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Regioselective Syntheses and Structural Characterizations of 2,3-Dibromo- and 2,3,7,8,12,13-Hexabromo-5,10,15,20-tetraphenylporphyrins

Laurent Jaquinod, Richard G. Khoury, Kalyn M. Shea and Kevin M. Smith*

Department of Chemistry, University of California, Davis, California 95616, USA

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Abstract: The title dibromoporphyrins **4/5** and hexabromoporphyrins **11/12** are prepared from H_2(2-NO_2TPP) **1** and Cu(2-NO_2TPP) **8**, respectively. The β-nitro group confines the 18-π-annulene system of a tetraphenylporphyrin to its $N_{22}H$-$N_{24}H$ aromatic delocalization pathway which induces the localization of an antipodal double bond on the porphyrin periphery and enhances its susceptibility to electrophilic attack. Dibromination of H_2(2-NO_2TPP) **1** occurs regioselectively affording the 12,13-dibromo-2-nitroporphyrin **2** which, upon Michael addition of $NaBH_4$ and re-aromatization of the resulting nitrochlorin **3**, provides an entry to 2,3-dibromoTPP **4/5** as well as an improved route to 2,3-dicyanoporphyrins **6/7**. Perbromination of Cu(2-NO_2TPP) **8** and denitration of **9** gave, after demetalation, 2,3,7,8,12,13-hexabromoTPP **12**. Both **4** and **12** are structurally characterized by X-ray crystallography. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

β-Bromo-substituted tetra-arylporphyrins are useful substrates for nucleophilic aromatic substitutions with cyanides,[1] thiolates,[2] benzaldoximate[3] or in palladium(0) mediated cross-coupling reactions with alkynes,[4] arylboronic acids,[5] and organozinc or organotributyltin reagents.[6] Some of their metal complexes (Fe, Cr, Mn, Ru) are also known to possess cytochrome P450-like properties because they catalyze both epoxidation of olefins and hydroxylation of unactivated hydrocarbons.[7] Tetra-arylporphyrins substituted with one, four or eight halogens at the β-pyrrole positions have traditionally been employed in these studies as they are readily prepared by direct bromination of the porphyrin periphery. Perbromination of metalloporphyrin with excess NBS or bromine affords octabromoporphyrins in good yields.[8] The antipodal[2] bromination of metal-free tetraphenylporphyrin [H_2(TPP)] with *N*-bromosuccinimide (NBS) in refluxing $CHCl_3$ produced H_2(2-BrTPP), H_2(2,3,12-Br_3TPP), H_2(2,3,12,13-Br_4TPP) and an intractable regioisomeric mixture (i.e. 2,3-, 2,12- and 2,13-) of dibromotetraphenylporphyrins.[1] As part of our ongoing research on the synthesis of fused porphyrinophthalocyanines (analogues of our recently described directly β-fused porphyrin oligomers),[9] fused

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* Corresponding author. E-mail: kmsmith@ucdavis.edu

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porphyrinotetrathiafulvalene and chiral porphyrins based on atropisomeric 2,3-disubstituted porphyrins, a regioselective entry to H_2(2,3-Br_2TPP) was desired. We report herein the development of such a synthesis from readily available 2-nitrotetraphenylporphyrins (2-NO_2TPPs); extension of this methodology also allows preparation of a pure regioisomer of hexabromo-TPP.

RESULTS AND DISCUSSION

2-Nitro-tetra-arylporphyrins are versatile starting materials in porphyrin chemistry which are stable towards demetalation/metalation sequences and can be prepared in high yields by chromatography-free procedures.[10,11] They display a unique set of reactivities which facilitate peripheral functionalizations (Figure 1). 2-Nitroporphyrins are similar to the simpler nitroalkenes in that they undergo Michael additions with a wide range of nucleophiles (hydride, alkoxides, active methylene compounds, etc.) affording 2-substituted and 2-nitro-3-substituted porphyrins,[12,13] pyrrolo[3,4-*b*]porphyrin[14] and *trans*-functionalized chlorins.[10] The β-nitro group is displaced with softer nucleophiles (thiolates, sodium salt of benzaldoxime, etc.)[15] without requiring assistance of another electron-withdrawing functionality to activate the macrocycle toward nucleophilic aromatic substitutions. In preliminary work, we showed that the nitro group directs electrophilic substitutions to the localized double bond on the antipodal pyrrole ring by confining the 18-π-annulene system to its $N_{22}H$-$N_{24}H$ tautomer.[16] Indeed, the bromination of H_2(2-NO_2TPP) **1** with 2.5 equiv of NBS in refluxing chloroform gave regioselectively H_2(2-NO_2-12,13-Br_2TPP) **2** in 75-85% yield.

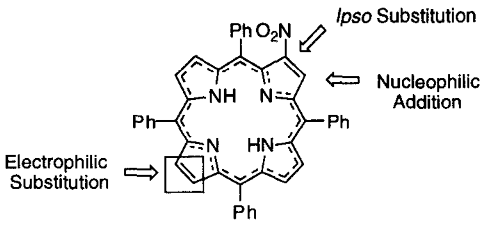
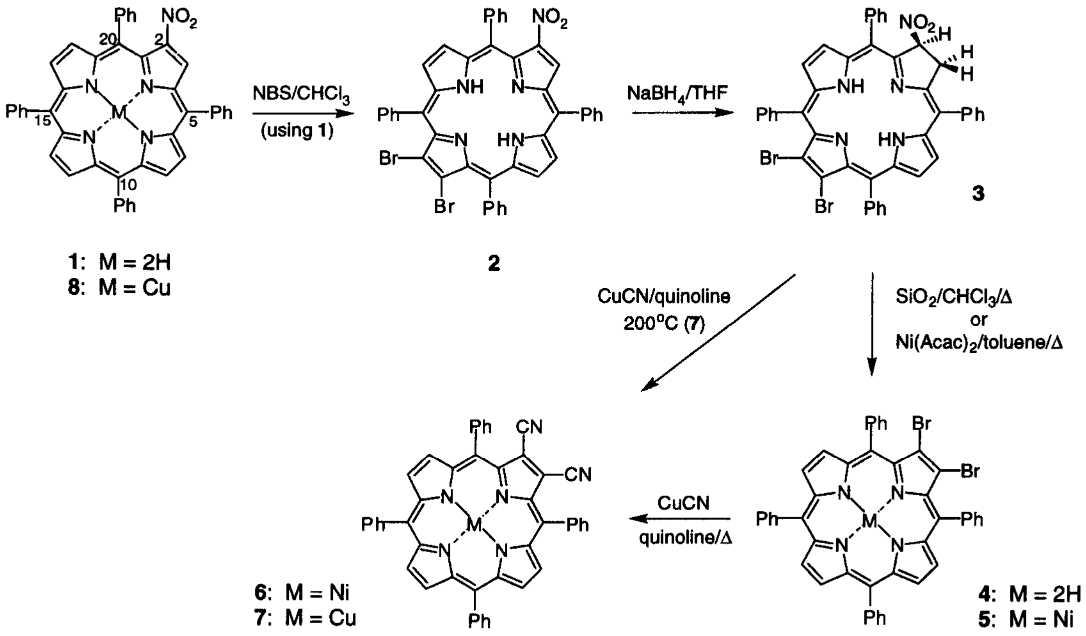


Figure 1: Reactivities of $N_{22}H$-$N_{24}H$ 2-NO_2TPP **1**.

In order to denitrate **2**, we took advantage of the facile nucleophilic addition of sodium borohydride to 2-NO_2TPPs to yield 2,3-dihydro-2-nitroporphyrins (chlorins).[13] These nitrochlorins were shown to eliminate nitrous acid to regenerate tetraphenylporphyrins or undergo reductive denitration with tributyltin hydride and AIBN to produce tetraphenylchlorins. Addition of $NaBH_4$ to a solution of **2** in THF gave nitrochlorin **3** in 84% yield. The ^1H NMR spectrum of **3** showed the C_2 and C_3 hydrogens as a three spin system identical with that found in 2-nitro-2,3-dihydroTPP.[16] Rearomatization of **3** via loss of HNO_2 was carried out in refluxing chloroform in the presence of silica gel or in refluxing toluene in the presence of nickel(II) acetylacetonate to afford, respectively, H_2(2,3-Br_2TPP) **4** and Ni(2,3-Br_2TPP) **5** in good yields. When the hydride addition was instead performed in DMSO, spontaneous rearomatization of nitrochlorin **3** occurred but H_2(2,3-Br_2TPP) **4** was isolated in lower yield. Addition of $NaBH_4$ to Ni(2-NO_2-12,13-Br_2TPP) (prepared from **2**) gave a nitrochlorin which extensively decomposed during attempts to initiate elimination of nitrous acid on silica gel, alumina, or by heating. 2,3-Dicyanoporphyrins **6** and **7** were prepared from Ni(2,3-Br_2TPP) or, more conveniently, from nitrochlorin **3** by nucleophilic substitution with excess cyanide ions (from CuCN) in refluxing quinoline. In the case of **3**, concomitant re-aromatization and metalation took place and copper(II) 2,3-dicyano-TPP **7** was isolated in 75 % yield.



1: M = 2H
8: M = Cu

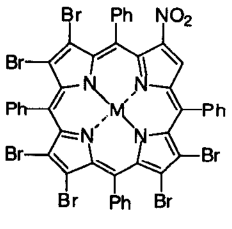
2

3

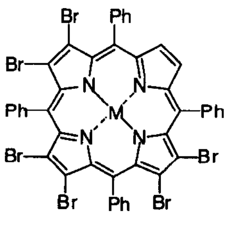
4: M = 2H
5: M = Ni

6: M = Ni
7: M = Cu

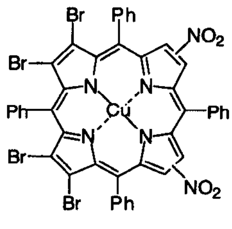
Substitution of $H_2(2\text{-}NO_2TPP)$ **1** with more than two halogens required the use of metalated porphyrins; otherwise decomposition was observed. For example, hexabromination of $Cu(2\text{-}NO_2TPP)$ **8** with excess NBS in boiling 1,2-dichloroethane gave $Cu(2,3,7,8,12,13\text{-}Br_6\text{-}17\text{-}NO_2TPP)$ **9** in 70% yield. Nucleophilic addition of $NaBH_4$ in DMSO converted **9** to the corresponding hexabromoporphyrin **11** via a spontaneous loss of HNO_2.



9: M = Cu
10: M = 2H



11: M = Cu
12: M = 2H



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When the metal-free nitro-compound **10** was submitted to the hydride addition reaction a fairly stable nitrochlorin was obtained which decomposed to give a low yield of $H_2(2,3,7,8,12,13\text{-}Br_6TPP)$ **12** during slow elution from an alumina column. Metal-free porphyrin **12** is best prepared by demetalation of **11** in sulfuric acid. The Soret band maximum of **12** (at 454 nm) is identical with that described for the regioisomeric mixture of six hexabromotetraphenylporphyrins prepared by direct bromination of Zn(TPP).[17] The two remaining β-pyrrolic protons appeared in the ^1H NMR spectrum as a singlet at δ 8.61 ppm. 2,3,7,8-

TetrabromoTPP was also regioselectively prepared by carrying out a double consecutive hydride addition/HNO_2 elimination sequence on a regioisomeric mixture of $Cu[Br_4\text{-}(NO_2)_2TPP]$ **13**; however, low yields and extensive chromatography separations hindered the reproducibility of this procedure.

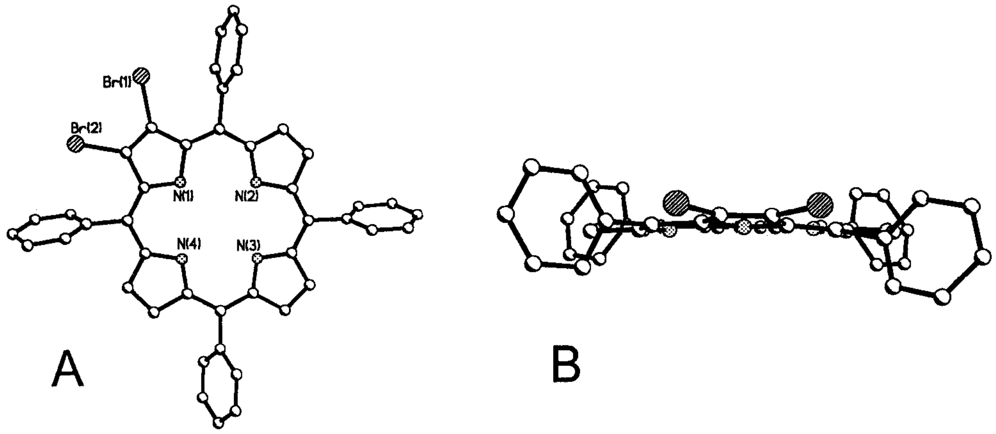

Figure 2: X-ray structure of **4**, (A) top view; (B) side view. Hydrogens have been omitted for clarity.

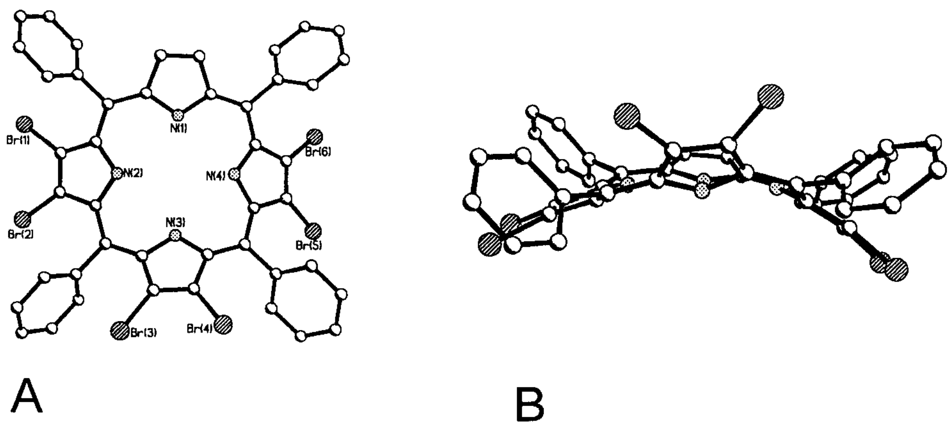

Figure 3: X-ray structure of **12**, (A) top view; (B) side view. Hydrogens have been omitted for clarity.

Molecular structures of **4** and **12** were determined by X-ray crystallography and, with the known structures of H_2(TPP),[18] H_2(2,3,12,13-Br_4TPP),[19] and H_2(Br_8TPP),[20] complete a series of tetraphenylporphyrins with graded degrees of β-bromination. Compound **12** exists in a saddle conformation with a mean plane deviation of 0.436(1) Å with respect to the 24 core atoms. The average displacement of the β-carbons of the three halogenated pyrrole rings is 0.930(3) Å. Octabrominated porphyrins display a similar saddle distortion and average displacement of the β-carbons.[21] A certain amount of redistribution of steric strain occurs as evidenced by the significant displacement of β-carbon atoms of the non-halogenated ring [0.795(3) Å]. This steric redistribution was also observed in a series of nonplanar TPPs with increasing β-ethyl substitution.[22] On the other hand, dibromoporphyrin **4** is quasi-planar with a mean plane deviation of only 0.079(1) Å. The average displacement of the β-carbon atoms of the halogenated subunit relative to the porphyrin mean plane is 0.209(3) Å. The average displacement of the β-carbons of the three other pyrrole rings is 0.103(3) Å.

CONCLUSIONS

Dibromination of $H_2(2\text{-}NO_2TPP)$ provides a regioselective route to 2,3-dibromo- and 2,3-dicyanoporphyrins. Exhaustive bromination of $Cu(2\text{-}NO_2TPP)$ followed by denitration led to the pure regioisomer 2,3,12,13,17,18-Br_6TPP. The nitro group, used to direct electrophilic attack and easily removed by nucleophilic addition of $NaBH_4$ plays, in porphyrin systems, the role of sulfo-groups in simpler aromatic compounds.

EXPERIMENTAL

M.p.s 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. $H_2(2\text{-}NO_2TPP)$ **1** and $Cu(2\text{-}NO_2TPP)$ **8** were synthesized as already described.[10,11]

Crystal Structure Data for 4 and 12: Single crystals of compound **4** ($C_{44}H_{28}N_4Br_2$) were grown from dichloromethane/methanol. The crystals were immersed in hydrocarbon oil and a single crystal was selected, mounted on a glass fiber, and placed in low-temperature N_2 stream generated by a LT-1 device. X-ray diffraction data for **4** were collected on a Siemens P4 rotating anode with a normal-focus sealed tube [(λ(Cu Kα) 1.54178 Å] at 130(2)K in θ/2 θscan mode to $2\theta_{max} = 112°$. The unit cell was monoclinic and of space group P2(1)/n with cell dimensions: $a = 13.985(4)$, $b = 18.518(3)$, $c = 14.577(5)$ Å, $\alpha,\gamma = 90°$, $\beta = 116.85(2)°$, $V = 3368(2)$ Å^3 and Z = 4 (FW = 772.52, $\rho_{calc} = 1.524$ g·cm^{-3}). Unit-cell parameters were derived from the setting angles of 38 reflections in the range of $55° \leq 2\theta \leq 60°$. Two standard reflections were measured every 198 reflections in a total reflections of 6503 of which 4237 were unique ($R_{int} = 0.08$); number of parameters = 457. Final R factors were $R1 = 0.078$ (based on observed data), and $wR2 = 0.215$ (based on all data). Single crystals of compound **12** $[(C_{44}H_{23.9}N_4Br_6)(Cu)_{0.05}(C_4H_4O)_{0.95}]$ were grown from tetrahydrofuran/methanol and were mounted following the procedure described for compound **4**. X-ray diffraction data for **12** were collected on a Siemens R3 diffractometer with a fine-focus sealed tube [(λ(MoK) 0.71073 Å] at 130(2)K in θ/2 θscan mode to $2\theta_{max} = 55°$. The unit cell was monoclinic and of space group P2(1)/c with cell dimensions: $a = 12.169(2)$, $b = 27.963(6)$, $c = 13.837(3)$ Å, $\alpha,\gamma = 90°$, $\beta = 113.64(3)°$, $V = 4313(2)$ Å^3 and Z = 4 (FW = 1155.52, $\rho_{calc} = 1.779$ g·cm^{-3}). Unit-cell parameters were derived from the setting angles of 37 reflections in the range of $30° \leq 2\theta \leq 40°$. Two standard reflections were measured every 198 reflections in a total reflections of 10565 of which 9899 were unique ($R_{int} = 0.058$); number of parameters = 536. Final R factors were $R1 = 0.079$ (based on observed data), and $wR2 = 0.2360$ (based on all data). The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied using XABS2;[23] extinction effects were disregarded. The structure solution of compound **4** and **12** were solved using direct methods and refined (based on F^2using 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. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC).

12,13-Dibromo-2-nitro-5,10,15,20-tetraphenylporphyrin 2. A mixture of $H_2(2\text{-}NO_2TPP)$ **1** (1.0 g, 1.52 mmol) and *N*-bromosuccinimide (0.68 g, 2.42 equiv) in dry chloroform (ethanol free, 150 mL) was heated under reflux overnight. After being cooled to room temperature, the reaction mixture was filtered through an alumina plug (Grade III; eluting with CH_2Cl_2). The filtrate was evaporated to dryness and the resulting residue was recrystallized from CH_2Cl_2/MeOH to give 1.01 g (82%) of a brown powder, mp > 300 °C; UV-Vis λ_{max} 436 nm (ε 152 000), 538 (11 200), 688 (7600); NMR δ_H (ppm) 8.97 (s, 1 H), 8.83 (m, 4 H), 8.25 (m, 8 H), 7.80 (m, 12 H), -2.55 (s, 1 H), -2.62 (s, 1 H); MS, m/z 817.9 (100%). Anal. Calcd for $C_{44}H_{27}N_5O_2Br_2 \cdot 2H_2O$: C, 61.92; H, 3.66; N, 8.20. Found C, 61.64; H, 3.33; N, 8.40.

12,13-Dibromo-2,3-dihydro-2-nitro-5,10,15,20-tetraphenylporphyrin 3. To a cold solution (ice/NaCl) of dried THF (30 mL) under argon was added a mixture of 2-nitro-12,13-dibromoTPP **2** (500 mg, 0.61 mmol) and $NaBH_4$ (40 mg, 1.11 mmol). The resulting reaction mixture is stirred for 2 h, the ice bath being removed after one h. The progress of the reaction was monitored by UV-Visible spectroscopy; after 2 h the Soret band had shifted from 436 to 424 nm. Dichloromethane (100 mL) was then added and the reaction mixture was poured into water. The organic phase was washed twice with water and evaporated to dryness. The residue was redissolved in dichloromethane and filtered through a short alumina plug (Grade V; eluting with CH_2Cl_2). After evaporation to dryness, the residue was recrystallized from CH_2Cl_2/MeOH to yield 420 mg (84%) of a brown amorphous powder, mp > 300 °C (decomposed with elimination of HNO_2 > 80 °C); UV-Vis λ_{max} 424 nm, 524, 555 sh, 592, 642 ; NMR δ_H (ppm) 8.85 (m, 2 H), 8.24 (m, 2 H), 8. 01 (m, 4 H), 7.70 (m, 14 H), 7.17 (dd, $J_{2\alpha,3\beta} = 2.1$ Hz, $J_{2\alpha,3\alpha} = 9.3$ Hz, H-2α), 4. 71 (1H, dd, J = 9.3 Hz, J = 18.6 Hz, H-3α), 4.49 (1H, dd, $J_{2\alpha,3\alpha} =$ 1.8 Hz, $J_{3\alpha,3\beta} = 18.6$ Hz, H-3β), -1.71 (s, 1 H), -1. 79 (s, 1 H); MS, m/z 773.2 (M - HNO_2, 100%). Anal. Calcd for $C_{44}H_{29}Br_2N_5O_2 \cdot 0.5H_2O$: C, 63.78; H, 3.65; N, 8.45. Found C, 63.81; H, 3.51; N, 8.29.

2,3-Dibromo-5,10,15,20-tetraphenylporphyrin 4. A mixture of nitrochlorin **3** (200 mg, 0.24 mmol), silica gel (20 g) and $CHCl_3$ (100 mL) was refluxed for 1 d under argon. The reaction mixture was cooled to room temperature and the silica gel was removed by filtration and washed thoroughly with CH_2Cl_2. After evaporation of the solvents to dryness, the residue was recrystallized from CH_2Cl_2/MeOH to yield 185 mg (98%) of a purple powder, mp > 300 °C; UV-Vis λ_{max} 424 nm (ε 169 000), 522 (1100), 560 (sh), 598 (4200), 656 (5100); NMR δ_H (ppm) 8.86 (m, 4 H), 8.71 (s, 2 H), 8.17 (m, 8 H), 7.85 (m, 12 H), -2.83 (s, 2 H); MS, m/z 770.1 (34%), 771.1 (50), 772.1 (88), 773.1 (100), 774.1 (86), 775.1 (65), 776.1 (28). Anal. Calcd for $C_{44}H_{28}Br_2N_4$: C, 68.41; H, 3.65; N, 7.25. Found C, 68.75 ; H, 3.95 ; N, 6.94.

Nickel(II) 2,3-Dibromo-5,10,15,20-tetraphenylporphyrin 5. A mixture of nitrochlorin **3** (500 mg, 0.61 mmol), nickel(II) acetylacetonate (95%, 1.2 g, 4.6 mmol) and toluene (100 mL) was heated under reflux overnight. The reaction mixture was cooled to room temperature and filtered through a short plug of silica gel (eluting with CH_2Cl_2). After evaporation to dryness, the residue was recrystallized from CH_2Cl_2/MeOH to yield 420 mg (83%) of a purple powder, mp > 300 °C; UV-Vis λ_{max} 422 nm (ε 124 000), 536 (9000); NMR δ_H (ppm) 8.71 (d, 2 H, J = 5.1 Hz), 8.68 (s, 2 H), 8.61 (d, 2 H, J = 5.1 Hz), 7.96 (m, 4 H), 7.83 (m, 4 H), 7.68 (m, 12 H); MS, m/z 829.3 (100%). Anal. Calcd for $C_{44}H_{26}Br_2N_4Ni$: C, 63.73; H, 3.16; N, 6.76. Found C, 63.22; H, 3.09; N, 6.62.

Nickel(II) 2,3-Dicyano-5,10,15,20-tetraphenylporphyrin 6. A mixture of **5** (400 mg, 0.48 mmol), copper(I) cyanide (550 mg, 5.6 mmol) and quinoline (15 mL) was heated at 200 °C for 2 h under argon. The reaction mixture was allowed to cool and CH_2Cl_2 (100 mL) was added. Excess copper cyanide was removed by filtration and the organic phase was washed with 10% HCl (3 x 100 mL), water (2x), dried over Na_2SO_4 and then evaporated to dryness. The residue was recrystallized from CH_2Cl_2/cyclohexane to yield 295 mg (85%) of a dark purple powder, mp > 300 °C; UV-Vis λ_{max} 434 nm (ε 165 000), 518 (6300), 554 (9700), 598 (22 000); NMR δ_H (ppm) 8.74 (d, 2 H, J = 5.1 Hz), 8.65 (s, 2 H), 8.58 (d, 2 H, J = 5.1 Hz), 7.91 (m, 8 H), 7.70 (m, 12 H). MS, m/z 721.2 (100%). Anal. Calcd for $C_{46}H_{26}N_6Ni$: C, 76.58; H, 3.63; N, 11.65. Found C, 76.97; H, 3.62 ; N, 11.65.

Copper(II) 2,3-Dicyano-5,10,15,20-tetraphenylporphyrin 7. A mixture of nitrochlorin **3** (500 mg, 0.61 mmol), copper(I) cyanide (1.1 g, 12 mmol) and quinoline (15 mL) was heated at 200 °C under argon for 2 h. The reaction mixture was allowed to cool and CH_2Cl_2 (100 mL) was added. Excess copper cyanide was removed by filtration and the organic phase was washed with 10% HCl (3 x 100 mL), water (2x), dried over Na_2SO_4 and then evaporated to dryness. The residue was recrystallized from CH_2Cl_2/cyclohexane to give 330 mg (75%) of a dark purple powder, mp > 300 °C; UV-Vis λ_{max} 434 nm (ε 185 000), 528 (6000), 562 (10 000), 606 (21 500); MS, m/z 726.2 (100%). Anal. Calcd for $C_{46}H_{26}CuN_6 \cdot H_2O$: C, 74.72; H, 3.82; N, 11.37. Found C, 74.36; H, 3.62; N, 11.05.

Copper(II) 2,3,7,8,12,13-Hexabromo-17-nitro-5,10,15,20-tetraphenylporphyrin 9. A mixture of Cu(2-NO_2TPP) **8** (1.53 g, 2.13 mmol), NBS (3.75 g, 10 equiv) in 1,2-dichloroethane (150 mL) was heated under reflux for 16 h under argon. After being cooled to room temperature, the reaction mixture was filtered through a silica gel plug (eluting with CH_2Cl_2). The filtrate was evaporated to dryness and the resulting residue was recrystallized from CH_2Cl_2/MeOH to give 1.76g (70%) of a dark green powder. Careful monitoring of the reaction by spectrophotometry was crucial as extended refluxing times led to slow degradation of the product and a concomitantly decreased yield. Mp > 300 °C; UV-Vis λ_{max} 460 nm (ε 124 000), 582 (14 500), 626 (8900); MS, m/z 1195.7 (100%). Anal. Calcd for $C_{44}H_{21}Br_6CuN_5O_2$: C, 44.24; H, 1.77; N, 5.86. Found C, 44.19; H, 1.67; N, 5.86.

2,3,7,8,12,13-Hexabromo-17-Nitro-5,10,15,20-tetraphenylporphyrin 10. In a 200 mL round bottom flask, Cu(2-NO_2-Br_6TPP) **9** (1.01 g, 0.85 mmol) was dissolved in a minimum of CH_2Cl_2 which was then evaporated to leave an oily film. Concentrated sulfuric acid (40 mL) was added. The reaction mixture was alternately stirred and sonicated for 1.5 h, then poured into ice/water and extracted with CH_2Cl_2. The organic phase was subsequently washed with water, saturated $NaHCO_3$, dried over Na_2SO_4 and then concentrated in vacuo to approximately 50 mL. Addition of MeOH (50 mL) and further concentration yielded, after filtration, 900 mg (94%) of a green amorphous powder. A green solution of **10** in CH_2Cl_2/5% Et_3N decomposed slowly, with isosbestic points at 490, 512, 670 nm, to give a red non-aromatic species displaying a broad band at 506 nm. (Note that compound **9** was stable under these conditions). Mp > 300 °C; UV-Vis λ_{max} 468 nm (ε 147 000), 572 (7400), 626 (12 000), 738 (6700); NMR δ_H (ppm) 8.59 (s, 1 H), 8.23 (m, 8 H), 7.78 (m, 12 H), -1.50 (br); MS, m/z 1133.6 (100%). Anal. Calcd for $C_{44}H_{23}Br_6N_5O_2 \cdot 2CH_3OH$: C, 46.15; H, 2.61; N, 5.85 . Found C, 45.73; H, 2.62; N, 5.54.

Copper(II) 2,3,7,8,12,13-Hexabromo-5,10,15,20-tetraphenylporphyrin 11. To a solution of dried DMSO (10 mL) under argon was added a mixture of **9** (400 mg, 0.33 mmol) and $NaBH_4$ (22 mg, 0.61 mmol). The resulting green solution turned brown after few min. The reaction mixture was stirred for 2 h and featured a 22 nm blue-shift of the Soret absorption band. Dichloromethane (200 mL) was then added and the reaction mixture was poured into water. The organic phase was washed several times with water, reduced to 10 mL and set aside in the fridge for few h. A dark brown precipitate was filtered off to give 220 mg (57%) of pure **11**, (the mother liquors contained more product, but further purification via chromatography was not attempted), mp > 300 °C; UV-Vis λ_{max} 438 nm (ε 158 000), 568 (16 500), 610 (9300); MS, m/z 1150.8 (100%). Anal. Calcd for $C_{44}H_{22}Br_6CuN_4 \cdot 2H_2O$: C, 44.57; H, 2.21; N, 4.73. Found C, 44.97; H, 2.38; N, 4.56.

2,3,7,8,12,13-Hexabromo-5,10,15,20-tetraphenylporphyrin 12. Demetalation of porphyrin **11** (160 mg, 0.14 mmol) was carried out in 20 mL of conc. sulfuric acid for 1 h as described for the preparation of **10**. Recrystallization from CH_2Cl_2/MeOH gave a dark purple powder (115 mg, 76%), mp: 303-305 °C; UV-Vis λ_{max} 454 nm (ε 171 000), 553 (9400), 604 (7800), 713 (6900); NMR δ_H (ppm) 8.61 (s, 2 H), 8.23 (m, 8 H), 7.80 (m, 12 H), -1.68 (br, 2 H); MS, m/z 1088.8 (100%). Anal. Calcd for $C_{44}H_{24}Br_6N_4$: C, 48.57; H, 2.22; N, 5.14. Found C, 48.60; H, 2.30; N, 5.15.

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