# Dihydroporphyrin Synthesis: New Methodology†

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Selective formation of *trans*-nitrochlorins **16**−**19**, cyclopropylchlorins **14**, **15**, and **20**−**23**, or functionalized *trans*-chlorins **5**−**13** by reaction of 2-nitro-5,10,15,20-tetraphenylporphyrin **1** with "active" methylene compounds such as malonates or malononitrile in the presence of base has been achieved. Reaction control is accomplished via sequential Michael additions, followed by *intra*-molecular nucleophilic displacement of a secondary nitro group. Steric as well as thermodynamic effects have been found to govern the selectivity of product formation. Ambient temperature or bulky carbanion substituents lead to nitrochlorins and/or cyclopropylchlorins. Increased reaction temperatures, combined with sterically less encumbered carbanion substituents, favor the formation of disubstituted *trans*-chlorins. Nucleophilic ring-opening reactions of cyclopropyl-derivative **14** afford disubstituted *trans*-chlorin products **5** and **25** and provide additional mechanistic evidence for the intermediacy of the cyclopropylchlorin. Use of porphyrins with modified *meso*-phenyl positions illustrates the generality of this methodology and allows a novel method for the preparation of a wide range of reduced porphyrins, which may find application in fields such as the photodynamic therapy (PDT) of cancer.

## Introduction

Chemical transformations of natural and synthetic porphyrin macrocycles and their peripheral substituents have been an area of intense interest for a number of years. Development of new methodologies to functionalize porphyrins and their derivatives can provide a variety of new compounds that could otherwise only be obtained by total synthesis.[1] Functionalization at the $\beta$-pyrrolic positions of tetrapyrroles is of particular interest due to the potential for additional bond construction as well as the direct alteration of the properties of the porphyrin macrocycle.

Previous methods for the preparation of reduced porphyrins (dihydroporphyrins) have allowed the synthesis of long-wavelength absorbing chromophores ($\lambda_{max}$ > 630 nm) that show potential application to the photodynamic therapy (PDT) modality for treatment of cancer.[2] This therapy makes use of localized, light-absorbing photosensitizer drugs for the treatment of malignant tumors.[3] For effectiveness of this treatment, it is important that the photosensitizer exhibit a strong long-wavelength absorption in order to minimize the photosensitizer dosage, reduce side effects, and achieve maximal tissue penetration with minimal light scattering. The conversion of tetraarylporphyrins into the corresponding tetraarylchlorins is known to increase the long-wavelength absorbance (>600 nm);[4] however, a general synthetic methodology that would produce a range of highly functionalized dihydroporphyrins is still needed to facilitate in-depth studies of the physical and structural properties of these photosensitizers.

Presently, effective techniques for the generation of functionalized *meso*-tetraarylchlorins (e.g., 5,10,15,20-tetraphenylchlorin, TPC) from *meso*-tetraphenylporphyrins (TPP) are limited to a small number of methods such as the diimide reduction procedure described by Whitlock et al. in 1969.[4] Bonnett et al. recently made use of this method to prepare a series of *meso*-tetrakis-(hydroxyphenyl)chlorins,[5] which show promise as second-generation PDT sensitizers.[6] Callot has also demonstrated that carbenes can be used to functionalize the TPP macrocycle, affording moderate yields of cyclopropanyl-annulated tetraphenylchlorins[7] that are similar to the compounds **14** and **15** described in the present paper. More recently, *meso*-arylporphyrins have been shown to act as dienophiles in the presence of *o*-benzoquinodimethane (a highly reactive diene generated in situ by exclusion of $SO_2$ from a sulfone) to produce chlorins, bacteriochlorins, and naphthochlorins.[8] Another route to naphthochlorins involves acid-catalyzed intramolecular

† Dedicated to Professor Wolfhart Rüdiger on the occasion of his 65th birthday.

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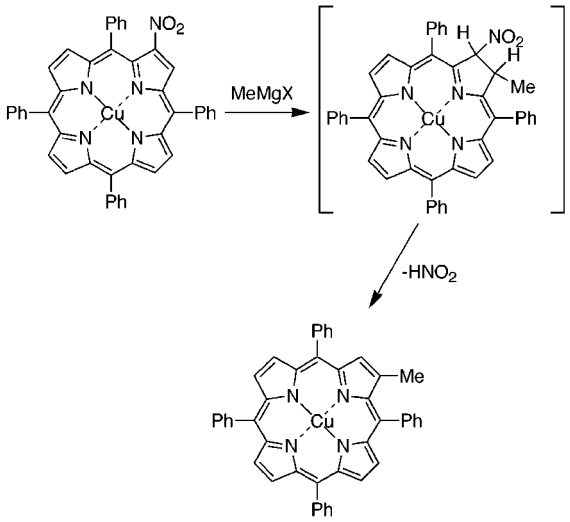
**Scheme 1. Synthesis of Cu(II) 2-Methyl-5,10,15,20-tetraphenylporphyrin from the Cu(II) 2-Nitro Analogue**




cyclization of Ni(II) 2-vinyltetraphenylporphyrin.[9] Vicinal $\beta,\beta'$-dihydroxylation of tetraphenylchlorin and tetraphenylporphyrin suffers from the low reactivity of TPP and the stoichiometric use of expensive and toxic $OsO_4$.[10]

2-Nitro-*meso*-tetraarylporphyrins are versatile starting materials for efficient incorporation of functionality into the $\beta$-pyrrolic positions of porphyrins through nitrochlorin intermediates.[11−13] These intermediates are unstable and readily eliminate nitrous acid to regenerate $\beta$-substituted porphyrins. For example, conjugate addition of Grignard and organolithium reagents to 2-nitrotetraphenylporphyrins proceeds through 2-alkyl-2,3-dihydro-3-nitroporphyrin (chlorin) intermediates. Elimination of nitrous acid affords 2-alkyltetraphenylporphyrin,[11] as outlined in Scheme 1. Reaction of metallo-2-nitro-5,10,15,20-tetraphenylporphyrins with sodium borohydride produces 2,3-dihydro-2-nitro-5,10,15,20-tetraphenylchlorin.[12] This chlorin intermediate can either eliminate nitrous acid to regenerate the porphyrin or undergo reductive denitration with tributyltin hydride and AIBN to produce 2,3-dihydroporphyrin. Reaction of copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin **2** with sodium methoxide affords the corresponding 2,2-dimethoxy-3-nitrochlorin via a nucleophilic-substitution nucleophilic-addition sequence.[13] Upon denitration, a blue-green 2,2-dimethoxychlorin eliminates methanol to afford the corresponding 2-methoxyporphyrin.

Although these routes involve chlorin intermediates, the preparation of stable functionalized dihydroporphyrin systems from nitroporphyrins has yet to be developed. In the present paper we report the convenient preparation of such novel dihydroporphyrins, discuss the versatility of the reaction, and describe the probable mechanism of formation of the products. This work stems from our recent synthesis of pyrroloporphyrins,[14] which involved reactions of metallo-2-nitro-5,10,15,20-tetraphenylporphyrin (2-$NO_2$TPP) with isocyanoacetates. Not only did this reaction provide the desired pyrroloporphyrin product but a Zn(II) cyclopropylchlorin was also isolated. These results prompted our development of the new methodology for preparation of dihydroporphyrins reported herein, based on the conjugate addition of carbon-centered nucleophiles to nitroalkenes. This approach offers the means to selectively generate carbon−carbon bonds for the preparation of novel highly functionalized chlorin systems by reaction of "active" methylene compounds with readily available $\beta$-nitroporphyrin precursors.

## Results and Discussion

A preliminary report[15] revealed the structure of two functionalized chlorin compounds prepared by the addition of "active" methylene compounds (characterized by X-ray crystallography). To extend this work, we have examined the reactivity of both metalated and metal-free 2-$NO_2$TPP with a variety of methylene compounds, bases, and solvents. In contrast to previous reports,[13] we find that metal-free nitroporphyrins can be used as substrates for nucleophilic reactions under basic conditions, without formation of a deactivated porphyrin anion.

**Reactions of 2-Nitro-5,10,15,20-tetraphenylporphyrin with Malononitrile and Alkylcyanoacetates.** Reaction of 2-nitro-5,10,15,20-tetraphenylporphyrin **1** with small methylene compounds, such as malononitrile and alkyl cyanoacetates, produced two chlorin products: cyclopropylchlorins and disubstituted functionalized *trans*-chlorins (Scheme 2).

At room temperature (~22 °C), reaction between **1** and malononitrile in the presence of $K_2CO_3$ produced cyclopropylchlorin **14** in 68% yield. A minor second product with higher polarity was also observed and identified as the functionalized *trans*-chlorin **5** (9% yield). Interestingly, by increasing the reaction temperature to 65 °C, only the *trans*-chlorin **5** was produced (71% yield).

The structures of the functionalized dihydroporphyrins **5** and **14** were assigned on the basis of their $^1$H NMR spectra. The less polar cyclopropylchlorin **14** displayed a singlet at $\delta$ 5.15 characteristic of the reduced $\beta$-pyrrolic protons, as well as two doublets ($\delta$ 8.55 and 8.75) and an additional singlet ($\delta$ 8.54) in the $\beta$-proton region. The mass spectrum of compound **14** showed the parent ion peak at 679.3 ($MH^+$). The $^1$H NMR spectrum of the more polar product **5** revealed a doublet at $\delta$ 4.35 corresponding to the malononitrile protons and a doublet at $\delta$ 5.38 corresponding to the reduced pyrrole $\beta$-protons (C2 and C3). The mass spectrum of the disubstituted chlorin showed the appropriate parent ion peak at 744.3 ($M^+$). The electronic absorbances for both compounds are characteristic of metal-free chlorins, with a long-wavelength peak at $\lambda_{max} = 646$ nm.

Stereoselectivity was observed with unsymmetric methylene compounds such as alkyl cyanoacetates. Reaction of **1** with methyl cyanoacetate ($K_2CO_3$, THF, 14

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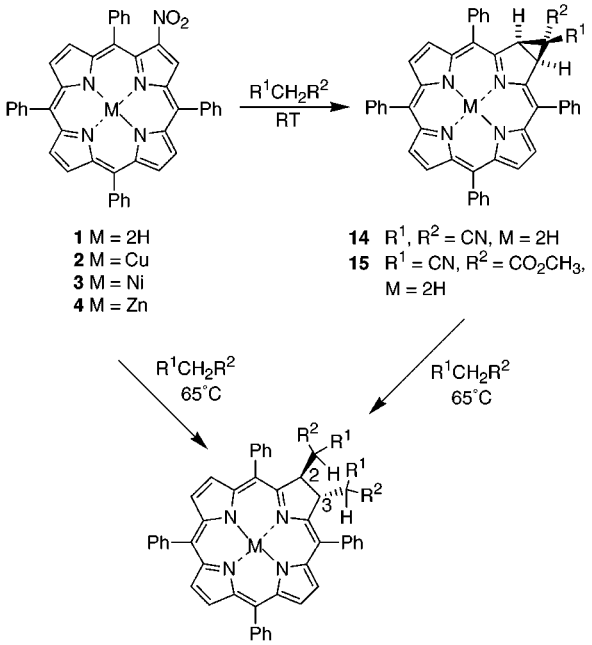
**Scheme 2. Synthesis of Cyclopropylchlorins and Functionalized *trans*-Chlorins via Employment of Carbanions with Small Methylene Substituents**

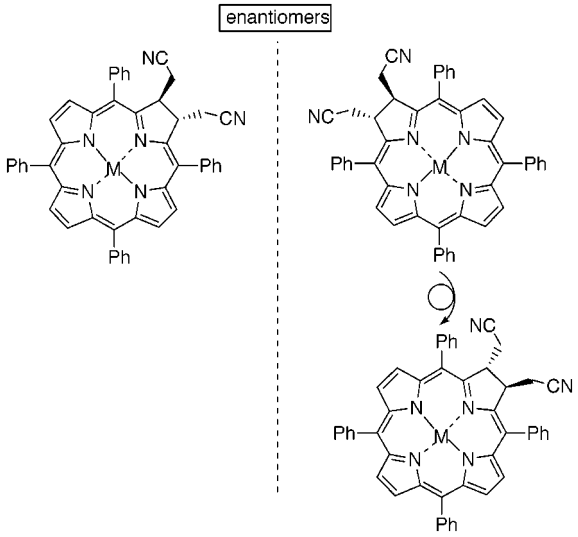



h) at room temperature produced the *exo*-cyclopropyl product **15** exclusively. A steric effect is thought to control the selective *exo* orientation of the bulkier group upon ring closure. Evidence for such stereoselectivity is revealed in the $^1$H NMR spectrum, which showed only one singlet at $\delta$ 3.93, corresponding to the ester methoxyl moiety.

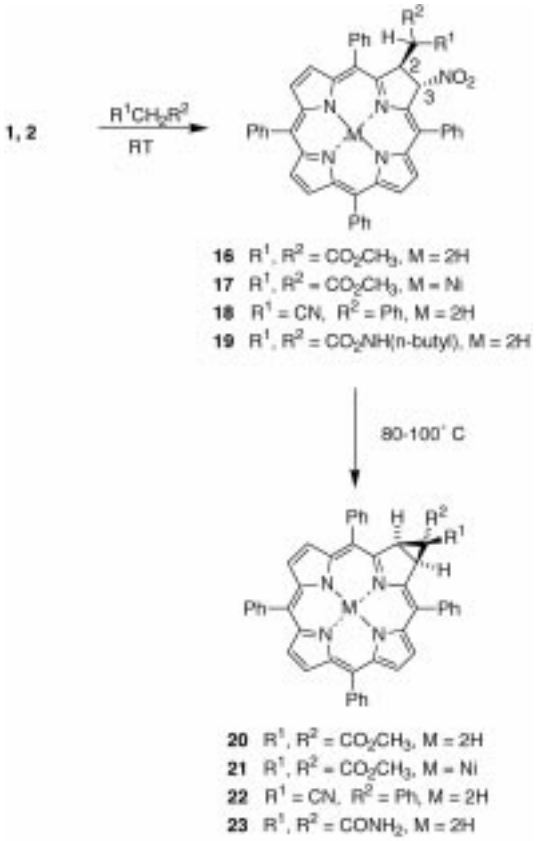
In contrast, addition of alkyl cyanoacetates to both **1** and **3** ($K_2CO_3$, THF) at 65 °C afforded a mixture of *trans*-chlorin diastereomers **10**−**13**. The $^1$H NMR spectrum indicated a mixture of four enantiomeric pairs of compounds. Decarboxymethylation of **10** with NaCl in wet DMSO at 140 °C yielded **9**, quantitatively and as a racemate. The reduced pyrrole subunit and its cyanomethyl substituents exhibit an ABX system in the $^1$H NMR spectrum, indicating that this compound is both chiral and $C_2$ symmetric (absence of mirror or inversion symmetry; Scheme 3).[16] The chirality of the functionalized *trans*-chlorin was further confirmed by X-ray crystallography data of compound **6**. Indeed, both enantiomers were found to be equally present in the crystal packing.[15] Compound **9** can be conveniently prepared in 75% yield by carrying out a one-pot sequential Michael addition, nitro substitution, and decarboxymethylation in DMSO.

**Reactions of 2-Nitro-5,10,15,20-tetraphenylporphyrin with Bulky "Active" Methylene Compounds.** Reaction of 2-$NO_2$TPP **1** with bulky methylene compounds, such as dimethyl malonate, afforded nitrochlorins and cyclopropylchlorins, but did not lead to disubstituted *trans*-chlorins (Scheme 4). At room temperature, reaction between **1** and dimethyl malonate in the presence of $K_2CO_3$ afforded the functionalized nitrochlorin **16** (66% yield). The nitrochlorin was surprisingly stable to warming, chromatography, and even mass spectral analysis. Earlier reports indicated that such stability of nitrochlorins was not observed, but rather elimination of $HNO_2$ and decomposition to the porphyrin occurred.[11,12] By increasing the temperature to 100 °C, reaction

**Scheme 3. Enantiomerism in *trans*-2,3-Bis(cyanomethyl)chlorins**




**Scheme 4. Synthesis of Nitrochlorins and Cyclopropylchlorins via Employment of Carbanions with Bulky Methylene Substituents**

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between **1** and dimethyl malonate ($K_2CO_3$, DMSO) afforded the cyclopropyl product **20** in 77% yield. Ni(II) 2-$NO_2$TPP **3** reacted similarly with dimethyl malonate to produce the metalated nitrochlorin **17** at room temperature and the metalated cyclopropyl analogue **21** at 100 °C.

The structures of nitrochlorins **16** and **17** were assigned on the basis of $^1$H NMR and mass spectral data. The $^1$H NMR spectrum of **16** showed singlets at $\delta$ 2.40 and 3.71 for the *endo* and *exo* methyl ester protons as well as doublets at $\delta$ 4.05 and 5.76 corresponding to the malonate proton and the C2 proton alpha to the nitro group, respectively. Similar to the metal-free nitrochlorin **16**, the $^1$H NMR spectrum of the Ni(II) nitrochlorin **17** revealed two doublets coupled to each other at $\delta$ 3.51 (malonate proton) and 5.40 (C2 proton). In addition, a singlet at $\delta$ 7.02 was observed, corresponding to the proton geminal to the nitro group (C3). Interestingly, there is an absence of coupling between the resonances at $\delta$ 5.40 and 7.02, thereby establishing the *trans* relationship of the substituents. Mass spectral analysis of **16** revealed a parent peak at *m*/*z* 792.3 and a fragment peak at 745.3, corresponding to the loss of $HNO_2$. The electronic absorbances of both compounds are characteristic of metal-free and metallochlorins, with long-wavelength peaks at $\lambda_{max}$ = 646 nm for **16** and 608 nm for **17**.

Use of benzylcyanide as the "active" methylene compound in a reaction with **1** at room temperature also produced a nitrochlorin **18**. Increasing the reaction temperature to 100 °C afforded the cyclopropylchlorin **22**. Reaction of **1** with di-*n*-butyl malonamide yielded nitrochlorin **19**, but only after extended reaction times (36 h) at elevated temperatures (100 °C). The corresponding cyclopropyl product was not observed. When malonamide was used in a reaction with **1** (50 h, 100 °C), the cyclopropylchlorin **23** was obtained. Unfortunately, the more rigorous conditions required to obtain the chlorin products reduced the yields of **19** and **23** and made product isolation more difficult.

**Central Metal Ion Effects.** Reaction of Cu(II), Ni(II), or Zn(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**2**−**4**, respectively) with malononitrile in the presence of base at 65 °C produced functionalized *trans*-chlorins **6**−**8** in similar yields (68, 70, and 63%, respectively). Reaction times varied from 3 h for the copper and nickel porphyrins to 24 h for the zinc porphyrin. Treatment of Ni(II) 2-nitro-5,10,15,20-tetraphenylporphyrin **3** with malononitrile at room temperature afforded exclusively the *trans*-chlorin **7**. This result is in direct contrast to the product distribution observed for the reaction of metal-free 2-$NO_2$TPP **1** at room temperature, which yielded mainly the cyclopropyl product **14**. Similarly, reaction of **3** with methyl cyanoacetate at room temperature afforded a diastereomeric mixture of the functionalized *trans*-chlorins **11**. Zn(II) 2-nitro-5,10,15,20-tetraphenylporphyrin **4** was found to be unreactive under the same conditions at room temperature, suggesting that moderately electronegative ions such as Cu(II) and Ni(II) facilitate nucleophilic attack of "active" methylene compounds, whereas less electronegative ions such as Zn(II) hinder such reactions. This pattern of 2-nitrometalloporphyrin reactivity has previously been observed with oxyanions[13] and is in good agreement with the results presented here.

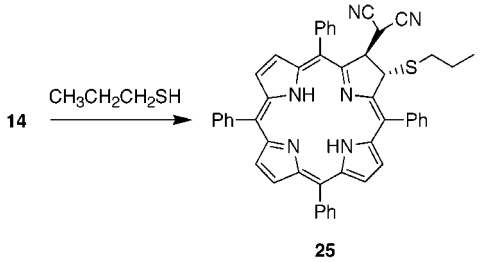
**Table 1. Effect of Reaction Temperature on Chlorin Formation: Method A, Malononitrile (10 equiv)/$K_2CO_3$/THF; Method B, Dimethyl Malonate (10 equiv)/$K_2CO_3$/THF**

| starting compound (method) | time (h) | temp (°C) | *trans*-chlorin (% yield) | cyclopropyl-chlorin (% yield) | nitro-chlorin (% yield) |
|---|---|---|---|---|---|
| **1** (A) | 12 | 22 | **5** (9) | **14** (68) | |
| **1** (A) | 10 | 35 | **5** (35) | **14** (41) | |
| **1** (A) | 7.5 | 50 | **5** (48) | **14** (27) | |
| **1** (A) | 6 | 65 | **5** (71) | | |
| **2** (A) | 8 | 22 | **7** (70) | | |
| **2** (A) | 3 | 65 | **7** (65) | | |
| **1** (B) | 12 | 22 | | **20** (4) | **16** (69) |
| **1** (B) | 5 | 80 | | **20** (46) | **16** (28) |
| **1** (B) | 3 | 100 | | **20** (72) | |

**Temperature Effects.** The selective formation of *trans*-nitrochlorins, cyclopropylchlorins, or functionalized *trans*-chlorins is highly temperature-dependent. We found that careful control of reaction temperature and close monitoring of product formation provided the desired product in good yield (Table 1). Temperature effects were studied in reactions of 2-$NO_2$TPP **1** with malononitrile (method A, Table 1) at 22, 35, 50, and 65 °C. At 22 °C, after 12 h (when all starting material had been consumed), 68% of the cyclopropylchlorin **14** and 9% of the functionalized *trans*-chlorin **5** were isolated. When these reactions were run at temperatures above room temperature, the combined yields of **14** and **5** were similar to the yields at room temperature, but the amount of **5** had increased with elevating temperature. In refluxing THF, only the functionalized *trans*-chlorin **5** was obtained.

Temperature effects were also studied in reactions of 2-$NO_2$TPP **1** with a bulky methylene compound, dimethyl malonate (method B, Table 1), at 22, 80, and 100 °C. Lower temperatures favored the formation of the nitrochlorin **16**, whereas at 80 °C, a mixture of the nitrochlorin **16** and cyclopropanylchlorin **20** was obtained. Increasing the temperature to 100 °C produced the cyclopropylchlorin **20** exclusively.

**Cyclopropyl Ring Opening.** To further understand the mechanism of these reactions cyclopropylchlorins **14** and **20** were subjected to nucleophilic attack in order to promote ring opening. Treatment of **14** with 10 equiv of malononitrile, with $K_2CO_3$ in THF at 65 °C, led to ring cleavage, affording the *trans*-chlorin **5** quantitatively. Use of 1-thiopropane afforded the highly functionalized product **25** in 82% yield. However, subjecting **20** to similar

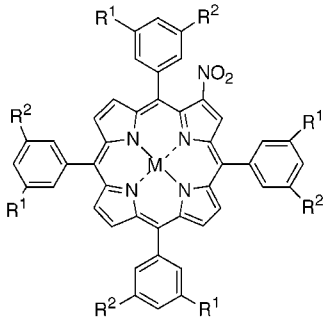



**25**

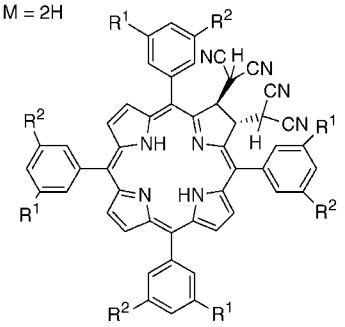
conditions (malononitrile, $K_2CO_3$, DMSO, 100 °C or 1-thiopropane, NaH, THF) did not result in ring opening, most likely due to steric hindrance by the bulky cyclopropyl substituents.

**Reactions of *meso*-Tetra[3,5-di(*tert*-butyl)phenyl]-2-nitroporphyrin and *meso*-Tetrakis(*m*-methoxyphenyl)-2-nitroporphyrin with "Active" Methylene**

**Compounds.** The generality of this methodology was investigated by modifying *meso*-aryl substituents. Nitration of Cu(II) *meso*-tetra[3,5-di(*tert*-butyl)phenyl]porphyrin **26** with dinitrogen tetraoxide ($N_2O_4$), followed by demetalation in $H_2SO_4$, provided *meso*-tetra[3,5-di(*tert*-butyl)phenyl]-2-nitroporphyrin **28**. As expected, reaction of **28** with malononitrile and $K_2CO_3$ in THF at 65 °C produced the functionalized *trans*-chlorin **30** (in 78% yield). Likewise, reaction of *meso*-tetra(*m*-methoxyphenyl)-2-nitroporphyrin **29** (prepared by similar nitration and demetalation procedures) with malononitrile afforded the *trans*-chlorin **31** in 64% yield. Modification of the six remaining chlorin $\beta$ positions by exhaustive bromination provided access to highly nonplanar dodecasubstituted chlorins for the first time.[17]



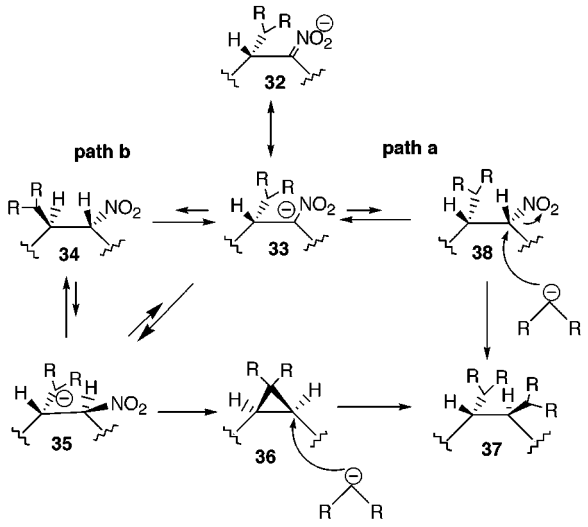
**26** $R^1$, $R^2$ = t-butyl, M = Cu
**27** $R^1 = OCH_3$, $R^2$ = H, M = Cu
**28** $R^1$, $R^2$ = t-butyl, M =2H
**29** $R^1 = OCH_3$, $R^2$ = H, M = 2H



**30** $R^1$, $R^2$ = t-butyl
**31** $R^1 = OCH_3$, $R^2$ = H

**Mechanism.** Two primary mechanisms may describe the reactions between "active" methylene compounds and either metal-free or metallo 2-nitro-5,10,15,20-tetraphenylporphyrins to produce the observed dihydroporphyrins. After initial Michael addition of a carbanion at the $\beta$-pyrrolic position adjacent to the carbon bearing the nitro group, the resulting nitronate **33** undergoes a protonation step via either path a or path b (Scheme 5), or perhaps a combination of these two pathways. In path a, protonation of nitronate **33** from the less crowded face would lead to the unlikely formation of the crowded stereoisomer, *cis*-nitrochlorin **38**. The nitro group, being then pseudobenzylic, could function as an electrophile to yield, via an *inter*molecular displacement of the nitro group by a second equivalent of carbanion, *trans*-chlorin **37** (as a racemic mixture). However, such intermolecular nucleophilic substitution of a nitro group is extremely rare. Indeed, reactions of primary and secondary nitroalkanes with base have been shown to result in the formation of a nitronate anion,[18] therefore preventing the nitro group from serving as a leaving group.

**Scheme 5. Possible Mechanistic Pathways for Formation of All Three Chlorin Products: Nitrochlorins, Cyclopropylchlorins, and Disubstituted *trans*-Chlorins**




A more feasible mechanistic route would rely on the formation of the less hindered *trans*-nitrochlorin, **34** (Scheme 5), followed by deprotonation to form **35**. Perhaps even more likely would be initial formation of **35** via intramolecular proton exchange, as illustrated in the conversion of **33** to **35**. Ring closure via intramolecular displacement of the nitro group would then produce the cyclopropylchlorin **36**. This type of *intra*molecular displacement of a nitro group has been reported previously by Tamura et al.[19] during cyclopropanation of α-nitroalkenes with cyanoacetate and malononitrile. The stable cyclopropyl intermediate **36** either can be isolated or can undergo a ring-opening reaction with a second equivalent of nucleophile to produce the functionalized disubstituted *trans*-chlorin **37**.

Support for path b (Scheme 5) was obtained by isolation, characterization, and further reactions of certain key intermediates. Heating nitrochlorin **16** in the presence of base promoted ring closure and intramolecular nitro group displacement to produce the cyclopropylchlorin **20**. Additionally, nucleophilic ring opening of cyclopropylchlorin **14** afforded disubstituted *trans*-chlorin products **5** and **25**. These results suggest that the functionalized *trans*-chlorins are obtained via a cyclopropylchlorin intermediate (path b) and not through an *inter*molecular displacement of a nitro group as illustrated by path a.

It can thus be seen that Michael addition of a carbanion at the $\beta$-pyrrolic position adjacent to the carbon bearing the nitro group followed by *intra*molecular proton exchange, *intra*molecular nitro group displacement, and ring opening of the cyclopropyl intermediate can account for formation of all three chlorin products: nitrochlorins, cyclopropylchlorins, and disubstituted *trans*-chlorins.

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## Conclusions

New methodology based on the conjugate addition of carbon-centered nucleophiles with nitroalkenes as a new route to the selective preparation of a variety of 5,10,15,20-tetraaryldihydroporphyrin compounds is reported. Product distribution can be controlled by altering the size of the carbanion substituents or varying reaction time and/or temperature, as well as the absence or presence of a chelated metal in the starting material. Increased temperatures, combined with smaller carbanion substituents, favor the formation of the disubstituted *trans*-chlorins, whereas ambient temperatures or bulky carbanion substituents afford *trans*-nitrochlorins and cyclopropylchlorins. Furthermore, it is shown that this methodology can be adapted to nitrotetraphenylporphyrins with other *meso*-phenyl substituents, thereby providing a general method for the preparation of new sensitizers for PDT of tumors.

## Experimental Section

General experimental conditions were as described previously.[20] Mass spectra were obtained at the University of California, San Francisco, Mass Spectrometry Resource. Tetraarylporphyrins were prepared via condensation of an aldehyde (benzaldehyde, 3,5-di-*tert*-butylbenzaldehyde,[21] or 3-methoxybenzaldehyde) with pyrrole in refluxing propionic acid according to Adler and Longo.[22]

**Nitration of Cu(II) Tetraarylporphyrins. Preparation of $N_2O_4$.** $N_2O_4$ gas was prepared by dropwise addition of concentrated $HNO_3$ (150 mL) from a dropping funnel into a 500 mL three-neck flask (with an argon inlet) containing zinc metal (50 g). The gas was pushed by a slow stream of argon toward a trap containing $P_2O_5$ to remove any water or $HNO_3$. The $P_2O_5$ trap was connected to a hose leading to a container of petroleum ether (~150 mL, cooled by liquid $N_2$), and $N_2O_4$ was bubbled through the cold ether. The petroleum ether dissolved $N_2O_4$ quickly, producing a blue-colored solution at low temperatures and a dark orange color at room temperature.

**Preparation of 2-Nitrotetraarylporphyrins.** A suspension of Cu(II) tetraarylporphyrin (e.g., CuTPP, 25.0 g) in dichloromethane (2.0 L) was stirred vigorously. The $N_2O_4$ solution was added dropwise over 2−3 h. The addition was performed rapidly at the beginning, but was slowed near completion of the reaction to avoid over-nitration. Close reaction monitoring by TLC ($Al_2O_3$, $CHCl_3$/cyclohexane 1:2) was crucial. If done properly, all Cu(II) tetraarylporphyrin was converted into the mononitro product with minimal dinitro product formation. The reaction mixture was filtered to remove any unreacted CuTPP. The mixture was then evaporated to 100 mL, and the product (2-$NO_2$CuTPP,[23] 22.0 g, 88%) was precipitated by addition of methanol.

***trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetraphenylporphyrin 5.** A mixture of $K_2CO_3$ (336 mg, 2.43 mmol) and malononitrile (200 $\mu$L, 3.03 mmol) in dry THF (5 mL) was stirred for 1 h at reflux under argon. The reaction mixture was cooled to room temperature, and 2-$NO_2$TPP **1** (200 mg, 0.303 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 starting material and intermediate cyclopropylchlorin had disappeared (monitored by TLC). The reaction mixture was cooled, diluted with dichloromethane (200 mL), washed with $H_2O$ (3 ×), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The crude chlorin was purified by chromatography on a short silica gel column eluted with dichloromethane/cyclohexane (2:1), and the red band was collected. Recrystallization from dichloromethane/*n*-hexane afforded the title product in 71% yield (161 mg), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 408 nm ($\epsilon$ 227 000), 516 (29 000), 544 (30 000), 590 (22 000), 642 (40 000); $\delta$ ($CDCl_3$) −1.82 (br s, 2 H), 4.35 (d *J* 3.9 Hz, 2 H), 5.38 (d *J* 3.9 Hz, 2 H), 7.8 (m, 12 H), 8.04 (m, 8 H), 8.31 (d *J* 4.8 Hz, 2 H), 8.52 (s, 2 H), 8.71 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 744.3 ($M^+$). Anal. Calcd for $C_{50}H_{32}N_8$: C, 80.63; H, 4.33; N, 15.04. Found: C, 80.49; H, 4.50; N, 14.91.

**Copper(II) *trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetraphenylporphyrin 6.** Sodium hydride (80% dispersion in mineral oil, 26 mg, 1.12 mmol) was placed in a two-neck flask equipped with a rubber septum and condenser. Sodium hydride was washed (3 ×) with pentane and removed through the septum with a syringe. DMF (2 mL) was added, followed by malononitrile (88 $\mu$L, 1.39 mmol), and the mixture was allowed to stir for 1 h at 60 °C. The mixture was cooled to room temperature, and compound **2** (100 mg, 0.139 mmol) was added; the mixture was then stirred for 6 h. The reaction mixture was diluted with dichloromethane, washed with $H_2O$ (6 ×), filtered, and evaporated to dryness. The crude copper chlorin was purified by chromatography on a short silica gel column eluted with dichloromethane, and the blue band was collected. Recrystallization from dichloromethane/*n*-hexane afforded the title product in 68% yield (76 mg), mp 298−300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 412 nm ($\epsilon$ 300 000), 514 (27 000), 606 (56 000); MS (LSIMS) *m*/*z* 806.2 ($M^+$). Anal. Calcd for $C_{50}H_{30}CuN_8 \cdot 0.5H_2O$: C, 73.69; H, 3.84; N, 13.76. Found: C, 73.87; H, 4.01; N, 13.54.

**Nickel(II) *trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetraphenylporphyrin 7.** A solution of $K_2CO_3$ (155 mg, 1.12 mmol) and malononitrile (88 $\mu$L, 1.40 mmol) in dry THF (5 mL) was stirred under argon for 1 h at reflux. The reaction mixture was cooled to room temperature, and compound **3** (100 mg, 0.140 mmol) was added; the mixture was then stirred for 6 h. The mixture was diluted with dichloromethane, washed with $H_2O$ (3 ×), filtered, and evaporated to dryness. The crude nickel chlorin was purified by chromatography on a short silica gel column eluted with dichloromethane, and the blue band was collected. Recrystallization from dichloromethane/*n*-hexane afforded the nickel chlorin in 70% yield (79 mg), mp 245−248 °C; $\lambda_{max}$ ($CH_2Cl_2$) 414 nm ($\epsilon$ 181 000), 504 (22 000), 604 (45 000); $\delta$ ($CDCl_3$) 3.88 (d *J* 4.5 Hz, 2 H), 5.03 (d *J* 4.5 Hz, 2 H), 7.15 (d *J* 7.8 Hz, 2 H), 7.63 (m, 10 H), 7.83 (m, 8 H), 8.2 (s, 2 H), 8.35 (d *J* 4.8 Hz, 2 H), 8.40 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 801.6 ($M^+$). Anal. Calcd for $C_{50}H_{30}N_8Ni \cdot 0.5H_2O$: C, 74.15; H, 3.86; N, 13.84. Found: C, 73.99; H, 3.75; N, 13.63.

**Zinc(II) *trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetraphenylporphyrin 8.** Sodium hydride (31.8 mg, 1.106 mmol) was prepared as described above. DMSO (2 mL) and malononitrile (87.6 $\mu$L, 1.38 mmol) were added, and the mixture was allowed to stir for 1 h at 60 °C. Compound **4** (100 mg, 0.138 mmol) was added, and stirring was continued for an additional 24 h at 80 °C. The mixture was cooled, diluted with dichloromethane (100 mL), washed with $H_2O$ (3 ×), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The crude zinc chlorin was purified by chromatography on a short silica gel column eluted with dichloromethane. Recrystallization of the green band from dichloromethane/*n*-hexane afforded the title chlorin product in 63% yield (70 mg), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 414 nm ($\epsilon$ 245 000), 514 (9000), 582 (15 000) 608 (44 000); $\delta$ ($CDCl_3$) 4.38 (d *J* 3.9 Hz, 2 H), 5.27 (d *J* 3.9 Hz, 2 H), 7.72−8.15 (m, 20 H), 8.23 (d *J* 4.8 Hz, 2 H), 8.45 (s, 2 H), 8.58 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 809 ($M^+$). Anal. Calcd for $C_{50}H_{30}N_8Zn$: C, 74.31; H, 3.74; N, 13.86. Found: C, 73.95; H, 3.93; N, 13.49.

***trans*-2,3-Dihydro-2,3-bis(cyanomethyl)-5,10,15,20-tetraphenylporphyrin 9.** Sodium hydride (35.1 mg, 1.22 mmol) was washed as described above. DMSO (5 mL) and methyl cyanoacetate (108 $\mu$L, 1.52 mmol) was added, and the mixture was allowed to stir for 1 h at 60 °C. Compound **1** (100 mg,

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0.152 mmol) was added with stirring at 80 °C for 3 h. Eight drops of $H_2O$ and NaCl (89 mg, 1.52 mmol) were added, and the temperature was increased to 140 °C for 14 h. The mixture was cooled, diluted with dichloromethane (200 mL), washed with $H_2O$ (6 ×), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with 20% cyclohexane in dichloromethane. Recrystallization from dichloromethane/*n*-hexane afforded the title product in 75% yield (79 mg), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 410 nm ($\epsilon$ 168 000), 516 (13 800), 544 (13 400), 592 (6700), 644 (26 000); $\delta$ ($CDCl_3$) −1.81 (br s, 2 H), 2.54 (dd *J* 17.1 Hz, *J* 8.1 Hz, 2 H), 2.81 (dd *J* 17.1 Hz, *J* 4.2 Hz, 2 H), 4.98 (dd *J* 8.1 Hz, *J* 4.2 Hz, 2 H), 7.61−8.23 (m, 22 H), 8.51 (s, 2 H), 8.67 (d *J* 4.8 Hz, 2 H). Anal. Calcd for $C_{48}H_{34}N_6$: C, 82.96, H, 4.94 N, 12.10. Found: C, 83.11; H, 4.82; N, 11.97.

**5,10,15,20-Tetraphenyl-[2:3]-dicyanomethanoporphyrin 14.** A solution of $K_2CO_3$ (3.34 g, 24.2 mmol) and malononitrile (1.9 mL, 30.3 mmol) in dry THF (100 mL) was stirred for 1 h at reflux under argon. The mixture was cooled to −20 °C, followed by addition of compound **1** (2.0 g, 3.03 mmol), and the mixture was stirred for 1 h. The reaction mixture was allowed to slowly warm to room temperature and stirred for an additional 12 h. Close monitoring by TLC was necessary to isolate the cyclopropyl product before the reaction proceeded to give the disubstituted *trans*-chlorin **5**. The mixture was diluted with dichloromethane (400 mL), washed with $H_2O$ (3 ×), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane/cyclohexane (2:1). The first red band was collected, and the residue after evaporation was recrystallized from dichloromethane/*n*-hexane, affording the title product in 68% yield (1.40 g), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 414 nm ($\epsilon$ 251 000), 522 (15 300), 592 (7000), 646 (16 000); $\delta$ ($CDCl_3$) −2.11 (br s, 2 H), 5.15 (s, 2 H), 7.74−8.17 (m, 20 H), 8.54 (s, 2 H), 8.55 (d *J* 5.1 Hz, 2 H), 8.75 (d *J* 5.1 Hz, 2 H); MS (LSIMS) *m*/*z* 679.3 ($MH^+$). Anal. Calcd for $C_{47}H_{30}N_6$: C, 83.15; H, 4.46; N, 12.39. Found: C, 83.30; H, 4.61; N, 12.23. A more polar red band was isolated and identified as **5** (in 9% yield).

**5,10,15,20-Tetraphenyl-[2:3]-[(cyano)(methoxycarbonyl)methano]porphyrin 15.** A solution of $K_2CO_3$ (155 mg, 1.12 mmol) and methyl cyanoacetate (152 $\mu$L, 1.70 mmol) in dry THF (5 mL) was stirred for 1 h at reflux under argon. The mixture was cooled to room temperature, followed by addition of compound **1** (100 mg, 0.152 mmol), and the solution was allowed to stir for 14 h. Close monitoring by TLC was necessary to isolate the cyclopropyl product before it proceeded to the disubstituted *trans*-chlorin **10**. The mixture was diluted with dichloromethane, washed with $H_2O$ (3 ×), filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane/cyclohexane (2:1). Recrystallization of the material from the major band using dichloromethane/*n*-hexane afforded the title compound in 63% yield (68 mg), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 416 nm ($\epsilon$ 249 000), 518 (16 000), 548 (11 200), 592 (7000), 646 (15 700); $\delta$ ($CDCl_3$) −2.03 (br s, 2 H), 3.93 (s, 3 H), 4.98 (s, 2 H), 7.73 (m, 12 H), 7.97 (m, 2 H), 8.13 (m, 6 H), 8.51 (d *J* 4.8 Hz, 2 H), 8.52 (s, 2 H), 8.72 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 712.3 ($MH^+$). Anal. Calcd for $C_{48}H_{33}N_5O_2 \cdot H_2O$: C, 79.17; H, 4.71; N, 9.52. Found: C, 78.98; H, 4.84; N, 9.60.

***trans*-2,3-Dihydro-2-[bis(methoxycarbonyl)methyl]-3-nitro-5,10,15,20-tetraphenylporphyrin 16.** A solution of $K_2CO_3$ (169 mg, 1.22 mmol) and dimethyl malonate (143 $\mu$L, 1.52 mmol) in dry THF (5 mL) was stirred for 1 h at reflux under argon. The mixture was cooled to room temperature, followed by addition of compound **1** (100 mg, 0.152), and then stirred for 12 h. The mixture was diluted with dichloromethane (100 mL), washed with $H_2O$ (3 ×), filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane/cyclohexane (2:1). Recrystallization from dichloromethane/*n*-hexane afforded the title product in 66% yield (79 mg), mp 209−211 °C; $\lambda_{max}$ ($CH_2Cl_2$) 410 nm ($\epsilon$ 182 000), 516 (16 300), 544 (17 500), 592 (9400), 642 (24 400); $\delta$ ($CDCl_3$) −192 (s, 1 H), −186 (d, 1 H), 2.40 (s, 3 H), 3.79 (s, 3 H), 4.05 (d *J* 4.2 Hz, 1 H), 5.76 (d *J* 4.2 Hz, 1 H), 7.71 (m, 13 H), 8.20 (m, 8 H), 8.32 (d *J* 4.8 Hz, 1 H), 8.36 (d *J* 4.8 Hz, 1 H) 8.52 (m, 2 H), 8.69 (m, 2 H); MS (LSIMS) *m*/*z* 792.3 ($MH^+$, 40), 745.3 (−$HNO_2$, 100). Anal. Calcd for $C_{49}H_{37}N_5O_6 \cdot H_2O$: C, 72.66; H, 4.86; N, 8.65. Found: C, 72.71; H, 4.72; N, 8.77.

**Nickel(II) *trans*-2,3-Dihydro-2-[bis(methoxycarbonyl)methyl]-3-nitro-5,10,15,20-tetraphenylporphyrin 17.** A solution of $K_2CO_3$ (310 mg, 2.25 mmol) and dimethyl malonate (320 $\mu$L, 2.79 mmol) in dry THF (10 mL) was stirred for 1 h at reflux under argon. The mixture was cooled to room temperature, followed by addition of Ni(II) 2-$NO_2$TPP **3** (200 mg, 0.279 mmol), and the solution was allowed to stir for 12 h. The mixture was diluted with dichloromethane (200 mL), washed with $H_2O$ (3 ×), filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane. Recrystallization from dichloromethane/*n*-hexane afforded the title compound in 61% yield (144 mg), mp 194−197 °C; $\lambda_{max}$ ($CH_2Cl_2$) 416 nm ($\epsilon$ 156 000), 532 (5600), 608 (19 200); $\delta$ ($CDCl_3$) 2.14 (s, 3 H), 3.51 (d *J* 4.5 Hz, 1 H), 3.68 (s, 3 H), 5.40 (d *J* 4.5 Hz, 1 H), 7.02 (s, 1 H), 7.63−7.85 (m, 20 H), 7.98 (d *J* 4.8 Hz, 2 H), 8.21 (s, 2 H), 8.34 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 848.3 ($M^+$, 30), 801.1 (−$HNO_2$, 100). Anal. Calcd for $C_{49}H_{35}N_5NiO_6 \cdot 0.5\ H_2O$: C, 68.68; H, 4.24; N, 8.18. Found: C, 68.68; H, 4.11 N, 8.05.

***trans*-2,3-Dihydro-2-[(cyano)(phenyl)methyl]-3-nitro-5,10,15,20-tetraphenylporphyrin 18.** A solution of $K_2CO_3$ (168 mg, 1.22 mmol) and benzylcyanide (175 $\mu$L, 1.52 mmol) in dry THF (5 mL) was stirred for 1 h at reflux under argon. The mixture was cooled to room temperature, followed by addition of compound **1** (100 mg, 0.152 mmol), and the solution was allowed to stir for 48 h. The reaction mixture was diluted with dichloromethane (100 mL), washed with $H_2O$ (3 ×), filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane/cyclohexane (2:1). Recrystallization from dichloromethane/*n*-hexane afforded the title product in 61% yield (72 mg), mp 187−189 °C; $\lambda_{max}$ ($CH_2Cl_2$) 410 nm ($\epsilon$ 174 000), 571 (13 200), 546 (15 300), 592 (7800), 642 (22 900); $\delta$ ($CDCl_3$) −1.75 (br s, 2 H), 4.58 (d *J* 3.6 Hz, 1 H), 5.45 (dd *J* = 3.6, 0.6 Hz, 1 H), 6.95 (d *J* 7.8 Hz, 2 H), 7.03 (s, 1 H), 7.40 (m, 3 H), 7.75 (m, 12 H), 8.04 (m, 4 H), 8.27 (m, 4 H), 8.36 (d *J* 4.8 Hz, 1 H), 8.44 (d *J* 4.8 Hz, 1 H), 8.52 (m, 2H), 8.69 (d *J* 4.8 Hz, 1 H), 8.75 (d *J* 4.8 Hz, 1 H); MS (LSIMS) *m*/*z* 777.2 ($MH^+$, 45), 730.2 (−$HNO_2$, 25). Anal. Calcd for $C_{52}H_{36}N_6O_2 \cdot H_2O$: C, 78.56; H, 4.82; N, 10.58. Found: C, 78.61; H, 4.89 N, 10.61.

***trans*-2,3-Dihydro-2-[bis(*n*-butylaminocarbonyl)methyl]-3-nitro-5,10,15,20-tetraphenylporphyrin 19.** A solution of $K_2CO_3$ (168 mg, 1.22 mmol) and di(*n*-butyl)malonamide (326 mg, 1.52 mmol) in DMSO (5 mL) was stirred for 1 h at 60 °C under argon. 2-$NO_2$TPP **1** (100 mg, 0.152 mmol) was added, the temperature was raised to 100 °C, and the solution was stirred for 36 h. The reaction mixture was diluted with dichloromethane, washed with $H_2O$ (3 ×), filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with 2% methanol in dichloromethane. Recrystallization from dichloromethane/*n*-hexane afforded the title chlorin in 19% yield (25 mg), mp 221−224 °C; $\lambda_{max}$ ($CH_2Cl_2$) 412 nm ($\epsilon$ 180 000), 516 (8000), 546 (10 000), 594 (7000); $\delta$ ($CDCl_3$) −1.91 (br s, 2 H), −1.51 (m, 1 H), −1.32 (m, 2 H), −1.13 (t *J* 7.2 Hz, 3 H), −0.93 (m, 1 H), −0.78 (m, 1 H), 0.88 (t *J* 7.2 Hz, 3 H), 1.2−1.6 (m, 4 H), 2.99 (m, 2 H), 3.38 (m, 2 H), 4.52 (m, 1 H,), 5.72 (d *J* 3.6 Hz, 1 H), 7.41−8.23 (m, 22 H), 8.38 (m, 3 H), 8.56 (d *J* 4.8 Hz, 1 H), 8.63 (d *J* 4.8 Hz, 1 H); MS (LSIMS) *m*/*z* 874.3 ($M^+$). Anal. Calcd for $C_{55}H_{51}N_7O_4 \cdot 2H_2O$: C, 72.59; H, 6.09; N, 10.21. Found: C, 72.42; H, 6.03 N, 10.21.

**5,10,15,20-Tetraphenyl-[2:3]-[bis(methoxycarbonyl)methano]porphyrin 20.** A solution of $K_2CO_3$ (310 mg, 2.25 mmol) and dimethyl malonate (320 $\mu$L, 3.40 mmol) in DMSO (10 mL) was stirred for 1 h at 60 °C under argon. 2-$NO_2$TPP **1** (200 mg, 0.303 mmol) was added, and the solution was stirred for 3 h at 100 °C. The mixture was cooled, diluted with dichloromethane (200 mL), washed with $H_2O$ (6 ×), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane; the first red band was collected and evapo-

rated to dryness. Recrystallization from dichloromethane/*n*-hexane afforded the title product in 77% yield (174 mg), mp 271−273 °C; $\lambda_{max}$ ($CH_2Cl_2$) 416 nm ($\epsilon$ 266 000), 518 (15 800) 548 (12 900), 592 (6000), 644 (18 000); $\delta$ ($CDCl_3$) −2.02 (br s, 2 H), 2.45 (s, 3 H), 3.80 (s, 3 H), 4.75 (s, 2 H), 7.70 (m, 12 H), 8.13 (m, 8 H), 8.53 (s, 2 H), 8.62 (d *J* 4.8 Hz, 2 H), 8.71 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 744.3 ($M^+$). Anal. Calcd for $C_{49}H_{36}N_4O_4$: C, 79.00; H, 4.87; N, 7.53. Found: C, 78.72; H, 5.12; N, 7.23.

**Nickel(II) 5,10,15,20-Tetraphenyl-[2:3]-[bis(methoxycarbonyl)methano]porphyrin 21.** A solution of $K_2CO_3$ (155 mg, 1.38 mmol) and dimethyl malonate (160 $\mu$L, 1.40 mmol) in DMSO was stirred for 1 h at 60 °C under argon. Compound **3** (155 mg, 0.138 mmol) was added, and the solution was stirred for 2 h at 100 °C. The mixture was cooled, diluted with dichloromethane (100 mL), washed with $H_2O$ (6 ×), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane. Recrystallization from dichloromethane/*n*-hexane afforded the desired product in 76% yield (85 mg), mp 237−240 °C; $\lambda_{max}$ ($CH_2Cl_2$) 416 nm ($\epsilon$ 195 000), 526 (7400), 568 (7400), 602 (24 000);); $\delta$ ($CDCl_3$) 2.36 (s, 3 H), 3.84 (s, 3 H), 4.71 (s, 2 H), 7.61 (m, 12 H), 7.87 (m, 8 H), 8.17 (d *J* 4.8 Hz, 2 H), 8.29 (s, 2 H), 8.41 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 800.2 ($M^+$). Anal. Calcd for $C_{49}H_{34}N_4NiO_4$: C, 73.43; H, 4.39; N, 6.99. Found: C, 73.36; H, 4.39; N, 7.11.

**5,10,15,20-Tetraphenyl-[2:3]-[(cyano)(phenyl)methano]porphyrin 22.** A solution of $K_2CO_3$ (168 mg, 1.22 mmol) and benzylcyanide (175 $\mu$L, 1.52 mmol) in DMSO was stirred for 1 h at 60 °C under argon. 2-$NO_2$TPP **1** (155 mg, 0.138 mmol) was added, and the solution was stirred for 12 h at 100 °C. The mixture was cooled, diluted with dichloromethane (100 mg), washed with $H_2O$ (6 ×), filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with ethyl acetate/cyclohexane (1:3). Recrystallization from dichloromethane/*n*-hexane afforded the desired product in 58% yield (58 mg), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 420 nm ($\epsilon$ 218 000), 520 (15 000), 548 (10 000), 596 (6000), 650 (20 000); $\delta$ ($CDCl_3$) −1.81 (br s, 2 H), 4.67 (s, 2 H), 7.37 (m, 5 H), 7.72 (m, 12 H), 8.16 (m, 8 H), 8.45 (d *J* 4.8 Hz, 2 H), 8.51 (s, 2 H), 8.71 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 730.3 ($M^+$). Anal. Calcd for $C_{52}H_{35}N_5 \cdot 0.5H_2O$: C, 84.53; H, 4.91; N, 9.48. Found: C, 84.43; H, 4.96; N, 9.36.

**5,10,15,20-Tetraphenyl-[2:3]-[bis(aminocarbonyl)methano]porphyrin 23.** A solution of $K_2CO_3$ (168 mg, 1.22 mmol) and malonamide (155 mg, 1.52 mmol) in DMSO (5 mL) was stirred for 1 h at 60 °C under argon. 2-$NO_2$TPP **1** (100 mg, 0.152 mmol) was added, and the solution was stirred for 50 h at 100 °C. The mixture was cooled, diluted with dichloromethane (100 mL), washed with $H_2O$ (6 ×), dried over anhydrous $Na_2SO_4$, and evaporated to dryness. The crude chlorin was purified on a silica gel column, eluted with 3% methanol in dichloromethane, to yield the title product in 25% yield (31 mg), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 418 nm ($\epsilon$ 165 000), 520 (13 000), 548 (11 000), 594 (7000), 650 (16 000); $\delta$ ($CDCl_3$) −1.95 (br s, 2 H), 4.02 (br s, 1 H), 4.33 (br s, 1 H), 4.96 (s, 2 H), 5.49 (br s, 1 H), 7.59−8.21 (m, 21 H), 8.42 (d *J* 4.8 Hz, 2 H), 8.51 (s, 2 H), 8.72 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 715.2 ($M^+$).

***trans*-2,3-Dihydro-2-(dicyanomethyl)-3-(*S*-thiopropyl)-5,10,15,20-tetraphenylporphyrin 25.** Sodium hydride (3.5 mg, 0.110 mmol) was treated as described above. THF (5 mL) was added, followed by addition of propane-1-thiol (13.3 $\mu$L, 0.147 mmol), and the mixture was stirred for 1 h at 60 °C. The mixture was then transferred to a dropping funnel and added dropwise to a stirring solution of compound **13** (50 mg, 0.0736 mmol) in THF at 0 °C under argon. The mixture was allowed to stir for 12 h and was then diluted with dichloromethane (50 mL), washed with $H_2O$ (3 ×), dried over anhydrous $Na_2SO_4$, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with 25% ethyl acetate in cyclohexane. Recrystallization from dichloromethane/*n*-hexane afforded the title compound in 78% yield (43 mg), mp 196−198 °C; $\lambda_{max}$ ($CH_2Cl_2$) 412 nm ($\epsilon$ 188 000), 518 (13 000), 546 (13 000), 594 (6000), 646 (23 000); $\delta$ ($CDCl_3$) −1.69 (s, 1 H), −1.80 (s, 1 H), 0.778 (t *J* 7.2 Hz, 3 H), 1.2 (m, 2 H), 2.15 (m, 1 H), 2.47 (m, 1 H), 4.14 (d *J* 3.9 Hz, 1 H), 5.36 (d *J* 3.9 Hz, 1 H), 5.67 (s, 1 H), 7.65−8.30 (m, 20 H), 8.34 (d *J* 4.8 Hz, 2 H), 8.50 (m, 2 H), 8.66 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 756.0 ($MH^+$). Anal. Calcd for $C_{50}H_{38}N_6S$: C, 79.55; H, 5.07; N, 11.13. Found: C, 79.25; H, 5.10; N, 10.90.

**Copper(II) 5,10,15,20-Tetra[3,5-di(*tert*-butyl)phenyl]-2-nitroporphyrin 26.** The nitration of copper(II) 5,10,15,20-tetra[3,5-di(*tert*-butyl)phenyl]porphyrin (3.0 g) in 150 mL of $CH_2Cl_2$ was performed as described above. Recrystallization of the nitrated porphyrin in $CH_2Cl_2$/MeOH produced the title compound in 89% yield (2.70 g), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 426 nm ($\epsilon$ 247 000), 548 (28 000), 590 (23 000); MS (LSIMS) *m*/*z* 1169.5 ($M^+$). Anal. Calcd for $C_{76}H_{91}CuN_5O_2$: C, 78.01; H, 7.84; N, 5.98. Found: C, 77.70; H, 7.76; N, 5.94.

**Copper(II) 5,10,15,20-Tetrakis(*m*-methoxyphenyl)-2-nitroporphyrin 27.** Nitration of copper(II) 5,10,15,20-tetrakis(*m*-methoxyphenyl)nitroporphyrin (5.0 g) in $CH_2Cl_2$ (500 mL) was performed as described above. Recrystallization of the nitrated porphyrin in $CH_2Cl_2$/MeOH produced the title compound in 88% yield (4.7 g), mp 197−200 °C; $\lambda_{max}$ ($CH_2Cl_2$) 424 nm ($\epsilon$ 175 000), 548 (12 000), 590 (8000); MS (LSIMS) *m*/*z* 841.1 ($M^+$). Anal. Calcd for $C_{48}H_{35}CuN_5O_6$: C, 68.52; H, 4.19; N, 8.32. Found: C, 68.55; H, 4.27; N, 8.46.

**5,10,15,20-Tetrakis[3,5-di(*tert*-butyl)phenyl]-2-nitroporphyrin 28.** Demetalation of **26** (2.65 g) in 100 mL of concentrated $H_2SO_4$ and recrystallization of the nitrated porphyrin from $CH_2Cl_2$/MeOH gave the title compound in 85% yield (2.15 g), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 430 nm ($\epsilon$ 185 000), 528 (19 000), 562 (9000), 604 (7000), 664 (13 000); $\delta$ ($CDCl_3$) −2.57(br s, 2 H), 1.51 (s, 72 H), 7.80 (m, 4 H), 8.06 (m, 8 H), 8.78 (m, 2 H), 8.95 (m, 2 H), 9.06 (s, 1 H), 9.08 (m, 2 H); MS (LSIMS) *m*/*z* 1108.6 ($M^+$). Anal. Calcd for $C_{71}H_{93}N_5O_2$: C, 82.34; H, 8.46; N, 6.32. Found: C, 82.24; H, 8.45; N, 6.41.

**5,10,15,20-Tetrakis(*m*-methoxyphenyl)-2-nitroporphyrin 29.** Demetalation of **27** (2.0 g) in TFA/$H_2SO_4$ (4:1) and recrystallization from $CH_2Cl_2$/MeOH produced the title compound in 76% yield (1.4 g), mp 290−293 °C; $\lambda_{max}$ ($CH_2Cl_2$) 430 nm ($\epsilon$ 144 000), 526 (14 000), 602 (6000), 662 (7000); $\delta$ ($CDCl_3$) −2.60 (br s, 2 H), 4.00 (s, 12 H), 7.34−7.84 (m, 16 H), 8.75−9.01 (m, 7 H); MS (LSIMS) *m*/*z* 779.3 ($M^+$). Anal. Calcd for $C_{48}H_{37}N_5O_6$: C, 73.93; H, 4.78; N, 8.98. Found: C, 73.74; H, 4.91; N, 7.82.

***trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetrakis[3,5-di(*tert*-butyl)phenyl]porphyrin 30.** Sodium hydride (52 mg, 1.81 mmol) was prepared as described above; THF (10 mL) and malononitrile (143 $\mu$L, 2.26 mmol) were added, and the mixture was stirred for 1 h at 60 °C. Compound **28** (250 mg, 0.226 mmol) was added, and the mixture was stirred for an additional 5 h at 60 °C. The mixture was cooled, diluted with dichloromethane (200 mL), washed with $H_2O$ (3 ×), filtered, and evaporated to dryness. The crude chlorin was purified on a silica gel column eluted with dichloromethane/cyclohexane (2:3). Recrystallization from dichloromethane/methanol afforded the title product in 78% yield (140 mg), mp >300 °C; $\lambda_{max}$ ($CH_2Cl_2$) 412 nm ($\epsilon$ 204 000), 518 (12 000), 550 (17 000) 592 (9000), 642 (22 000); $\delta$ ($CDCl_3$) −1.79 (br s, 2 H), 1.7 (s, 72 H), 4.30 (d *J* 3.9 Hz, 2 H), 5.31 (d *J* 3.9 Hz, 2 H), 7.84 (m, 12 H), 8.14 (m, 8 H), 8.43 (d *J* 5.1 Hz, 2 H), 8.59 (s, 2 H), 8.75 (d *J* 5.1 Hz, 2 H); MS (LSIMS) *m*/*z* 1193.8 ($M^+$). Anal. Calcd for $C_{82}H_{96}N_8 \cdot H_2O$: C, 81.53; H, 8.01; N, 9.33. Found: C, 81.28; H, 8.15; N, 9.25.

***trans*-2,3-Dihydro-2,3-bis(dicyanomethyl)-5,10,15,20-tetrakis(*m*-methoxyphenyl)porphyrin 31.** A solution of $K_2CO_3$ (425 mg, 3.08 mmol) and malononitrile (244 $\mu$L, 3.85 mmol) in dry THF (15 mL) was stirred under argon for 1 h at reflux. Compound **29** (300 mg, 0.385 mmol) was added, and the solution was allowed to stir for an additional 10 h. The mixture was cooled, diluted with dichloromethane, washed with $H_2O$ (3 ×), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to dryness. The crude chlorin was chromatographed on a short silica gel column eluted with dichloromethane. Recrystallization from dichloromethane/*n*-hexane afforded the title product in 56% yield (187 mg), mp 205−208 °C; $\lambda_{max}$ ($CH_2Cl_2$) 410 nm ($\epsilon$ 165 000), 514 (15 000), 544 (14

000), 590 (9000), 642 (24 000); $\delta$ ($CDCl_3$) −1.92 (br s, 2 H), 3.52 (s, 3 H), 3.94 (s, 3 H), 4.02 (s, 6 H), 4.47 (d *J* 3.9 Hz, 1 H), 4.53 (d *J* 3.9 Hz, 1 H), 5.46 (d *J* 3.9 Hz, 1 H), 5.48 (d *J* 3.9 Hz, 1 H), 7.30−7.95 (m, 16 H), 8.40 (d *J* 4.8 Hz, 2 H), 8.57 (s, 2 H), 8.78 (d *J* 4.8 Hz, 2 H); MS (LSIMS) *m*/*z* 865.3 ($M^+$). Anal. Calcd for $C_{54}H_{40}N_8O_4$: C, 74.99; H, 4.66; N, 12.95. Found: C, 74.86; H, 4.61; N, 12.85.

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