48 h under nitrogen. After evaporation of the solvent, the resulting green material was purified by PTLC.

PcH_2-Dinitrile Bisadduct 29: From **22** (55 mg, 30.6 μmol) and **28** (33.9 mg, 0.1 mmol). Purification of **29** was accomplished by PTLC on silica gel to remove TPB (eluent: chloroform) and excess **28** (eluent: THF). The yield of **29** was 35.3 mg (70%). R_f (silica gel, THF): 0.81. − IR (KBr): $\tilde{\nu}$ = 3271 cm^{-1} (NH), 3096, 2959, 2934, 2871, 2565 (CN), 1602, 1580, 1528, 1495, 1464, 1339, 1279, 1146, 1119, 1063, 743. − UV/Vis ($CHCl_3$): λ_{max} = 720 nm, 647.5, 406, 337.5. − ^1H NMR ($CDCl_3$): δ = −3.52, −3.19 (2s, br, 2 H, NH), 0.95−1.08 (m, 12 H, CH_3^{DN}), 1.23−1.49 (m, 12 H, CH_3^{Pc}), 1.71−2.76 (m, 32 H, CH_2), 3.19 (s, 4 H, H-5, H-24), 3.99−5.21 (m, 16 H, OCH_2), 6.02, 6.19, 6.35 (3s, 8 H, H-4, H-6, H-23, H-25), 8.75−8.79 (m, br, 4 H, H-15−16), 9.48−9.68 (m, br, 2 H, H-13). − ^{13}C NMR (CD_2Cl_2): δ = 13.6 (CH_3^{DN}), 14.3, 14.5 (CH_3^{Pc}), 19.1, 19.2 (CH_2^{DN}), 20.0, 20.3, 20.4 (CH_2^{Pc}), 32.0 (CH_2^{DN}), 33.1, 33.3 (CH_2^{Pc}), 50.1, 50.8 (C-5, C-24), 74.0, 74.3, 74.5 (OCH_2), 76.6, 79.1,

80.3 (C-4, C-6, C-23, C-25), 108.3, 108.5 (C-1, C-28), 113.3 (CN), 117.7 (C-13), 122.2 (C-16), 124.3, 125.5 (C-15), 138.8, 138.9, 139.5, 139.8, 140.4, 142.1, 142.2, 143.3, 143.4 (C-9, C-10, C-12, C-17, C-19, C-20), 144.7, 144.9, 145.2, 145.4, 145.5, 145.6 (C-3, C-7, C-8, C-21, C-22, C-26), 148.7 (C-14), 149.4, 149.6 (C-2, C-27), 155.2, 155.4, 155.7, 155.8 (C-11, C-18). − FAB-MS; *m/z* (%): 1648 (56) [M^+], 1311 (20) [$M^+ - 38$]. − $C_{92}H_{92}N_{14}O_{16}$ (1648.7): calcd. C 66.98, H 5.62, N 11.89; found C 66.87, H 6.30, N 9.18.

PcH_2-Dinitrile Bisadduct 30: From **24** (77.7 mg, 42.8 μmol) and **28** (43.5 mg, 0.13 mmol). The purification of **30** was accomplished by PTLC on silica gel to remove the TPB and the excess of **28** (eluent: chloroform). The yield of **30** was 52.7 mg (74%). R_f (silica gel, chloroform): 0.39, 0.50 (isomers of **30**), 0.72 (TPB), 0.6 (**28**). − IR (KBr): $\tilde{\nu}$ 3323 cm^{-1} (NH), 3271 (NH), 2959, 2934, 2872, 2230 (CN), 1583, 1493, 1464, 1377, 1306, 1281, 1119, 1065, 829, 760. − UV/Vis ($CHCl_3$): λ_{max} = 741 nm, 702, 665, 633, 339. − ^{1}H NMR ($CDCl_3$): δ = −0.49, −0.46, −0.40 (3s, br, NH), 0.99−1.07 (m, 12 H, CH_3^{DN}), 1.18−1.29 (m, 12 H, CH_3^{Pc}), 1.77, 1.78 (2s, 18 H, $C(CH_3)_3$), 1.79−2.00 (m, 16 H, CH_2), 2.48−2.63 (m, 16 H, CH_2), 3.15 (s, 4 H, H-5,H-24), 4.16−4.32, 4.86−5.65 (m, 16 H, OCH_2), 5.94, 6.05, 6.16 (3s, 8 H, H-4, H-6, H-23, H-25), 8.34−8.37 (m, 2 H, H-16), 9.34−9.38 (dd, ^3J = 8.25 Hz, 2 H, H-15), 9.52 (s, 2 H, H-13). − ^{13}C NMR ($CDCl_3$): δ = 13.8 (CH_3^{DN}), 14.2, 14.3, 14.4 (CH_3^{Pc}), 19.0, 19.1 (CH_2^{DN}), 19.8, 20.0 (CH_2^{Pc}), 31.9 (CH_2^{DN}), 32.0 ($C(CH_3)_3$), 33.1, 33.4 (CH_2^{Pc}), 36.2 ($C(CH_3)_3$), 50.1, 50.5 (C-5, C-24), 74.5, 75.2, 75.2 (OCH_2), 76.3, 78.9, 80.2 (C-4, C-6, C-23, C-25), 108.4, 108.5 (C-1, C-28), 113.2 (CN), 119.4 (C-13), 122.7 (C-16), 128.5, 128.6, 128.7 (C-15), 130.6, 130.8, 133.7, 134.2, 136.1, 136.7, 139.2, 141.2, 143.4, 143.9, 144.7, 145.8, 149.5, 149.7, 154.5, 154.6, 154.7 (C-2−3, C-7−12, C-14, C-17−22, C-26−27). − FD-MS; *m/z* (%): 1672 (100) [M^+]. − $C_{100}H_{110}N_{12}O_{12}$ (1672.05): calcd. C 71.83, H 6.63, N 10.05; found C 71.17, H 6.48, N 9.56.

Synthesis of Ladder-Type PcH_2 Trimers 31 and 32. General Procedure: A solution of the PcH_2-tetracyclone bisadduct **22**, **24** and a threefold excess of the PcH_2 **20**, **9** in anhydrous toluene (20 mL) was stirred at 120°C for 48 h under nitrogen. After evaporation of the solvent, the trimers obtained were isolated by Soxhlet extraction.

PcH_2-Trimer 31: The crude material from **22** (47.5 mg, 26.5 μmol) and **20** (81.5 mg, 79.5 μmol) was purified by Soxhlet extraction with toluene, chloroform, ethyl acetate and methanol to remove TPB and excess of **20**. Trimer 31 was obtained as a green powder (57 mg, 72%). − IR (KBr): $\tilde{\nu}$ = 3273 cm^{-1} (NH), 3094, 2957, 2934, 2872, 1605, 1580, 1528, 1495, 1466, 1339, 1285, 1144, 1117, 1105, 1088, 1028, 920, 874, 841, 741. − UV/Vis [Poly(chlorotrifluoroethylene)]: λ_{max} = 745, 684 (br). − ^{13}C CP/MAS NMR: δ = 13.9 (CH_3), 19.9 (CH_2), 32.9 (CH_2), 51.0 (C-20), 74.3 (C-2, C-19, OCH_2), 123.5 (C-9, C-11−12), 142.5, 156.1 (C-1, C-3−8, C-10, C-13−18). − MALDI-TOF MS; **m**/*z* (%): 1012 (100) $[M + 6D]^{3+}$. − $C_{164}H_{152}N_{30}O_{30}$ (3023.2): calcd. C 65.16, H 5.97, N 13.90; found C 58.48, H 4.71, N 11.84.

PcH_2-Trimer 32: The crude material obtained from **24** (42 mg, 23.12 μmol) and **9** (72.5 mg, 69.37 μmol) was purified by Soxhlet-extraction with CCl_4 to remove TPB and excess of **13**. The residue was extracted with chloroform to give 54.3 mg (76%) of **32** as green powder. − IR (KBr): $\tilde{\nu}$ = 3319 cm^{-1}, 3271 (NH), 2957, 2934, 2870, 1609, 1580, 1491, 1466, 1362, 1302, 1281, 1246, 1101, 1069, 1049, 1007, 910, 831, 760. − UV/Vis ($CHCl_3$): λ_{max} = 750, 704, 663.5, 339. − ^{1}H NMR ($CDCl_3$): δ = 0.84−2.65 (br, 84 H, CH_3, CH_2), 3.12, 3.65 (br, H-20), 4.65−5.52 (br, 24 H, OCH_2), 6.09−6.71 (br, 12 H, H-2, H-19), 7.24−8.58 (br, 10 H, H-1, H-11), 9.07−9.74 (br, 10 H, H-9, H-12). − ^{13}C NMR DEPT 135 ($CDCl_3$): δ = 14.5 (CH_3), 19.7, 20.1, 22.7 (CH_2), 29.7, 33.4 (CH_2), 32.0 ($C(CH_3)_3$), 51.1 (C-20), 70.5, 70.2, 72.6, 74.8 (br, OCH_2), 81.3 (br, C-2, C-19), 119.1 (br, C-9), 122.9 (br, C-12), 127.5, 128.2, 128.9, 129.8 (br, C-11), 143.1 (br, C-1). − $C_{188}H_{206}N_{24}O_{18}$ (3087.8): calcd. C 73.13, H 6.66, N 10.89; found C 70.97, H 6.65, N 10.04.

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