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# Functionalization of 2,3-Disubstituted-2,3-dihydro-5,10,15,20-tetraphenylporphyrins

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**Abstract**—A reduced pyrrole subunit directs electrophilic functionalizations of dihydroporphyrins to the antipodal pyrrole ring by confining the chromophore 18-π-electron delocalization pathway to its N(22)*H*-N(24)*H* tautomer. The 2,3-disubstituents inhibit oxidation, this being exemplified by the synthesis of perbrominated dodecasubstituted metallochlorins. Regiospecific nitration (using $N_2O_4$) of metal-free chlorins provides access to Michael acceptors such as 12-nitro-2,3-disubstituted chlorins which are used in the preparation of highly functionalized tetraaryl-bacteriochlorins by conjugate addition of carbon-centered nucleophiles. 

## Introduction

2,3-Disubstituted-2,3-dihydroporphyrins (2,3-disubstituted chlorins) are readily prepared by way of nucleophilic attack of free-base or metallo-2-nitro-5,10,15,20-tetraphenylporphyrin with 'active' methylene compounds.[1] These novel derivatives are ideal candidates for investigation of the peripheral functionalization of free-base and metallotetraarylchlorins because they are stabilized toward chlorin-to-porphyrin oxidation by their bulky 2,3-substituents.

Most investigations of the chemical reactivity or functionalization of tetraarylchlorins or other 20-π electron analogues have focused on the reduced (or oxidized) pyrrole subunits. Deuteration studies showed that the four methylene protons of tetraphenylchlorin [$H_2$(TPC)] **1** can be exchanged via a simple protonation–deprotonation process. Under harsh conditions, all peripheral macrocyclic hydrogens were exchanged, revealing that 2,3-dihydroporphyrins are true tautomers of 5,22-dihydroporphyrin (phlorins).[2] 2,3-vic-Dihydroxy-tetraphenylchlorin can be dehydrated to give $H_2$(2-hydroxyTPP)[3] or converted into a dicarboxaldehyde-secoporphyrin,[4] which can in turn be decarbonylated to afford a tetraphenylchlorophin.[5] 2,3-Dione-porphyrins are readily condensed with aromatic *ortho*-diamines to give pyrazinoporphyrins,[6,7] with aromatic aldehydes and ammonium acetate to give aryl-substituted fused imidazoleporphyrin systems,[8] or undergo ring expansion when treated with excess diazomethane to yield oxypyriporphyrins.[9]

We now demonstrate that metal free 2,3-disubstituted-2,3-dihydroporphyrins are stable toward oxidation and therefore undergo regiospecific β-bromination and -nitration in high yields. Perbromination of their nickel(II) complexes gave highly nonplanar dodecasubstituted-2,3-dihydroporphyrins. Finally, a novel synthesis of tetraarylbacteriochlorins is described from the Michael addition of 'active' methylene compounds to β-nitrochlorins.

## Results and Discussion

β-Functionalization of free-base porphyrinoids occurs regioselectively via fixation of their 18-π electron delocalization pathway[10–13] with bond-fixing entities such as β-fused aromatic rings[6,11] and peripheral electron-withdrawing groups.[12,13] A reduced or β–β′-oxidized pyrrole subunit also causes a substantial antipodal bond-fixation by confining the electron delocalization pathway to a $N_{22}H$–$N_{24}H$ tautomer[14] (Fig. 1). Consequently, diimide reduction[15] or osmium tetroxide oxidation[16] of $H_2$(TPC) **1** produced bacteriochlorin analogues. *N*-Amination[17] and -alkylation[18] of tetraarylchlorins at the N(23) imine nitrogen stem also from a preferential $N_{22}H$–$N_{24}H$ tautomer. Dibromination of 2,3-dionetetraarylporphyrin, formally a 20 π-electron chlorin analogue, is also regioselective.[6] However, photoreduction of $H_2$(TPC) in the presence of pyrrolidine

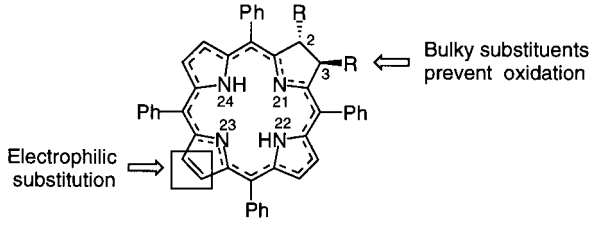


**Figure 1.** 2,3-Disubstituted 2,3-dihydro-$N_{22}H$–$N_{24}H$-5,10,15,20-tetraphenylporphyrin. R=H: **1**.

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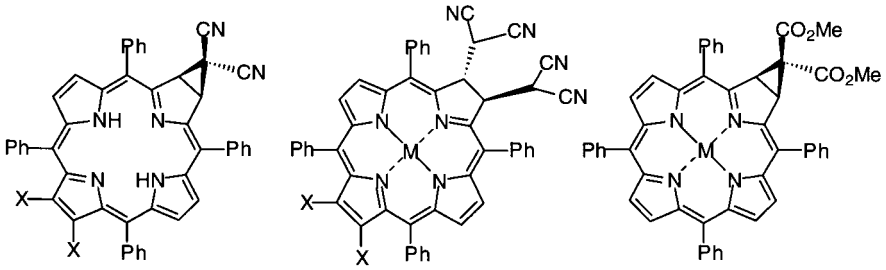


**2: X = H**
**3: X = Br**

**4: M = $H_2$; X = H**
**5: M = $H_2$; X = Br**
**6: M = Ni; X = H**

**7: M = Ni**
**11: M = $H_2$**

**Scheme 1.**

produces exclusively the tetraphenylisobacteriochlorin.[19] Core metalation also increases the reactivity of the pyrrole rings adjacent to the reduced pyrrole toward diimide reduction[15] or $OsO_4$ oxidation,[16] affording isobacteriochlorins.

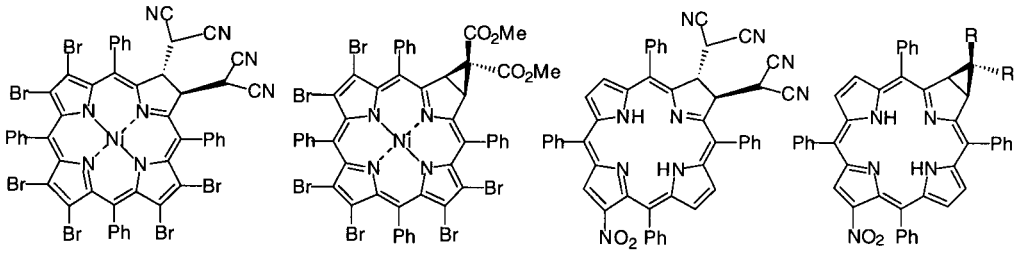
In preliminary work we showed that the fixed delocalization pathway of a chlorin allows regiospecific bromination to take place.[20] Indeed, the bromination of [2:3]-[di(cyano)-methano]-2,3-dihydro-5,10,15,20-tetraphenylporphyrin **2** with 2.5 equiv. of NBS in refluxing chloroform gave dibromochlorin **3** in 75% yield. Dropwise addition of 2.5 equiv. of bromine to **4** afforded the dibrominated product **5** in 91% yield (Scheme 1).

Alternatively, reaction of 2-nitro-12,13-dibromoTPP[13] with excess malononitrile and $K_2CO_3$ in THF at room temperature afforded the cyclopropyl derivative **3** in 65% yield. When the Michael addition was carried out at reflux temperature, the disubstituted chlorin **5** was obtained instead. The molecular structure of compound **5** was confirmed by X-ray crystallography.[20] The 2,3-substituents inhibited oxidation of the chlorin to the corresponding porphyrin even by such a strong oxidant as bromine. Attempts to regioselectively brominate the parent chlorin $H_2$(TPC) **1** with 2 equiv. of bromine or NBS (as another potential entry to 2,3-dibromotetraphenylporphyrin[13]) provided a mixture of brominated porphyrins.

Brief treatment of the nickel(II) chlorins **6** and **7** with excess bromine in chloroform afforded the desired hexabromochlorins **8** and **9**, providing a first route to dodecasubstituted dihydroporphyrins. The $^1$H NMR spectrum of **8** displayed two doublets, at $\delta$ 3.52 and 4.83 ppm, characteristic of the *trans* chlorin functionality,[1] and no peaks in the β-pyrrolic proton region. The molecular structure of compound **8** was confirmed by X-ray crystallography and displayed a significantly nonplanar conformation (Scheme 2).[20]

The $N_2O_4$ nitration of $H_2$(TPC) **1** in dichloromethane gave a mixture of $H_2$(TPP) and $H_2$(2-$NO_2$TPP). The 2-nitroporphyrin was certainly formed by oxidation of an intermediate β-nitrotetraphenylchlorin [which we did not attempt to isolate] as tetraphenylporphyrin does not react under these conditions, yielding solely the deactivated green dicationic species $[H_4TPP]^{2+}$. Nitration of hindered chlorin **4** was attempted and produced nitrochlorin **10** (as a racemic mixture) in 91% yield without any oxidation by-product being formed. The $^1$H NMR spectrum of **10** featured doublets at $\delta$ 4.22 and 4.24 for the malononitrile protons and doublets of doublets at $\delta$ 5.21 and 5.25 ppm for the reduced pyrrole β-protons. $N_2O_4$ nitration of **2** and **11** afforded β-nitrochlorins **12** and **13**, respectively, in excellent yields. As expected, nitration (as well as bromination) of the corresponding nickel(II) chlorins produced a regioisomeric mixture of nitrochlorins, confirming the need for metal-free compounds in order to ensure regioselectivity.

Our data suggest a reaction mechanism involving an ionic reaction pathway although electron transfer and radical mechanisms have been proposed.[21] The $N_2O_4$ nitration of porphyrinoids is fairly complex and might be similar to a nitrous acid catalyzed nitration.[21] Indeed, hydrolysis of $N_2O_4$ to HONO and $HONO_2$ has been shown to be catalyzed in dichloromethane by water and acids, and inhibited by non nucleophilic bases.[22] Upon $N_2O_4$ reaction with $H_2$(TPP), the porphyrin acted as a base which, upon protonation, cannot



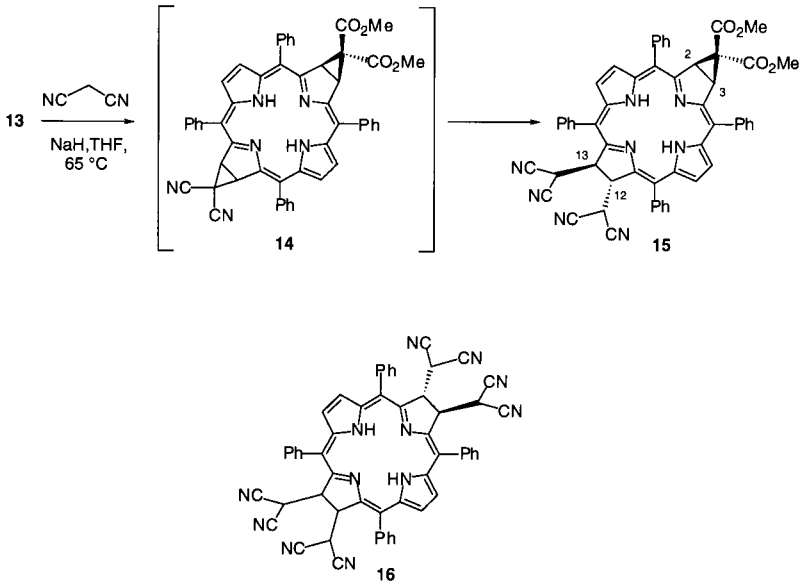
**8**

**9**

**10**

**12: R = CN**
**13: R = $CO_2$Me**

**Scheme 2.**




**Scheme 3.**

undergo further electrophilic attack of nitronium ions. Chlorins are weaker bases than the corresponding porphyrins, their diprotonation being not associated with marked resonance stabilization.[23] Under the $N_2O_4$ nitration conditions, they did not protonate and therefore underwent nitration at their nucleophilic sites in high yields. Again, stability towards oxidation was provided by the bulky 2,3-disubstituents, which also make these novel nitrochlorins (**10**,**12**) potential precursors of yet unknown 12,13-dione-2,3-dihydroporphyrins as building blocks for the synthesis of pyrazino-fused-oligoporphyrins.[7]

With these β-nitrochlorins in hand, we sought to extend the preparation of disubstituted chlorins by conjugate addition of carbon-centered nucleophiles to β-nitroporphyrins to provide access to highly functionalized bacteriochlorins. The conversion of tetraarylporphyrins into tetraarylchlorins causes red-shifts of their long-wavelength absorbance maxima, and further reduction to give bacteriochlorin analogues induces an even more pronounced optical effect. Use of these potentially therapeutic agents[24] has been limited, due to their low stability and because of the few synthetic methodologies available for their preparation. Hence, their syntheses could be achieved by application of all tetra-arylchlorin methodologies (diimide reduction, $OsO_4$ oxidation, pericyclic reactions) albeit in modest to low yields.[25] However, addition of malononitrile to a regioisomeric mixture of $[Cu(NO_2)_2TPP]$[7] led to extensive decomposition, but optical and mass spectrometry revealed that some tetra-functionalized bacteriochlorins were indeed formed. Synthesis of such bacteriochlorins was smoothly achieved by reacting nitrochlorin **13** with excess malononitrile in THF in the presence of NaH. Bacteriochlorin **15** was obtained in 77% yield as a racemic mixture (Scheme 3) (Fig. 2).

Michael addition of a malononitrile anion to the nitrochlorin and subsequent ring-closure by intramolecular displacement

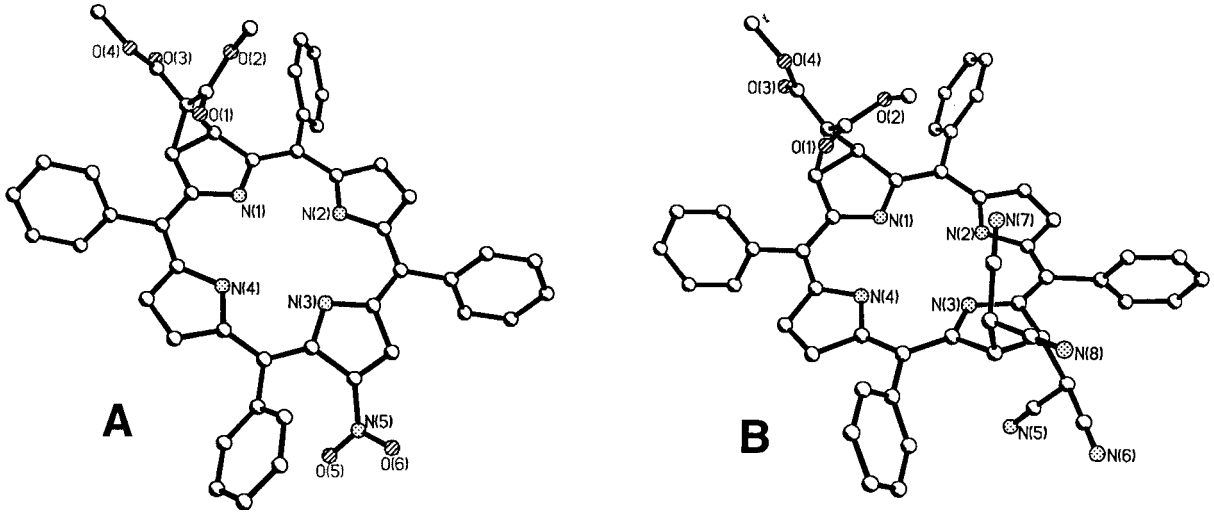



**Figure 2.** Molecular structures of compounds **13** (A) and **15** (B). Hydrogen atoms have been omitted for clarity.

of the nitro group led to a diastereomeric mixture of dicyclopropyl intermediates **14**. Owing to the remarkable stability of the methyl (cyclopropano 1,1-dicarboxylate) chlorins toward nucleophilic attack,[1] a selective opening of the dicyanocyclopropyl ring by a second equiv. of malononitrile gave bacteriochlorin **15**. In the case of nitrochlorin **10**, addition of malonitrile produced a diastereomeric mixture of tetra-*trans*-functionalized bacteriochlorins **16** (characterized by mass spectrometry). The faster ring-opening then previously observed in the case of dicyanocyclopropyl annulated-chlorins[1] made attempts to isolate the racemic intermediate cyclopropyl bacteriochlorin (at 0°C) unsuccessful.

The molecular structures of compounds **13** and **15** were confirmed by X-ray crystallography (Fig. 2). Whereas those compounds are formed as racemic mixtures, a spontaneous resolution occurred within individual single crystals as shown by the examination of their crystal packing.

## Conclusions

The stability of 2,3-disubstituted chlorins towards oxidation, the regioselectivity of their nitration and bromination reactions, and their ready availability make them attractive for additional bond constructions en route to larger systems. β-Nitrochlorins are excellent Michael-acceptors and therefore provide a novel bacteriochlorin synthesis via a key Michael addition of a carbon centered nucleophile to the nitroalkene subunit.

## Experimental

Melting points were measured on a Thomas/Bristoline microscopic hot stage apparatus and were uncorrected. Silica gel 60 (70–230 mesh, Merck) was used for column chromatography. $^1$H NMR spectra were obtained in $CDCl_3$ at 300 MHz using a General Electric QE300 spectrometer; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Elemental analyses were performed at the Midwest Microlab. Inc., Indianapolis, IN. Electronic absorption spectra were measured in dichloromethane solution using a Hewlett–Packard 8450A spectrophotometer. Mass spectra were obtained at the Mass Spectrometry Facility, University of California, San Francisco, CA. Chlorins **1**, **2**, **4, 6**, **7**, **11** and petroleum ether solutions of $N_2O_4$ were prepared according to the literature.[1,15]

### Crystal structure determinations[26]

**Compound 13.** Crystals were grown from $CH_2Cl_2$/cyclohexane. Crystal data for $[C_{49}H_{35}N_5O_6{\cdot}(CH_2Cl_2)]$ at 130 K (Cu $K_\alpha$ radiation, $\lambda$=1.54178 Å, $2\theta_{max}$=113°), monoclinic, space group $P2_1$, $a$=14.919(3), $b$=8.690(3), $c$=16.149(3) Å, β=96.05(2)°, $V$=2082(7) Å$^3$, $Z$=2, $R$=0.063, $wR$=0.207, $S$=1.009 for 2812 for 4320 reflections with $F>4.0\sigma(F)$ and 576 parameters. **Compound 15.** Crystals were grown from $CHCl_3$/*n*-hexane. Crystal data for $[C_{55}H_{38}N_8O_4{\cdot}(CHCl_3)]$ at 130 K (Cu $K_\alpha$ radiation, $\lambda$=1.54178 Å, $2\theta_{max}$=113°), monoclinic, space group $P2_1/n$, $a$=15.319(3), $b$=8.461(2), $c$=37.822(8) Å, β=92.43(3)°, $V$=4898(2) Å$^3$, $Z$=4, $R$=0.053, $wR$=0.132, $S$=1.087 for 5242 reflections with $F>2.0\sigma(F)$ and 648 parameters. An absorption correction was applied using XABS2;[27] extinction effects were disregarded. The structure solutions of compounds **13** and **15** were solved using direct methods and refined (based on $F^2$ using all independent data) by full matrix least squares methods (Siemens SHELXTL V. 5.02). Hydrogen atoms were included at calculated positions by using a riding model.

**2,3-Dihydro-[2:3]-[dicyanomethano]-12,13-dibromo-5,10,15,20-tetraphenylporphyrin 3.** *Route 1:* A light-shielded solution of NBS (131 mg, 0.738 mmol) and compound **2** (200 mg, 0.295 mmol) in $CHCl_3$ (100 mL) were refluxed under argon for 12 h. The mixture was filtered over a short silica plug (eluted with $CH_2Cl_2$) The brown band was collected and evaporated to dryness. Recrystallization from $CH_2Cl_2$/*n*-hexane afforded the title compound in 98% yield (241 mg).

*Route 2:* A suspension of $K_2CO_3$ (135 mg, 0.98 mmol) and malononitrile (77 μL, 1.22 mmol) in dry THF (5 mL) was refluxed under argon for 1 h. The reaction mixture was cooled to room temperature followed by the addition of 2-nitro-12,13-dibromotetraphenylporphyrin[13] (100 mg, 0.122 mmol) and then stirred for an additional 12 h. The reaction mixture was diluted with $CH_2Cl_2$, washed with water (3×) and evaporated to dryness. The crude product was purified by chromatography on a short silica gel column (eluted with $CH_2Cl_2$) and the brown band was collected. Recrystallization from $CH_2Cl_2$/*n*-hexane afforded **3** in 65% yield (66 mg). Mp >300°C; $\lambda_{max}$ 426 nm ($\epsilon$ 221 000), 528 (17 000), 596 (10 000), 646 (7000); $^1$H NMR $\delta$ −2.15 (br s, 2 H), 5.10 (s, 2 H), 7.60–8.16 (m, 20 H), 8.44 (dd, $J$=5.1 Hz, $J$=1.5 Hz, 2 H), 8.71 (dd, $J$=5.1 Hz, $J$=1.5 Hz, 2 H); MS (LSIMS) $m/z$ 823.1 ($MH^+$); Anal. Calcd for $C_{46}H_{28}Br_2N_6$: C, 67.01; H, 3.42; N, 10.19; Found: C, 67.24; H, 3.39; N, 9.95.

***trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-12,13-dibromo-5,10,15,20-tetraphenylporphyrin 5.** *Route 1:* A solution of $Br_2$ (8.7 μL, 0.168 mmol) in $CHCl_3$ (5 mL) was added dropwise over a 10 min period to a solution of *trans*-2,3-dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetraphenylporphyrin **4** (50 mg, 0.067 mmol), pyridine (3 drops), and $CHCl_3$ (25 mL) shielded from the light. The reaction mixture was allowed to stir for an additional 20 min followed by addition of $CH_2Cl_2$ (100 mL). The mixture was washed twice with saturated sodium bisulfite, evaporated to dryness and purified on a short silica gel column (eluted with $CH_2Cl_2$). Recrystallization from $CH_2Cl_2$/*n*-hexane afforded the title compound in 91% yield (55 mg).

*Route 2:* A suspension of $K_2CO_3$ (271 mg, 1.96 mmol) and malononitrile (155 μL, 2.45 mmol) in dry THF (10 mL) was refluxed under argon for 1 h. 2-Nitro-12,13-dibromotetraphenylporphyrin[13] (200 mg, 0.245 mmol) was added and the reaction mixture was refluxed for 8 h. The mixture was diluted with $CH_2Cl_2$, washed with water (3×), filtered and evaporated to dryness. The crude residue was purified by chromatography on a short silica gel column (eluted with $CH_2Cl_2$) and the brown band was collected. Recrystallization

from dichloromethane/*n*-hexane afforded **5** in 62% yield (137 mg). Mp >300°C; $\lambda_{max}$ 418 nm ($\epsilon$ 189 000), 522 (15 000), 592 (9000), 642 (13 000); $^1$H NMR $\delta$ −1.87 (br s, 2 H), 4.28 (d, *J*=3.9 Hz, 2 H), 5.31 (d, *J*=3.9 Hz, 2 H), 7.71–7.92 (m, 18 H), 8.21 (dd, *J*=5.1 Hz, *J*=1.8 Hz, 2 H), 8.28 (d, *J*=7.8 Hz, 2 H), 8.67 (dd, *J*=5.1 Hz, *J*=1.8 Hz, 2 H); MS (LSIMS) *m/z* 903.0 ($M^+$); Anal. Calcd for $C_{50}H_{30}Br_2N_8 \cdot 0.5H_2O$: C, 66.00; H, 3.44; N, 12.32; Found: C, 65.87; H, 3.53; N, 11.77.

**Nickel(II) *trans*-2,3-dihydro-2,3-bis(dicyanomethyl)-7,8,12,13,17,18-hexabromo-5,10,15,20-tetraphenyl-porphyrin 8.** A solution of $Br_2$ (100 μL, 1.94 mmol) in $CHCl_3$ (5 mL) was added dropwise over a 10 min period to a solution of nickel(II) *trans*-2,3-dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetraphenylporphyrin **6** (50 mg, 0.062 mmol) in $CHCl_3$ (25 mL) shielded from the light. The reaction mixture was allowed to stir for an additional 3 min before addition of $CH_2Cl_2$ (100 mL) and immediate washing with saturated sodium bisulfite solution (2×). The mixture was evaporated to dryness and purified on a short silica gel column (eluted with $CH_2Cl_2$). Recrystallization from $CH_2Cl_2$/*n*-hexane afforded the title compound in 88% yield (70 mg). Mp >300°C; $\lambda_{max}$ 440 nm ($\epsilon$ 144 000), 640 (33 000); $^1$H NMR $\delta$ 3.55 (d, *J*=5.1 Hz, 2 H), 4.95 (d, *J*=5.1 Hz, 2 H), 7.4–8.2 (m, 20 H); MS (LSIMS) *m/z* 1275.5 ($M^+$) Anal. Calcd for $C_{50}H_{24}Br_6N_8Ni$: C, 47.11; H, 1.90; N, 8.79; Found: C, 47.40; H, 2.03; N, 8.79.

**Nickel(II) 2,3-dihydro-[2:3]-[di(methoxycarbonyl)-methano]-7,8,12,13,17,18-hexabromo-5,10,15,20-tetraphenylporphyrin 9.** A solution of $Br_2$ (100 μL, 1.94 mmol) in $CHCl_3$ (5 mL) was added dropwise over a 10 min period to a solution of nickel(II) 2,3-dihydro-[2:3]-[bis(methoxycarbonyl)methano]-5,10,15,20-tetraphenylporphyrin **7** (50 mg, 0.063 mmol) in $CHCl_3$ (25 mL) shielded from the light. The reaction mixture was allowed to stir for 5 min before addition of $CH_2Cl_2$ (100 mL) and immediate washing with saturated sodium bisulfite (2×). The mixture was evaporated to dryness and purified on a short silica gel column (eluted with $CH_2Cl_2$). Recrystallization from $CH_2Cl_2$/*n*-hexane afforded the title compound in 84% yield (67 mg). Mp >300°C; $\lambda_{max}$ 444 nm ($\epsilon$ 144 000), 640 (40 000); $^1$H NMR $\delta$ 2.32 (s, 3 H), 3.64 (s, 3 H), 4.55 (s, 2 H), 7.55–7.80 (m, 20 H); MS (LSIMS) *m/z* 1274.0 ($M^+$); Anal. Calcd for $C_{49}H_{28}Br_6N_4Ni$: C, 46.16; H, 2.21; N, 4.39; Found: C, 45.83; H, 1.95; N, 4.51.

***trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-12-nitro-5,10,15,20-tetraphenylporphyrin 10.** A suspension of *trans*-2,3-dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetraphenylporphyrin **4** (5.0 g, 6.72 mmol) in dichloromethane (500 mL) was stirred vigorously. The $N_2O_4$ solution was added dropwise over 2 h. Monitoring by TLC (silica gel, $CH_2Cl_2$/cyclohexane 1:2) was crucial to avoid over-nitration. The mixture was then evaporated to 50 mL and the product precipitated by addition of methanol to give the title compound in 78% yield (4.14 g). Mp >300°C; $\lambda_{max}$ 432 nm ($\epsilon$ 167 000), 536 (21 000), 588 (18 000), 636 (14 000); $^1$H NMR $\delta$ −1.49 (s, 1 H), −1.48 (s, 1 H), 4.22 (d, *J*=3.9 Hz, 1 H), 4.24 (d, *J*=3.9 Hz, 1 H), 5.21 (dd, *J*=3.9 Hz, *J*=1.2 Hz, 1 H), 5.25 (dd, *J*=3.9 Hz, *J*=1.2 Hz, 1 H), 7.5–8.3 (m, 20 H), 8.60 (d, *J*=4.8 Hz, 1 H), 8.62 (d, *J*=4.8 Hz, 1 H), 8.66 (s, 1 H), 8.68 (d, *J*=4.8 Hz, 1 H), 8.70 (dd, *J*=4.8 Hz, 1 H); MS (LSIMS) *m/z* 790.6 ($M^+$); Anal. Calcd for $C_{50}H_{31}N_9O_2$: C, 76.03; H, 3.96; N, 15.96. Found: C, 75.77; H, 4.08; N, 15.74.

**2,3-Dihydro-[2:3]-[dicyanomethano]-12-nitro-5,10,15,20-tetraphenylporphyrin 12.** A suspension of 2,3-dihydro-[2:3]-[dicyanomethano]-5,10,15,20-tetraphenylporphyrin **2** (1 g, 1.47 mmol) in $CH_2Cl_2$ (100 mL) was stirred vigorously. The $N_2O_4$ solution was added dropwise over 2 h. Monitoring by TLC (silica gel, $CH_2Cl_2$/cyclohexane 1:2) was important to avoid over-nitration. The mixture was filtered and the filtrate was then reduced to 20 mL and the product was precipitated by addition of methanol to give the title compound in 77% yield (819 mg). Mp >300°C; $\lambda_{max}$ 436 nm ($\epsilon$ 165 000), 538 (21 000), 594 (16 000), 642 (10 000); $^1$H NMR $\delta$ −1.79 (br s, 2 H), 5.07 (s, 2 H), 7.7–8.3 (m, 20 H), 8.61 (d, *J*=4.8 Hz, 1 H), 8.64 (d, *J*=4.8 Hz, 1 H), 8.69 (s, 1 H), 8.72 (d, *J*=4.8 Hz, 1 H), 8.75 (d, *J*=4.8 Hz, 1 H); MS (LSIMS) *m/z* 724.3 ($M^+$); Anal. Calcd for $C_{47}H_{29}N_7O_2 \cdot 2H_2O$: C, 74.30; H, 4.38; N, 12.90. Found: C, 73.92; H, 4.20 N, 12.50.

**2,3-Dihydro-[2:3]-[di(methoxycarbonyl)methano]-12-nitro-5,10,15,20-tetraphenylporphyrin 13.** A suspension of 2,3-dihydro-[2:3]-[di(methoxycarbonyl)methano]-5,10,15,20-tetraphenylporphyrin **11** (7 g, 9.41 mmol) in $CH_2Cl_2$ (700 mL) was stirred vigorously. The $N_2O_4$ solution was added dropwise over 2 h and monitored by TLC (silica gel, $CH_2Cl_2$/cyclohexane 1:2). The mixture was filtered and the filtrate was then evaporated to a volume of 50 mL and the product was precipitated by addition of methanol to give the title compound in 75% yield (5.58 g). Mp 227–230°C; $\lambda_{max}$ 440 nm ($\epsilon$ 160 000), 540 (18 000), 596 (15 000), 644 (9000); $^1$H NMR $\delta$ −1.68 (br s, 2 H), 2.45 (s, 3 H), 3.86 (s, 3 H), 4.75 (s, 2 H), 7.7 –8.4 (m, 20 H), 8.66 (d, *J*=4.5 Hz, 1 H), 8.68 (d, *J*=4.5 Hz, 1 H), 8.75 (s, 1 H), 8.76 (d, *J*=4.5 Hz, 1 H), 8.78 (d, *J*=4.5 Hz, 1 H); MS (LSIMS) *m/z* 790.3 ($M^+$); Anal. Calcd for $C_{49}H_{35}N_5O_6 \cdot 0.5H_2O$: C, 73.67; H, 4.54; N, 8.77. Found: C, 73.68; H, 4.65; N, 8.75.

***trans*-2,3-*cis*-12,13-Tetrahydro-2,3-bis(dicyanomethyl)-[12:13]-[di(methoxycarbonyl)methano]-5,10,15,20-tetraphenylporphyrin 15.** A mixture of $K_2CO_3$ (473 mg, 3.43 mmol) and malononitrile (215 μL, 3.43 mmol) in dry THF (15 mL) was refluxed for 1 h under argon. The reaction mixture was cooled to room temperature and porphyrin **13** (300 mg, 0.343 mmol) was added to the mixture. The temperature was slowly increased to 65°C and the mixture was allowed to stir for 6 h until all the starting material had disappeared (monitored by TLC). The reaction mixture was diluted with $CH_2Cl_2$ (200 mL), washed with water (3×), filtered and evaporated to dryness. The crude chlorin was purified by chromatography on a short silica gel column (eluted with $CH_2Cl_2$/cyclohexane 2:1) and the major red band was collected. Recrystallization from $CH_2Cl_2$/*n*-hexane afforded the title porphyrin in 77% yield (230 mg). Mp 268–270°C; $\lambda_{max}$ 396 nm ($\epsilon$ 230 000), 534 (45 000), 700 (83 000); $^1$H NMR $\delta$ −2.31 (br s, 2 H), 2.56 (s, 3 H), 3.85 (s, 3 H), 4.30 (d, *J*=3.9 Hz, 1 H), 4.32 (d, *J*=3.9 Hz, 1 H), 4.70 (s, 2 H), 5.25 (m, 2 H), 7.6–7.9 (m, 16 H), 8.14–8.25 (m, 4 H), 8.32–8.38 (m, 2H), 8.47 (d, *J*=7.5 Hz, 1 H),

8.65 (d, $J$=7.5 Hz, 1 H); MS (LSIMS) $m/z$: 874 ($M^+$); Anal. Calcd for $C_{55}H_{38}N_8O_4 \cdot 0.5H_2O$: C, 74.73; H, 4.45; N, 12.68. Found: C, 74.48; H, 4.37 N, 12.62.

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