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Chemical Transformations of Mono- and Bis(buta-1,3-dien-1-yl)porphyrins: A New Synthetic Approach to Mono- and Dibenzoporphyrins

Ana M. G. Silva,[a][‡] Kleber T. de Oliveira,[a] Maria A. F. Faustino,[a] Maria G. P. M. S. Neves,[a] Augusto C. Tomé,[a] Artur M. S. Silva,[a] José A. S. Cavaleiro,*[a] Paula Brandão,[b] and Vítor Felix[b]

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β-Butadienyl- and β,β′-dibutadienylporphyrins were prepared by the Wittig reaction of β-formyl- and β,β′-diformyl-*meso*-tetraphenylporphyrins with allylic phosphorus ylide. Subsequent treatment of β-butadienylporphyrin with dienophiles afforded the corresponding Diels–Alder adducts. In the absence of dienophiles, β-butadienylporphyrin underwent electrocyclization, followed by oxidation, to give monobenzoporphyrin in good yield. Similarly, adjacent and opposite dibenzoporphyrins were successfully synthesized from adjacent and opposite β,β′-dibutadienylporphyrins, respectively. This is the first report of electrocyclization of β-butadienylporphyrins. The structures of mono- and dibenzoporphyrin nickel complexes, as well as of a Diels–Alder adduct, were determined by single-crystal X-ray diffraction; a strong distortion from the planarity of the porphyrin core was observed.

Introduction

The synthesis and functionalization of porphyrins have received much attention within the scientific community in recent years.[1] This has been undoubtedly due to the promising applications of such compounds in several areas. Their use as oxidative catalysts, as photosensitizes in cancer treatments (photodynamic therapy),[2] as materials with novel electrical properties, and as biomimetic model systems of the primary processes of natural photosynthesis[1c,3] are certainly of great significance. There is therefore a need for porphyrinic systems with new and well-defined substitution patterns. This can be accomplished by the development of novel synthetic methodologies to transform easily available *meso*-arylporphyrins into novel molecular frameworks. In this context, porphyrins with π-extended conjugation such as benzoporphyrins have received much attention in recent years.[4] Benzoporphyrins and related derivatives can be synthesized by total synthesis[5] or by Diels–Alder reactions[6] of vinylporphyrins or tetraarylporphyrins; however, the regioselective syntheses of mono- and dibenzoporphyrins (two isomers) are still a challenge.

Recently, Smith et al. reported the synthesis of mono-, di-, and tribenzoporphyrins by allylation of polybromoporphyrins by using Suzuki coupling, followed by ring-closure metathesis and oxidation.[7]

In previous reports, we described the synthesis, separation, and characterization of β-formyl- and β,β′-diformylporphyrins[8] and their conversion into pyrroloporphyrins by 1,5-dipolar electrocyclization reactions.[9] Now we report the use of these aldehydes as precursors for the synthesis of mono- and dibutadienylporphyrins (**1**, **2**, and **3**), which can be further converted into β-substituted porphyrins **4** through Diels–Alder reactions or into mono- or dibenzoporphyrins (**5**, **6**, and **7**) by thermal electrocyclization reactions (Scheme 1). This approach allows easy and selective access to monobenzo-, adjacent dibenzo-, and opposite dibenzoporphyrins.

In addition, the present work relates to previous studies, where a β-(buta-1,3-dien-2-yl)porphyrin was used in Diels–Alder reactions with several electron-deficient dienophiles to furnish β-substituted porphyrins.[10] One of those Diels–Alder adducts was used in the synthesis of porphyrin–phthalocyanine dyads with hindered rotation.[11]

Results and Discussion

The starting mono- and dibutadienylporphyrins required for the Diels–Alder and electrocyclization reactions were conveniently prepared from the corresponding formyl derivatives[8] by Wittig reactions (Scheme 2).[12] Thus, the

[a] Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
Fax: +351-234-370-084
E-mail: jcavaleiro@ua.pt
[b] Department of Chemistry and CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[‡] Present address: REQUIMTE, Department of Chemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal
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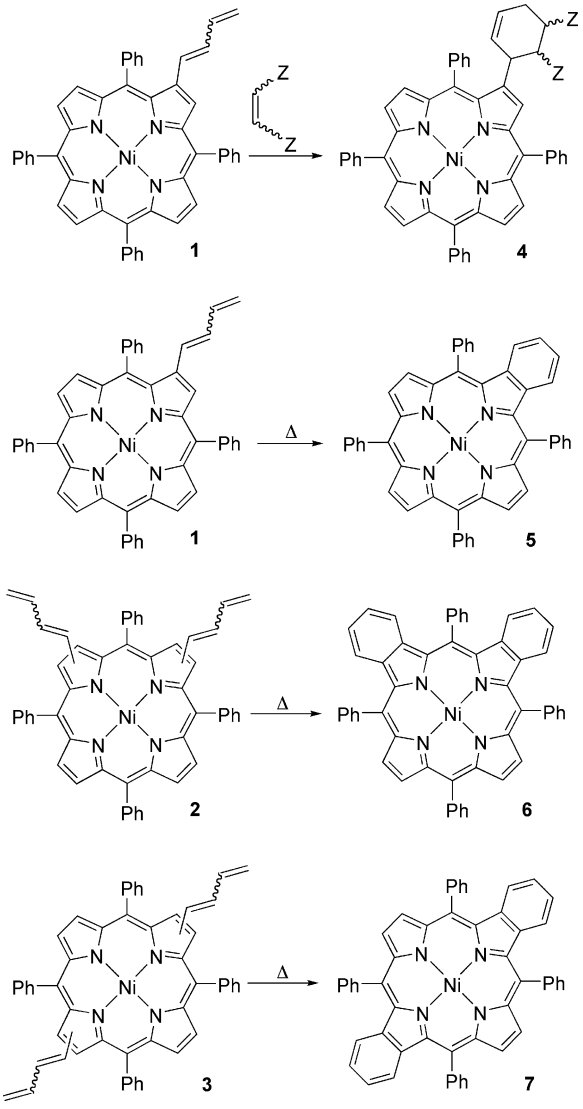
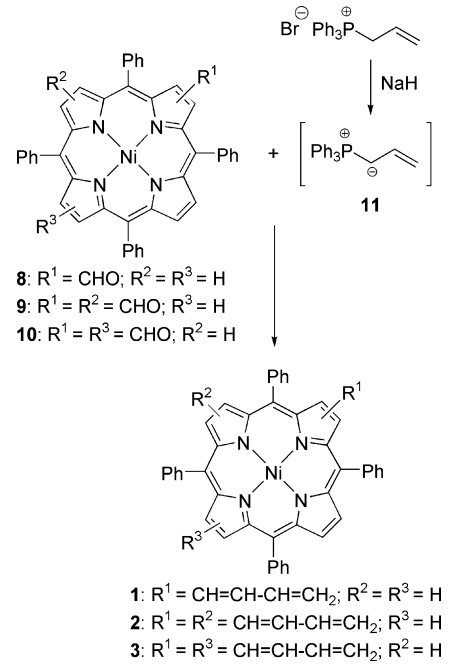
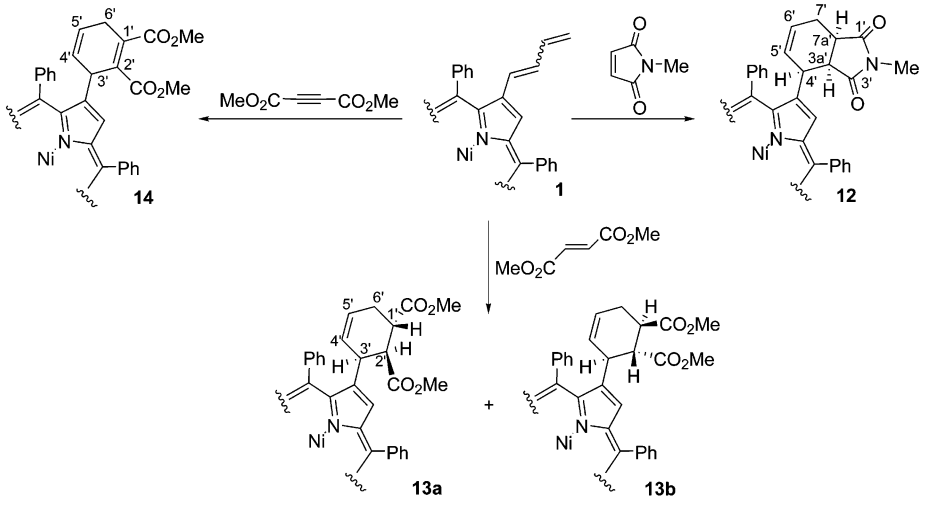


Scheme 1. General transformations of butadienylporphyrins **1**–**3**.

nickel(II) complex of β-butadienylporphyrin **1** was obtained in 74% yield from the reaction of the nickel(II) complex of β-formylporphyrin **8** with allylic ylide **11** generated in situ from allylphosphonium bromide and sodium hydride in toluene. The ^{1}H NMR spectrum of **1** shows that it is composed of a mixture of *cis*/*trans* isomers in a 1:1.5 ratio. The reaction of diformylporphyrins **9** (present as a mixture of adjacent isomers)[8] with allylic ylide **11** afforded the corresponding dibutadienylporphyrins **2** in 56% yield. Similarly, the reaction of diformylporphyrins **10** (a mixture of opposite isomers) afforded dibutadienylporphyrins **3** in 78% yield.



Scheme 2. Wittig reaction with formylporphyrins **8**, **9**, and **10**.



Scheme 3. Reactions of butadienylporphyrin **1** with activated dienophiles.

β-Butadienylporphyrins in Diels–Alder Reactions

Porphyrin **1** (mixture of *cis*/*trans* isomers) was treated with three different electron-deficient dienophiles: *N*-methylmaleimide, dimethyl fumarate, and dimethyl acetylenedicarboxylate (Scheme 3). Typically, the reactions were performed by heating porphyrin **1** with a dienophile (6 equiv.) in refluxing toluene for 48 h. The reaction with *N*-methylmaleimide furnished, after chromatographic purification, *endo* adduct **12** in 46% yield. From the analysis of the ^{1}H NMR spectrum, 2D COSY, and NOE experiments, it was possible to assign unequivocally all of the resonances of the isoindole protons and their relative stereochemistries.

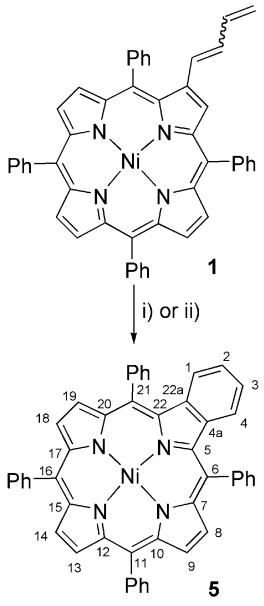
The observed close proximity between 3a′-H and 4′-H indicates that these protons are in a *cis* configuration. This is consistent with the *endo* configuration of the product. The structure of adduct **12** was also confirmed by single-crystal X-ray crystallography (Figure 5).

The reaction of **1** with dimethyl fumarate gave two diastereomeric adducts, which were separated by column chromatography and further purified by preparative TLC. Analysis of their NMR spectra allowed us to identify the diastereomer with the higher R_f value as **13a** (28% yield) and the diastereomer with lower R_f value as **13b** (13% yield). The ^{1}H NMR spectra of both diastereomers show seven signals corresponding to the resonances of the cyclohexene protons and two distinct singlets that arise due to the CO_2CH_3 groups. In the spectrum of diastereomer **13a**, the resonance of the 2′-CO_2CH_3 group appears at a lower frequency (δ = 2.10 ppm) than the one corresponding to the 1′-CO_2CH_3 group (δ = 3.61 ppm), which suggests that the former is closer to the porphyrin ring. In addition, NOE experiments show a close proximity between 2′-H and 3′-H, which allowed us to establish the *cis* relationship between these protons. In the spectrum of diastereomer **13b**, the resonances of the 2′-CO_2CH_3 and 1′-CO_2CH_3 groups (δ = 3.15 and 3.56 ppm, respectively) and the close proximity between 3′-H and 1′-H are consistent with a *trans* arrangement of the 2′-H and 3′-H protons.

The reaction with dimethyl acetylenedicarboxylate gave a single product, which was isolated and identified as the expected adduct **14** (28% yield). Its ^{1}H NMR spectrum shows the characteristic signals corresponding to the CO_2CH_3 groups and five signals corresponding to the resonances of the cyclohexadiene protons.

β-Butadienylporphyrins in Electrocyclization Reactions

During the Diels–Alder reactions with porphyrin **1**, we observed that when the reaction temperature was raised (180 °C in 1,2-dichlorobenzene) a new product was obtained in addition to the expected adducts. Full spectroscopic characterization of the new product showed it to be benzoporphyrin **5**, which was formed from the electrocyclization of butadienylporphyrin **1**, followed by oxidation (Scheme 4). Thus, when a 1,2,4-trichlorobenzene solution of **1** was heated at reflux for 16 h, in the absence of a dienophile, benzoporphyrin **5** was obtained in 68% yield after



Reagents and conditions:
(i) 1,2,4-trichlorobenzene, reflux, 16h (68% yield)
(ii) nitrobenzene, reflux, 12h (78% yield)

Scheme 4. Electrocyclizations performed with butadienylporphyrin **1**.

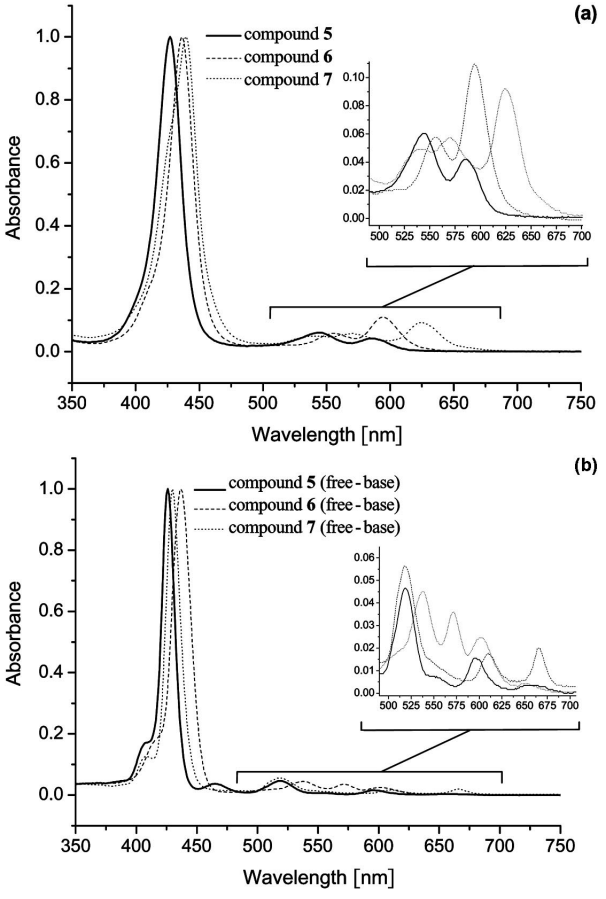


Figure 1. Normalized UV/Vis spectra ($CHCl_3$) of benzoporphyrins **5**, **6**, and **7** (a) and the corresponding free bases (b).

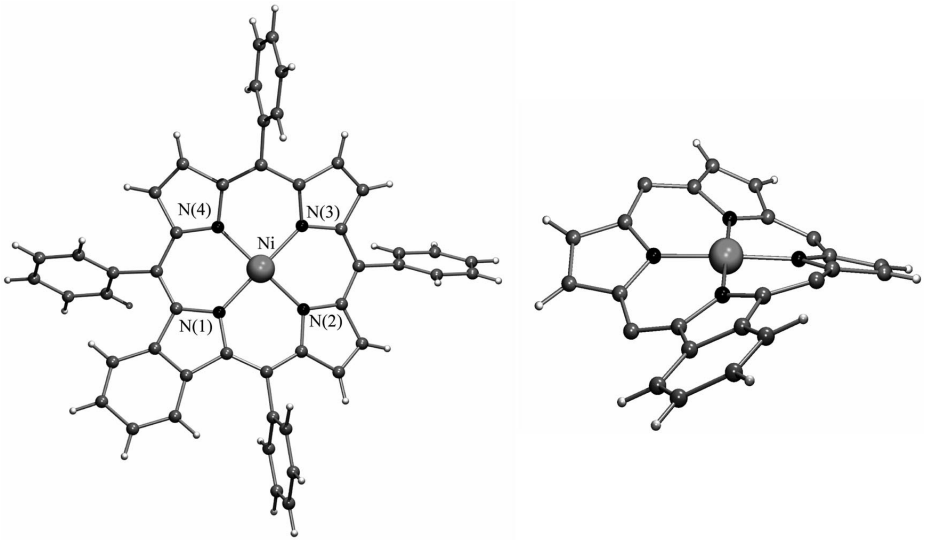


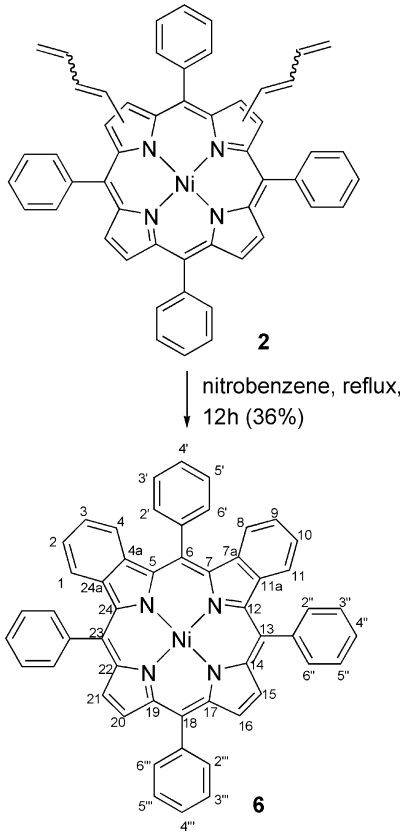
Figure 2. Molecular structure of benzoporphyrin **5** in two different views showing the overall structure (left) and the absence of planarity in the porphyrin core (right). In the right view the phenyl rings are omitted for clarity.

chromatographic purification. Following this discovery, we decided to optimize the conditions in order to prepare benzoporphyrin **5**, since during our studies we had observed that the use of shorter reaction times led to the formation of traces of non-oxidized intermediates. Under these conditions, after 12 h in refluxing nitrobenzene, the yield was increased to 78%.[13] This result suggests that the use of an oxidant favours the formation of benzoporphyrin **5**.

Comparison of the UV/Vis spectrum of starting porphyrin **1** (λ_{max} = 536 nm) with that of benzoporphyrin **5** (λ_{max} = 542 and 584 nm) shows a redshift in the Q bands in the benzoporphyrin, as expected (Figure 1). The symmetry of the molecule results in a simple NMR spectrum. In the ^{1}H NMR spectrum, the most important features are: two multiplets at ca. δ = 7.10 and 7.31 ppm that correspond to the resonances of 1-H/4-H and 2-H/3-H, respectively, and two singlets at δ = 8.66 and 8.64 ppm that correspond to the resonances of 8-H/9-H/18-H/19-H and 13-H/14-H, respectively. The structure of benzoporphyrin **5** was also confirmed by X-ray crystallography (Figure 2).

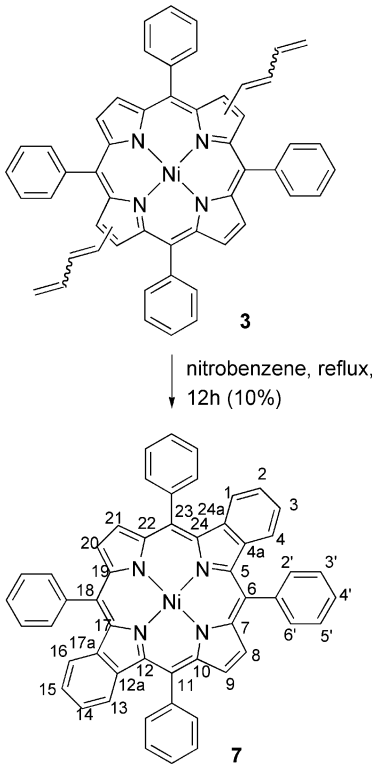
β,β′-Dibutadienylporphyrins in Electrocyclization Reactions

Initial attempts to convert porphyrins **2** and **3** into dibenzoporphyrins **6** and **7** in refluxing 1,2,4-trichlorobenzene were unsuccessful, as mixtures of **6** or **7** containing a substantial amount of nonoxidized electrocyclization products were obtained. However, when the reactions were carried out in refluxing nitrobenzene (12 h), dibenzoporphyrins **6** and **7** were obtained in 36 and 10% yields, respectively (Schemes 5 and 6). The difference in the yields of these two dibenzoporphyrins is consistent with the results observed during the formation of dipyrroloporphyrins.[9]



Scheme 5. Electrocyclization of β,β′-dibutadienylporphyrin **2**.

The most important features of the ^{1}H NMR spectrum of dibenzoporphyrin **6** are: two doublets at δ = 7.00 and 7.05 ppm (J = 8.0 Hz in both) that correspond to 1-H/11-H and 4-H/8-H, two doublets of doublets of doublets at δ = 7.22 and 7.27 (J = 8.0 Hz, J = 7.1 Hz, and J = 1.2 Hz)



Scheme 6. Electrocyclization of β,β′-dibutadienylporphyrin **3**.

that correspond to 2-H/10-H and 3-H/9-H, and an AB system (two doublets) at δ = 8.53 and 8.55 ppm that correspond to the β-pyrrolic protons 15-H/21-H and 16-H/20-H. These ^{1}H NMR results are consistent with the molecular structure determined by X-ray crystallography (Figure 3).

The NMR spectra of dibenzoporphyrin **7** are very simple and allow full assignment of all proton and carbon signals. The signals corresponding to protons 1-H, 4-H, 13-H, and 16-H appear as a multiplet at δ = 7.07–7.11 ppm. Similarly, the signals of protons 2-H, 3-H, 14-H, and 15-H appear at δ = 7.27–7.30 ppm. The signals corresponding to the resonance of the protons on the phenyl groups appear between δ = 7.65 and 7.95 ppm and are doublets and triplets, as expected for this system. The β-pyrrolic protons 8-H, 9-H, 20-H, and 21-H appear as multiplets at δ = 8.63–8.66. This splitting is due to the pronounced torsion of the porphyrinic ring of compound **7** (see X-ray structure, Figure 4).

In order to obtain the free bases of benzoporphyrins **5**, **6**, and **7**, analytical samples of the corresponding Ni complexes were treated with sulfuric acid in dichloromethane. The demetallated derivatives were obtained in neart quantitative yields and their structures were confirmed by MS and UV/Vis spectroscopy. Figure 1 shows the electronic absorption spectra of mono- and dibenzoporphyrins (Ni complexes and free bases) in chloroform. The spectra of the free bases of **5** and **7** are identical to those shown by Smith et al.[7] As expected, a redshift in the Soret and Q bands is observed for the dibenzoporphyrins.

X-ray Structures of Porphyrins 5, 6, 7, and 12

The molecular structures of porphyrins **5**, **6**, **7**, and **12**, as determined by single-crystal X-ray diffraction, are shown in Figures 2–5. Furthermore, the asymmetric unit of **5** is composed of two independent molecules of nickel benzoporphyrin, and the molecular diagram presented in Figure 2 corresponds to the structure of the first of these. The two dibenzoporphyrins have C_2 symmetry and possess a twofold crystallographic axis running along the C(5), Ni, and C(15) atoms in **6** and the N(2), Ni, and N(4) atoms in **7**. Selected bond lengths and angles in the nickel coordination sphere are listed in Table S1 (Supporting Information). In these four complexes, the metal center is coordinated to the four nitrogen donors of the porphyrin macrocycle in a distorted square planar fashion with similar Ni–N distances, which

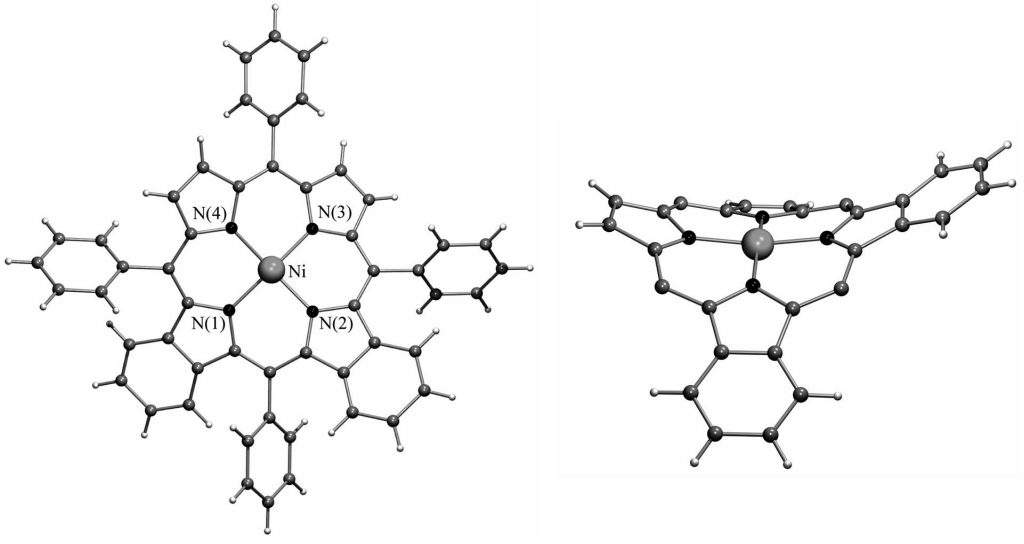


Figure 3. Molecular structure of dibenzoporphyrin **6**. The * corresponds to the symmetry operation: x, 1 – y, –z. The remaining details as given in Figure 2.

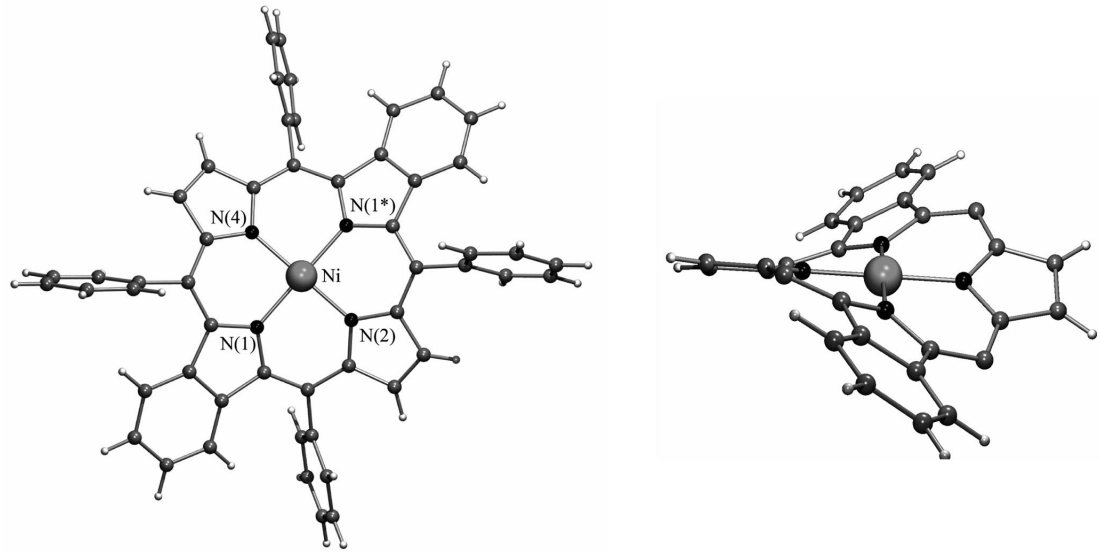


Figure 4. Molecular structure of dibenzoporphyrin **7**. The * corresponds to the symmetry operation: $-x + 1$, y, $-z + 3/2$. The remaining details as given in Figure 2.

are within the expected values for d^8 nickel porphyrin complexes.[14] Significant structural differences between these four complexes are obtained from the tetrahedral distortion, which is determined by the deviation of the nitrogen donors from the least–squares N_4 macrocyclic plane.

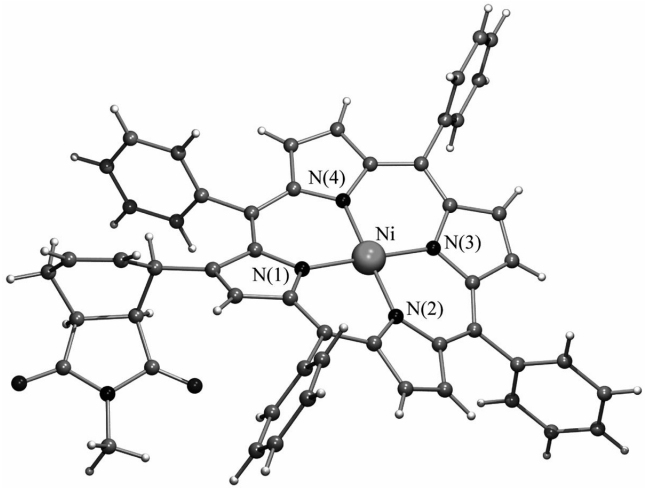


Figure 5. Molecular structure of adduct **12** emphasizing the nickel coordination geometry and stereochemistry of the tetrahydroisoindole-1,3-dione fragment.

Asymmetric dibenzoporphyrin **6** has an average tetrahedral distortion of ±0.197(1) Å, whereas in symmetric isomer **7**, the four nitrogen atoms are in the N_4 coordination plane and this distortion is absent. Porphyrin **5**, with one isoindole unit, and adduct **12**, with one tetrahydroisoindole-1,3-dione moiety, display small tetrahedral distortions. The pyrrole rings are tilted relative to each other, which leads to dihedral angles between consecutive rings that range from 26.5(1) to 34.2(1)° for **6**, from 25.7(1) to 35.0(1)° for **7**, and 21.8(2)° for **12**. In benzoporphyrin **5**, the dihedral angles vary between 29.9(2) and 36.1(3)° for the first independent molecule and between 23.7(3) and 28.6(4)° for the second one. This structural feature is illustrated in Figures 2–4 for mono- and dibenzoporphyrin derivatives (right views). The loss of planarity of the porphyrinic aromatic core in all four complexes is due to the minimization of the steric repulsions between neighboring phenyl and pyrrole rings. Indeed, in tetrabenzoporphyrin derivatives that possess no *meso*-phenyl substituents, the porphyrinic system is perfectly planar.[15] In contrast, the *meso*-tetraphenyltetrabenzoporphyrin derivative exhibits a tetrahedral distortion of ±0.21 Å, which is comparable to that of porphyrin **5**, and dihedral angles of 36.0° between the pyrrole rings.[16]

Conclusions

We showed that mono- and dibutadienylporphyrins can be prepared conveniently from the corresponding β-formyl derivatives. Monobutadienylporphyrin **1** reacts with activated dienophiles to afford the corresponding Diels–Alder adducts in moderate yields and it can be converted into benzoporphyrin **5** in very good yield. Similarly, dibutadienylporphyrins **2** and **3** can be converted into dibenzoporphyrins **6** and **7**, respectively, by electrocyclization in refluxing nitrobenzene. In conclusion, by starting from a very simple porphyrin (TPP) and by using a sequence of conventional reactions (formylation, Wittig, Diels–Alder or electrocyclization), we can synthesize a range of porphyrin derivatives that possess different electronic properties. The single–crystal X-ray diffraction analysis of the new compounds shows strong distortion from the planarity of the porphyrin core.

Experimental Section

General: ^{1}H NMR spectra were recorded with a Bruker Avance 300 at 300.13 MHz or a Bruker Avance 500 at 500.13 MHz and ^{13}C

NMR spectra at 75.47 or 125.77 MHz, respectively, with $CDCl_3$ as solvent and TMS as internal reference. Chemical shifts are expressed in δ (ppm), and coupling constants (J) are expressed in Hertz (Hz). Unequivocal ^1H assignments were made with the aid of 2D *g*COSY (^1H–^1H) and *g*NOESY spectra (mixing time of 800 ms), whereas ^{13}C assignments were made on the basis of 2D *g*HSQC (^1H–^{13}C) and *g*HMBC experiments (delay for long-range J C–H couplings were optimized for 7 Hz). Mass spectra and HRMS were recorded with FAB (VG AutoSpec Q instrument) and ESI (APEX Qe instrument) and LD-MS (4800 MALDI-TOF/TOF Applied Biosystems) techniques. Microanalyses were carried out with a LECO 932 CHNS analyser. UV/Vis spectra were recorded with $CHCl_3$ as solvent (UV-2501PC SHIMADZU instrument). Flash chromatography was carried out with silica gel (Merck, 230–400 mesh), and preparative thin-layer chromatography was carried out on 20 × 20 cm glass plates coated with Merck silica gel 60 (1 mm thick). Analytical TLC was carried out on precoated sheets with silica gel (0.2 mm thick, Merck). All chemicals and solvents used herein were obtained from commercial sources and used without further purification, except the toluene, which was dried by using standard procedures.[17] β-Formyl- and β,β′-diformylporphyrins were prepared according to the published procedures.[8]

{2-(Buta-1,3-dien-1-yl)-5,10,15,20-tetraphenylporphyrinato}nickel(II) (1): Sodium hydride (50% dispersion in oil, 11.0 mg, 0.46 mmol) was added to a suspension of allylphosphonium bromide (88.0 mg, 0.23 mmol) in dry toluene (5 mL) under a nitrogen atmosphere. The resulting mixture was heated at reflux until the appearance of an orange color was observed (15 min) to indicate the formation of the ylide. The nickel complex of β-formyl-*meso*-tetraphenylporphyrin **8** (40.0 mg, 57.0 μmol) was then added, and the reaction mixture was heated at reflux for 4 h. A second solution of phosphorus ylide was prepared, as before, by adding sodium hydride 50% (11.0 mg, 0.46 mmol) to a suspension of allylphosphonium bromide (88.0 mg, 0.23 mmol) in dry toluene (2.5 mL) and heating at reflux for 15 min. This solution was added to the reaction mixture. After 2 h, the reaction mixture was washed with water. The porphyrinic material was extracted with dichloromethane and dried (Na_2SO_4), and the solvent was then evaporated. Purification by flash chromatography (silica, toluene) afforded β-butadienyl porphyrin **1** (*cis*/*trans* mixture, 30.6 mg, 74% yield). This mixture was used in the Diels–Alder reactions and in the electrocyclizations. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 5.06–5.15 (m, 1 H, 4′-H), 5.26–5.34 (m, 1 H, 4′-H), 5.96–6.13 (m, 2 H, 1′-H and 3′-H), 6.75–6.95 (m, 1 H, 2′-H), 7.46–7.74 and 7.86–8.00 (2 m, 20 H, Ph-H), 8.66–8.72 (m, 6 H, β-H), 8.76 (s, 1 H, 3-H) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 422 (5.35), 536 (4.23) nm. MS (FAB+): m/z = 723 $[M + H]^+$, 722 $[M]^{+\cdot}$. MS (ESI-TOF): calcd. for $C_{48}H_{33}N_4Ni^+$ $[M + H]^+$ 723.2007; found 723.2002.

[β,β′-Bis(buta-1,3-dien-1-yl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) (2): Sodium hydride (95%, 27.0 mg, 1.03 mmol) was added to a suspension of allylphosphonium bromide (403.0 mg, 1.05 mmol) in dry toluene (10 mL) under a nitrogen atmosphere. The resulting mixture was heated at reflux until the appearance of an intense orange color was observed (ca. 30 min) to indicate the formation of the ylide. The isomeric mixture of β,β′-diformyl-*meso*-tetraphenylporphyrin **9** (50.0 mg, 68.7 μmol) was added, and the reaction mixture was heated at reflux for 2 h more. The reaction mixture was then poured over ice/water (ca. 30 g). The porphyrinic material was extracted with dichloromethane and dried (Na_2SO_4), and the solvent was evaporated. Purification by flash chromatography (toluene) afforded the isomeric mixture of β,β′-dibutadienyl porphyrin **2** (30.1 mg, 56% yield). MS (LD): m/z = 775 $[M + H]^+$.

[β,β′-Bis(buta-1,3-dien-1-yl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) (3): Sodium hydride (95%, 14.5 mg, 0.57 mmol) was added to a suspension of allylphosphonium bromide (223.0 mg, 0.58 mmol) in dry toluene (6 mL) under a nitrogen atmosphere. The resulting mixture was heated at reflux until the appearance of an intense orange color was observed (ca. 30 min) to indicate the formation of the ylide. The isomeric mixture of β,β′-diformyl-*meso*-tetraphenylporphyrin **10** (28.0 mg, 38.5 μmol) was then added, and the reaction mixture was heated at reflux for 2 h more. Ice/water (ca. 30 g) was added to the reaction mixture. The porphyrinic material was extracted with dichloromethane and dried (Na_2SO_4), and the solvent was evaporated. Purification by flash chromatography (toluene) afforded the isomeric mixture of β,β′-dibutadienyl porphyrin **3** (23.4 mg, 78% yield). MS (LD): m/z = 775 $[M + H]^+$.

General Procedure for the Diels–Alder Reactions: A solution of **1** (14 μmol) and the dienophile (84 μmol) in toluene (0.5 mL) was heated at reflux for 48 h under a nitrogen atmosphere. After cooling to room temperature, the solution was purified by flash chromatography (toluene, then toluene/ethyl acetate, 99:1) to remove starting porphyrin **1** and the adducts. Adducts **12**–**14** were further purified by preparative TLC (silica, toluene/ethyl acetate, 99:1). The isolated adducts were then crystallized from dichloromethane/methanol.

[2-(3a,4,7,7a-Tetrahydro-2-methyl-1,3-dioxoisoindol-4-yl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) (12): ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.71–1.96 (m, 1 H, 7′-H), 2.63–2.77 (m, 2 H, 7′-H and 7′a-H), 2.77 (s, 3 H, CH_3), 3.13 (dd, J = 8.6 Hz, J = 6.1 Hz, 1 H, 3′a-H), 3.85–3.86 (m, 1 H, 4′-H), 5.88–5.95 (m, 1 H, 6′-H), 6.37 (dt, J = 9.2 Hz, J = 3.4 Hz, 1 H, 5′-H), 7.54–7.81 and 7.99–8.16 (2 m, 20 H, Ph-H), 8.61–8.73 (m, 7 H, β-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 24.0 (C-7′), 24.6 (CH_3), 35.7 (C-4′), 40.6 (C-7′a), 47.8 (C-3′a), 117.1, 118.3, 118.8, 119.1, 126.75, 126.81, 126.9, 127.26, 127.29, 127.6, 127.7, 128.4, 131.7, 132.07, 132.11, 132.3, 132.5, 132.6, 132.8, 133.0, 133.66, 133.68, 134.1, 134.2, 135.9, 139.1, 140.60, 140.62, 140.8, 141.1, 142.0, 142.2, 142.4, 142.5, 142.7, 143.2, 144.5, 176.6 (1′-C=O), 179.5 (3′-C=O) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 418 (5.40), 533 (4.25) nm. MS (FAB+): m/z = 833 $[M]^{+\cdot}$. HRMS (FAB): calcd. for $C_{53}H_{37}N_5O_2Ni$ $[M]^{+\cdot}$ 833.2301; found 833.2302. $C_{53}H_{37}N_5O_2Ni$ (834.59): calcd. C 76.27, H 4.47, N 8.39; found C 75.94, H 4.30, N 8.27.

[2-(1,2-Dimethoxycarbonylcyclohex-4-en-3-yl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) (13a and 13b): 13a: ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.04–2.14 (m, 1 H, 6′-H), 2.10 (s, 3 H, 2′-CO_2CH_3), 2.49–2.58 (m, 1 H, 6′-H), 2.99 (dd, J = 11.7 Hz, J = 7.1 Hz, 1 H, 2′-H), 3.15 (dt, J = 11.7 Hz, J = 5.5 Hz, 1 H, 1′-H), 3.61 (s, 3 H, 1′-CO_2CH_3), 4.07–4.09 (m, 1 H, 3′-H), 5.76–5.81 (m, 1 H, 5′-H), 5.97–6.01 (m, 1 H, 4′-H), 7.65–7.71 and 7.99–8.02 (2 m, 20 H, Ph-H), 8.58–8.70 (m, 7 H, β-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 28.1 (C-6′), 35.0 (C-3′), 37.5 (C-1′), 46.0 (C-2′), 50.4 (2′-CO_2CH_3), 51.9 (1′-CO_2CH_3), 118.2, 118.3, 118.7, 119.0, 123.3 (C-5′), 126.9, 127.7, 128.3, 128.4 (C-4′), 131.5, 131.9, 132.1, 132.3, 132.49, 132.55, 133.1, 133.7, 133.8, 133.9, 134.0, 134.3, 140.0, 140.6, 140.66, 140.70, 142.3, 142.56, 142.64, 142.7, 143.8, 145.6 (C-2), 172.5 (2′ C=O), 176.0 (1′ C=O) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 419 (5.43), 533 (4.28) nm. MS (FAB+): m/z = 866 $[M]^{+\cdot}$. HRMS (FAB): calcd. for $C_{54}H_{40}N_4O_4Ni$ $[M]^{+\cdot}$ 866.2403; found 866.2401. **13b**: ^1H NMR (500.13 MHz, $CDCl_3$): δ = 2.34–2.38 (m, 2 H, 6′-H), 2.73 (dt, J = 10.6 Hz, J = 6.6 Hz, 1 H, 1′-H), 3.15 (s, 3 H, 2′-CO_2CH_3), 3.25 (t, J = 10.6 Hz, 1 H, 2′-H), 3.56 (s, 3 H, 1′-CO_2CH_3), 3.79–3.81 (m, 1 H, 3′-H), 5.48–5.52 (m, 1 H, 5′-H), 5.73 (dq, J = 9.9 Hz, J = 2.0 Hz, 1 H, 4′-H), 7.57–7.78

and 7.97–7.99 (2 m, 20 H, Ph-H), 8.64–8.72 (m, 7 H, β-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 27.8 (C-6′), 39.0 (C-3′), 43.0 (C-1′), 48.3 (C-2′), 51.4 (2′-CO_2CH_3), 51.9 (1′-CO_2CH_3), 118.1, 118.2, 118.6, 119.1, 121.8 (C-5′), 126.91, 126.95, 127.1, 127.7, 127.8, 128.2, 131.1 (C-4′), 131.6, 132.08, 132.11, 132.3, 132.5, 132.7, 132.8, 133.0, 133.2, 133.7, 133.8, 139.3, 140.1, 140.6, 140.7, 140.9, 142.1, 142.3, 142.4, 142.5, 142.6, 143.4, 147.3, 174.2 (2′-C=O), 174.5 (1′-C=O) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 418 (5.42), 532 (4.26) nm. MS (FAB+): *m*/*z* = 866 $[M]^{+\cdot}$. HRMS (FAB): calcd. for $C_{54}H_{40}N_4O_4Ni$ $[M]^{+\cdot}$ 866.2403; found 866.2401.

[2-(1,2-Dimethoxycarbonylcyclohexa-1,4-dien-3-yl)-5,10,15,20-tetraphenylporphyrinato]nickel(II) (14): ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.91 (dddd, *J* = 23.4 Hz, *J* = 7.8 Hz, *J* = 3.8 Hz, *J* = 1.7 Hz, 1 H, 6′-H), 3.16 (ddt, *J* = 23.4 Hz, *J* = 7.8 Hz, *J* = 2.7 Hz, 1 H, 6′-H), 3.35 (s, 3 H, CO_2CH_3), 3.80 (s, 3 H, CO_2CH_3), 4.46–4.53 (m, 1 H, 3′-H), 5.48–5.54 (m, 1 H, 5′-H), 5.82–5.88 (m, 1 H, 4′-H), 7.61–7.72 and 7.86–8.08 (2 m, 20 H, Ph-H), 8.55 (s, 1 H, 3-H), 8.62–8.73 (m, 6 H, β-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 27.8 (C-6′), 37.3 (C-3′), 51.8 (OCH_3), 52.3 (OCH_3), 118.0, 118.3, 118.6, 118.9 (C-5′), 119.1, 126.8, 126.9, 127.1, 127.7, 128.2 (C-4′), 128.6, 131.7, 132.1, 132.2, 132.49, 132.53, 132.7, 133.1, 133.3, 133.7, 134.0, 134.2, 135.4, 138.4, 139.9, 140.5, 140.6, 140.7, 142.2, 142.3, 142.4, 142.5, 142.6, 143.3, 147.3, 167.8 (C=O), 168.8 (C=O) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 418 (5.35), 533 (4.17) nm. MS (FAB+): *m*/*z* = 864 $[M]^{+\cdot}$. HRMS (FAB): calcd. For $C_{54}H_{38}N_4O_4Ni$ $[M]^{+\cdot}$ 864.2247; found 864.2229. $C_{54}H_{38}N_4O_4Ni$ (865.60): calcd. C 74.93, H 4.42, N 6.47; found C 74.73, H 4.42, N 6.37.

Electrocyclization Reactions

(6,11,16,21-Tetraphenylbenzo[*b*]porphyrinato)nickel(II) (5)

Method A: A solution of β-butadienyl porphyrin **1** (10.2 mg, 14 μmol) in 1,2,4-trichlorobenzene (2 mL) was heated at reflux under a nitrogen atmosphere for 16 h. The reaction mixture was then purified by flash chromatography (light petroleum, then toluene) to remove 1,2,4-trichlorobenzene and benzoporphyrin **5**. Product **5** was further crystallized from dichloromethane/methanol to give the pure compound (6.9 mg,68% yield). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.08–7.11 (m, 2 H, 1-H, 4-H), 7.30–7.33 (m, 2 H, 2-H, 3-H), 7.65–7.78 (m, 12 H, Ph-H$_{meta}$, Ph-H$_{para}$), 7.90–7.93 and 7.97–8.00 (2 m, 8 H, Ph-H$_{ortho}$), 8.64–8.66 (m, 6 H, β-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 115.0 and 120.0 (C-6, C-21 and C-11, C-16), 124.1 (C-1, C-4), 125.7 (C-2, C-3), 126.9, 127.8, 128.0, 128.3 (C$_{meta}$-Ph, C$_{para}$-Ph), 131.0 and 131.3 (C-8, C-19 and C-9, C-18), 132.4 (C-13, C-14), 132.7 and 133.5 (C$_{ortho}$-Ph), 137.9, 140.4, 140.46, 140.48, 140.9, 141.5, 143.9 ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 426 (5.35), 542 (4.14), 584 (3.95) nm. MS (FAB+): *m*/*z* = 720 $[M]^+$. MS (ESI-TOF): calcd. for $C_{48}H_{31}N_4Ni^+$ $[M + H]^+$ 721.1850; found 721.1848.

Method B: A solution of β-butadienyl porphyrin **1** (9.9 mg, 13.7 μmol) in nitrobenzene (10 mL) was heated at reflux under a nitrogen atmosphere for 12 h. The nitrobenzene was then removed by distillation under reduced pressure, and the remaining residue was purified by preparative TLC (silica, light petroleum/dichloromethane, 8:2). Recrystallization from dichloromethane/methanol afforded benzoporphyrin **5** (7.8 mg, 79% yield) as red crystals. M.p. >320 °C.

(6,13,18,23-Tetraphenyldibenzo[*b*,*g*]porphyrinato)nickel(II) (6). Method B: A solution of dibutadienyl porphyrin **2** (isomeric mixture, 20.0 mg, 25.8 μmol) in nitrobenzene (20 mL) was heated at reflux for 12 h under a nitrogen atmosphere. The nitrobenzene was removed by distillation under reduced pressure, and the remaining residue was purified by preparative TLC (silica, light petroleum/dichloromethane, 9:1). Recrystallization from dichloromethane/methanol afforded dibenzoporphyrin **6** (7.2 mg, 36% yield) as green crystals. M.p >320 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 7.00 (d, *J* = 8.0 Hz, 2 H) and 7.05 (d, *J* = 8.0 Hz, 2 H, 1-H, 11-H and 4-H, 8-H), 7.22 (ddd, *J* = 8.0 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 2 H) and 7.27 (ddd, *J* = 8.0 Hz, *J* = 7.1 Hz, *J* = 1.2 Hz, 2 H, 2-H, 10-H and 3-H, 9-H), 7.64–7.68 (m, 3 H, 4′′-H, 4′′′-H), 7.69–7.80 (m, 8 H, Ph-H$_{meta}$), 7.87 (tt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1 H, 4′-H), 7.90–7.98 (m, 8 H, Ph-H$_{ortho}$), 8.53 (d, *J* = 4.9 Hz, 1 H) and 8.55 (d, *J* = 4.9 Hz, 1 H, 15-H, 16-H, 20-H, 21-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 113.2 and 115.9 (C-6, C-18 and C-13, C-23), 123.6 and 124.8 (C-1, C-11 and C-4, C-8), 125.0 and 125.7 (C-2, C-10 and C-3, C-9), 127.0, 128.1 and 128.3 (C$_{meta}$-Ph), 127.8, 129.0 and 129.1 (C-4′, C-4′′, C-4′′′), 129.5 and 131.3 (C-15, C-16, C-20, C-21), 132.8, 133.1 and 133.4 (C$_{ortho}$-Ph), 136.0 (C-5, C-7, C-12, C-24), 139.8 and 143.3 (C-14, C-22 and C-17, C-19), 140.0 and 140.1 (C-4a, C-7a and C-11a, C-24a), 140.6 and 141.1 (C1′, C-1′′, C-1′′′) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 435 (5.25), 556 (4.02), 594 (4.27) nm. MS (LD): *m*/*z* = 771 $[M + H]^+$. MS (ESI-TOF): calcd. for $C_{52}H_{33}N_4Ni^+$ $[M + H]^+$ 771.2007; found 771.2002.

(6,11,18,23-Tetraphenyldibenzo[*b*,*l*]porphyrinato)nickel(II) (7). Method B: A solution of dibutadienyl porphyrin **3** (isomeric mixture, 13.0 mg, 16.6 μmol) in nitrobenzene (13 mL) was heated at reflux under a nitrogen atmosphere for 12 h. Nitrobenzene was then removed by distillation under reduced pressure, and the remaining residue was purified by preparative TLC (silica, light petroleum/dichloromethane, 8:2). Recrystallization from dichloromethane/methanol afforded dibenzoporphyrin **7** (1.3 mg, 10% yield) as green crystals. M.p. >320 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 7.07–7.11 (m, 2 H, 1-H, 4-H), 7.27–7.30 (m, 2 H, 2-H, 3-H), 7.71 (t, *J* = 7.7 Hz, 8 H, 3′-H, 5′-H), 7.76 (t, *J* = 7.7 Hz, 4 H, 4′-H), 7.92 (d, *J* = 7.7 Hz, 8 H, 2′-H, 6′-H), 8.63–8.66 (m, 4 H, 8-H, 9-H, 20-H, 21-H) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 116.2 (C-6, C-11, C-18, C-23), 123.8 (C-1, C-4, C-13, C-16), 125.3 (C-2, C-3, C-14, C-16), 128.9 (C-3′, C-5′), 128.3 (C-4′), 131.0 (C-8, C-9, C-20, C-21), 132.7 (C-2′, C-6′), 136.7 (C-5, C-12, C-17, C-24), 140.1 (C-4a, C-12a, C-17a, C-24a), 140.6 (C-1a), 141.7 (C-7, C-10, C-19, C-22) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 439 (5.31), 540 (3.98), 570 (4.04), 624 (4.26) nm. MS (LD): *m*/*z* = 771 $[M + H]^+$. MS (ESI-TOF): calcd. for $C_{52}H_{33}N_4Ni^+$ $[M + H]^+$ 771.2007; found 771.1995.

Demetalation of Benzoporphyrins 5, 6, and 7: A few milligrams of benzoporphyrin was dissolved in CH_2Cl_2 (1 mL) and concentrated H_2SO_4 (3 drops) was added. The mixture was stirred at room temperature for 5 min and then water was added. The mixture was neutralized with $NaHCO_3$, and the organic layer was separated and dried with Na_2SO_4; the solvent was removed under reduced pressure. The free-base benzoporphyrins were purified by preparative TLC (petroleum ether/dichloromethane, 7:3). The free-base compounds were analyzed by UV/Vis and MS (LD): *m*/*z* = 665.2 $[M + H]^+$, free-base **5**; 715.2 $[M + H]^+$, free-base **6**; 715.2 $[M + H]^+$, free-base **7**.

Crystallography: The pertinent crystallographic data for compounds **5**, **6**, **7**, and **12** are given in Table S2 (Supporting Information). The X-ray data was collected at 150 K with a CCD Bruker APEX II by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystals were positioned at 35 mm from the CCD and the spots were measured by using an appropriate counting time. Data reduction and empirical absorption were carried out with the SAINT-NT from Bruker aXS. Structures were solved by a combination of Patterson methods and subsequent difference Fourier

syntheses and refined by full-matrix least-squares on F^2 using the SHELX-97 suite.[18] The X-ray structure determinations of **5** and **12** show the presence of disordered solvent molecules in their crystal structures, specifically $CHCl_3$ in **5** and CH_3CH_2OH and CH_2Cl_2 in **12**. The $CHCl_3$ was found to be disordered over two tetrahedral sites, and the hydrogen and chlorine atoms occupy two alternative positions, which were included in the refinement with occupancies of x and $1 - x$, where x is equal to 0.62. The CH_2Cl_2 was also disordered over two positions related by a crystallographic inversion center. In addition, in the asymmetric unit, the two solvate molecules were separated by a short distance, which was incompatible with the establishment of intermolecular contacts between their atoms. Therefore, these molecules were included together in the refinement with occupancies of x for CH_2Cl_2 and $1 - x$ for CH_3CH_2OH, where x is equal to 0.33. Anisotropic thermal parameters were used for all non-hydrogen atoms of the complex molecules. The thermal movement of the non-hydrogen atoms of the solvent molecules were described with individual isotropic thermal parameters, with the exception of the chlorine atoms of CH_2Cl_2 molecule, which were also refined with anisotropic parameters. Hydrogen atoms that were bonded to carbon atoms were placed at calculated positions with $U_{iso} = 1.2U_{eq}$ of the parent atom. In the final difference Fourier maps of all complexes, the highest peak was less than 1 e Å^{-3} with the exception of **6**. However, in this case the highest peak of 1.49 e Å^{-1} was 0.86 Å within the nickel coordination sphere. Molecular diagrams were drawn with PLATON.[19] CCDC-660526 (for **5**), -660527 (for **6**), -660528 (for **7**), and -660529 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected distances and angles in the nickel coordination sphere for porphyrins **5**, **6**, **7**, and **12**; crystal data and pertinent refinement details for compounds **5**, **6**, **7**, and **12**; and ^{1}H and ^{13}C NMR spectra (uni- and bidimensional analysis).

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