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Introduction of a Third Meso Substituent into 5,10-Diaryl Chlorins and Oxochlorins

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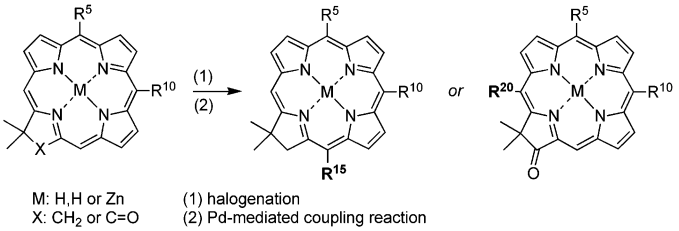

Chlorins/oxochlorins bearing distinct patterns of substituents are valuable compounds in bioorganic and materials chemistry. Treatment of a 5,10-diaryl-substituted chlorin or oxochlorin with TFA-d_1 resulted in selective deuteriation of the remaining meso positions (15, 20) rather than any of the β-pyrrolic positions. Electrophilic iodination or bromination of a 5,10-diaryl-substituted chlorin proceeded with high regioselectivity, affording the 5,10-diaryl-15-halo-substituted chlorin. Iodination or bromination of a free base 5,10-diaryloxochlorin gave a mixture of products arising through halogenation at the 15-, 20-, and β-pyrrolic positions, while bromination of a zinc 5,10-diaryloxochlorin selectively gave the 5,10-diaryl-20-bromo-substituted oxochlorin. The Suzuki coupling reaction of a phenyl boronic acid derivative and a 5,10-diaryl-15-iodooxochlorin or 5,10-diaryl-20-bromooxochlorin gave the corresponding 5,10,15- or 5,10,20-triaryloxochlorin. The introduction of a third aryl substituent into the chlorin or oxochlorin causes an ~5-nm red shift of the long wavelength Q_y absorption band. Two phenylethyne-linked oxochlorin−oxochlorin dyads in distinct metalation states (zinc/free base, free base/zinc) were prepared by Sonogashira coupling reactions of a 5,10-diaryl-20-bromooxochlorin and a 10-substituted ethynylphenyl oxochlorin. This study provides access to new chlorins/oxochlorins that can be utilized in diverse applications.

Introduction

A chlorin differs from a porphyrin in containing one pyrrole ring that is reduced at the β-positions. One manifestation of the reduction is the stronger absorption in the red spectral region compared with that of a porphyrin, imbuing chlorins with their characteristic green color.[1] Chlorophyll *a* and chlorophyll *b* are the best known chlorins, though other naturally occurring chlorins also are known, including Faktor I and bonellin (Chart 1).[2] The characteristic spectral features of chlorins have caused these hydroporphyrins to be sought as diagnostic and therapeutic agents in medicinal chemistry and as light-absorbing components in materials chemistry.

The naturally occurring chlorins bear a rich pattern of substituents at the six β-positions of the pyrrolic rings, typically leaving three if not four meso positions unsubstituted. One of the chief challenges to syntheses of the natural chlorins, in addition to constructing the dihydroporphyrin macrocycle, lies in assembling the appropriate pattern of substituents. Total syntheses of chlorin e_6 (a precursor to chlorophylls),[3] Faktor I,[4] and bonellin[5] have been developed. Routes to chlorins for biological and materials chemistry applications typically employ one of two distinct strategies: (1) derivatization of naturally occurring chlorins or (2) reduction of syn-

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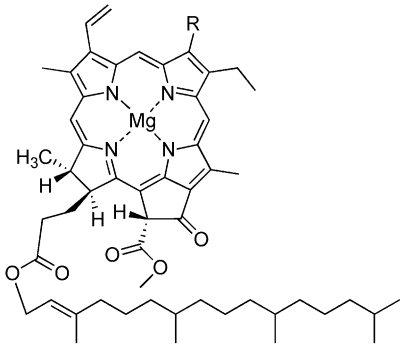
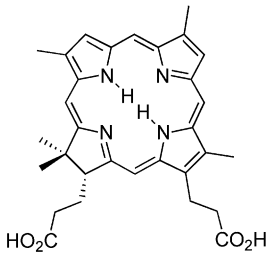
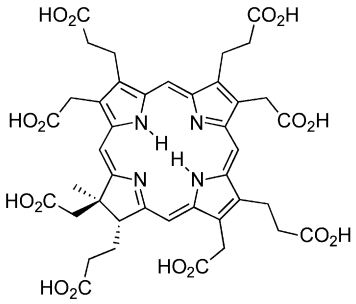
CHART 1



R = CH_3, Chlorophyll *a*
R = CHO, Chlorophyll *b*

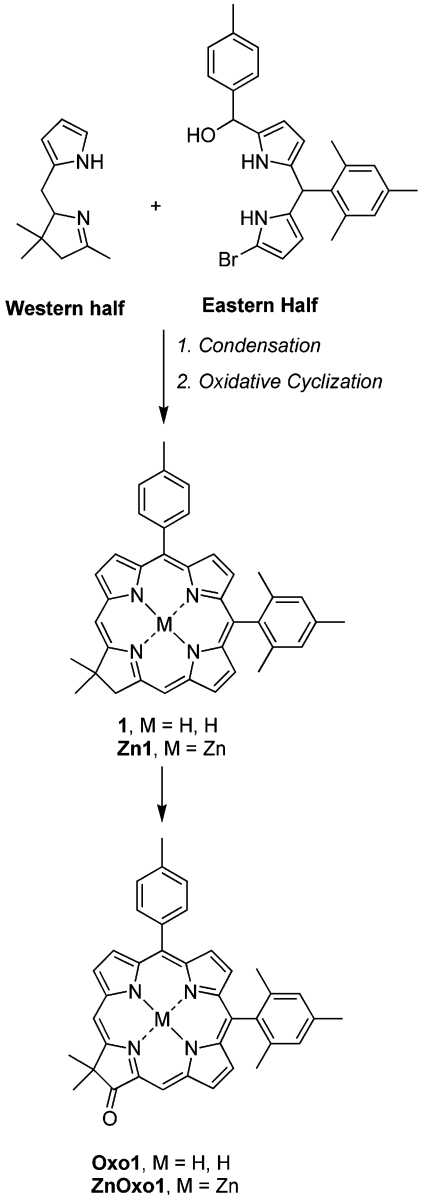


Bonellin



Faktor I

SCHEME 1



thetic porphyrins. The former route has access to large quantities of starting materials but restricts control over the pattern of substituents. The latter route is compatible with diverse substituents (though regioisomers may form) yet often suffers from adventitious dehydrogenation that regenerates the porphyrin.

Over the past few years, we have developed a *de novo* synthesis of chlorins (Scheme 1).[6−8] The chlorin incorporates a geminal dimethyl group in the reduced ring to lock in the chlorin reduction level, thereby precluding adventitious dehydrogenation to give the porphyrin. The geminal dimethyl motif in the reduced pyrroline ring is not found in chlorophylls but is present in other chlorins such as Faktor I and bonellin. Indeed, our synthetic plan was inspired by Battersby's synthetic approaches to bonellin and Faktor I[4,5] but in its simplest guise employs pyrrole synthons that lack β-substituents. The synthesis entails reaction of an Eastern half and a Western half (Scheme 1). The Eastern half is readily available and provides a substrate for introduction of diverse substituents at the 5- and 10-positions of the chlorin.[6] The Western half is less amenable to synthetic manipulation, though we have carried out lengthy syntheses to introduce substituents in the pyrrolic ring (corresponding to the chlorin 2-position)[7] or a spirohexyl group[9] in place of the geminal dimethyl groups. Lengthy syntheses of Eastern-half derivatives have led to chlorins bearing substituents at the 8- or 12-positions.[7] Oxidation of the chlorin affords the corresponding oxochlorin, where a keto group is present adjacent to the geminal dimethyl group in the reduced ring (17-position).[9] The oxochlorin has greater redox stability compared to the chlorin. Thus, substitution of chlorins has been achieved at positions 2, 5, 8, 10, 12, 17, and 18. With the exception of the 17-oxo group, all substituents have been introduced through the use of substituted Eastern-half and/or Western-half precursors.

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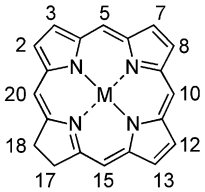
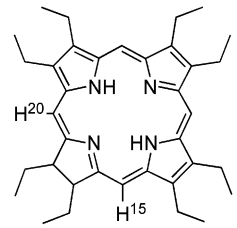


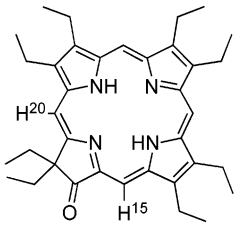
An effective synthetic strategy in porphyrin chemistry has been to prepare a porphyrin and introduce additional substituents by derivatization of the macrocycle. This approach is particularly effective with porphyrins containing one or two free meso positions; subsequent halogenation and Pd-mediated coupling enable introduction of diverse meso substituents.[10−15] We thought a similar strategy could be meritorious for the synthesis of trisubstituted chlorins/oxochlorins. A key for the success of this strategy is the ability to control the position of halogenation. Because most naturally occurring chlorins contain a full (or nearly full) complement of β-substituents, relatively little is known about substitution chemistry of chlorins containing free meso and β-positions, at least in comparison to that of porphyrins.[16] The studies to date concerning functionalization of chlorins have employed the following chlorin derivatives: (1) octaethylchlorin, where all β-positions are blocked;[17] (2) chlorophyll derivatives, such as chlorin-e_6 trimethyl ester where all β-positions and one meso (15) position are blocked;[18,19] and (3) *meso*-tetraphenylchlorin derivatives, where all meso positions are blocked.[20]

In this paper, we report studies aimed at understanding the substitution chemistry of 5,10-diarylchlorins and oxochlorins. The studies include examination of the relative reactivity of meso and β-sites of free base chlorins/oxochlorins upon deuteriation, and of free base or zinc chlorins/oxochlorins upon bromination or iodination. The identification of substrates and reagents that afford selective halogenation provided an entrée into the synthesis of triaryl-substituted chlorins and oxochlorins via Pd-mediated coupling reactions. The absorption spectral properties of the triaryl derivatives have been noted as part of an effort to understand substituent effects in chlorin chemistry. This work provides the foundation for the rational synthesis of synthetic chlorins bearing defined substituent patterns.

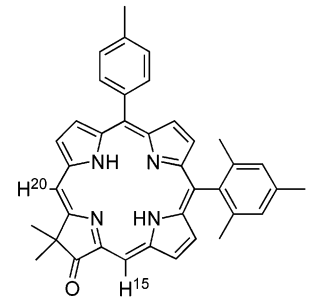
CHART 2



OEC



Oxo-OEC



Oxo1

Results and Discussion

I. Deuteriation of Chlorin/Oxochlorins. Woodward first reported that deuteriation of chlorins occurs predominantly at the meso sites flanking the reduced, pyrroline ring (15- and 20-positions).[18] Such studies were performed using chlorins wherein all four meso positions are free and a nearly if not completely full set of β-substituents is present (Chart 2).[18,21−26] The relative reactivity of the meso positions flanking the pyrroline ring of various hydroporphyrinic species has been exam-

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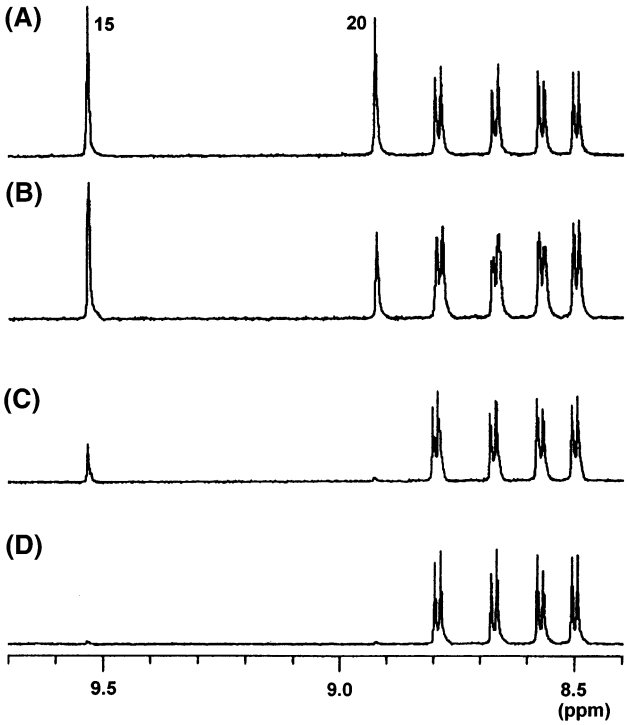

FIGURE 1. Deuteriation of the 15- and 20-position of oxochlorin **Oxo1** in TFA-d_1 at 50 °C. The four multiplets (8.5−8.8 ppm) correspond to four of the six pyrrolic β-protons: (A) 0 min, (B) 64 min, (C) 325 min, (D) 10 h.

ined by early molecular orbital calculations,[24,27] but to our knowledge no calculations concerning meso versus β-substitution have been reported (although frontier molecular orbital densities[28] are well-known). At the outset of our studies, we needed to establish whether substitution would occur preferentially at the open meso versus β-positions in the synthetic chlorins, a phenomenon not possible in the systems investigated previously. Chlorin **1**[7] or oxochlorin **Oxo1**[9] was treated in neat deuteriotrifluoroacetic acid (TFA-d_1) at 50 °C. The signals from H^{15} and H^{20} steadily diminished over a few hours. By contrast, the signals from the β-protons remained intact for up to 100 h. This study indicated the preferential reactivity of the meso versus β-sites in the diaryl-substituted chlorin and oxochlorin.

The ^{1}H NMR spectra of free base oxochlorin **Oxo1** in TFA-d_1 at 50 °C (Figure 1) enabled estimation of the pseudo-first-order rate constants for deuterium exchange. Kinetic measurement was made to at least 75% deuterium exchange of the meso protons. The rate of exchange of H^{20} was three times faster than for H^{15} in **Oxo1**. The similar molecule octaethyloxochlorin **Oxo-OEC**[25] exhibits overall faster rates of exchange, but the same trend in reactivity (H^{20} ∼ three times faster than for H^{15}) is observed (Table 1). Similar studies of chlorin **1** were attempted. Approximately 75% of the meso protons (H^{15} and H^{20}) in chlorin **1** underwent exchange with deuterium within 100 min, but rate constants could not be calculated due to the overlapping resonances of H^{15} and H^{20} (see the Supporting Information). It is noteworthy

TABLE 1. Pseudo-First-Order Rate Constants for Deuterium Exchange of Chlorin/Oxochlorin Meso Protons

compound	meso protons	k^a (s^{-1})	$t_{1/2}{}^a$ (min)
OEC[b]	15, 20	5.7×10^{-5} [c]	200[c]
Oxo-OEC	15	1.5×10^{-5} [d]	780[d]
Oxo-OEC	20	4.8×10^{-5} [d]	240[d]
Oxo1	15	7.8×10^{-5}	150
Oxo1	20	1.8×10^{-4}	64

[a] In TFA-d_1 at 50 °C. [b] Stereochemistry of **OEC** is not clear. [c] Reference 25. [d] Reference 26.

that deuteriation of chlorophyll *a* at the open meso position flanking the reduced ring has been observed under neutral conditions with CD_3OD, but the free base analogue (pheophytin *a*) showed hardly any reactivity.[21,22,24] We attempted similar studies under neutral conditions of **Zn1** and **ZnOxo1**, but in both cases exposure to $CD_3OD/CDCl_3$ at 37 °C for 16 h gave no observable deuteriation of the meso positions (H^{15} and H^{20}).

II. Halogenation of Chlorins/Oxochlorins. Prior to examining the electrophilic halogenation of chlorins/oxochlorins, all meso and β-pyrrolic protons of chlorins/oxochlorins were assigned by NMR spectroscopy (HH-COSY, NOE, and NOESY). The assignments for **1**, **Zn1**,[7,8] **Oxo1**, and **ZnOxo1**[9] are summarized in the Supporting Information. The ^{1}H NMR spectrum of each chlorin/oxochlorin shows a singlet for each of the two meso protons and a doublet for each of the six β-pyrrolic protons. The resonances of the β-pyrrolic protons (H^7 and H^8) on the ring diametrically opposed to the reduced, pyrroline ring were shifted upfield compared to other β-pyrrolic protons. The resonances of **Zn1** or **ZnOxo1** are overlapped compared to those of the free base species **1** or **Oxo1**, due to the upfield shift of the meso protons (H^{15} and H^{20}). In oxochlorins, the resonance of H^{15} and of H^{20} was shifted downfield compared to that of chlorins. These assignments facilitate determination of the substitution pattern of halogenated chlorins/oxochlorins.

Halogenation was performed using literature procedures for reaction with NBS,[29] I_2/AgO_2CCF_3,[29] and $I_2/(CF_3CO_2)_2IC_6H_5$.[15] We first examined the bromination of chlorin **1** using NBS (eq 1). The reaction of **1** with 1 equiv of NBS was essentially complete within 1 h, affording the 15-bromochlorin **1-Br15** (70% yield), the dibromo-substituted chlorins **1-Br15,20** (8%) and **1-Br7,15** (4%), and a small amount of unreacted starting material **1** (5%). The 15-bromochlorin **1-Br15** was readily isolated (entry 1, Table 2). The bromochlorins were assigned by ^{1}H NMR spectroscopy as shown in the Supporting Information. The substitution pattern was established by (1) disappearance of the resonance upon bromo substitution and (2) downfield shift of the resonance stemming from the hydrogen positioned adjacent to the bromo atom. No other monobromo-substituted chlorins such as a 20- or β-bromo-substituted chlorin were observed.

Further halogenation studies were performed with the free base chlorin **1** and zinc chlorin **Zn1**. Iodination of **1** afforded the 15-substituted iodochlorin in 81% yield (entry 2, Table 2). Bromination of zinc chlorin **Zn1** afforded the 15-bromo zinc chlorin, also in 81% yield

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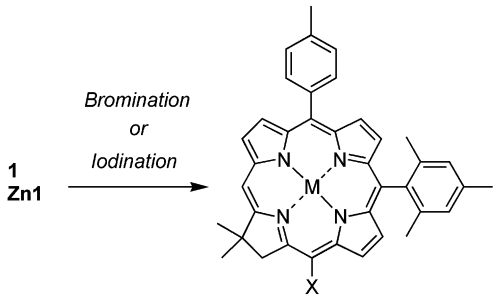
TABLE 2. Halogenation of Chlorins 1 and Zn1

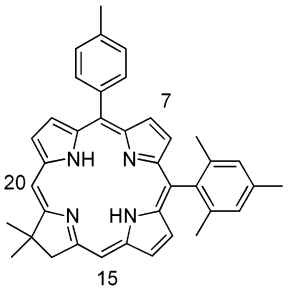


1-Br15 **Zn1-Br15**
1-I15 **Zn1-I15**

entry	starting material	M	X	product	yield (%)
1[a]	**1**	H, H	Br	**1-Br15**	70
2[b]	**1**	H, H	I	**1-I15**	81
3[a]	**Zn1**	Zn	Br	**Zn1-Br15**	81
4[c]	**Zn1**	Zn	I	**Zn1-I15**	22

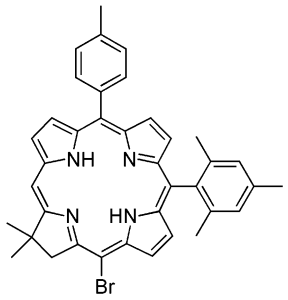
[a] NBS in THF. [b] $I_2/(CF_3CO_2)_2IC_6H_5$ in $CHCl_3$/pyridine. [c] I_2/CF_3CO_2Ag in THF.

(entry 3). Iodination of **Zn1** afforded the 15-iodo product **Zn1-I15** in only 22% isolated yield (entry 4); accordingly, we also synthesized **Zn1-I15** by zincation of **1-I15**. In addition to the 15-halochlorin produced, each halogenation reaction gave dihalo-substituted chlorins together



1

NBS (1 equiv)
THF (1)



1-Br15 70%

+

di-bromo chlorins

1-Br7,15 4%

1-Br15,20 8%

+

Recovery of **1** 5%

SCHEME 2

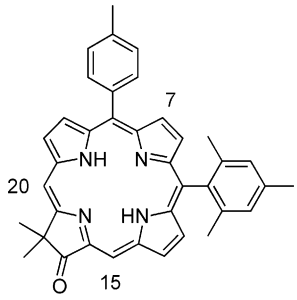
mono-bromo oxochlorins + di-bromo oxochlorins

Oxo1-Br7 12% **Oxo1-Br7,15** 1%

Oxo1-Br15 4% **Oxo1-Br7,20** 7%

Oxo1-Br20 13% **Oxo1-Br15,20** 2%

Bromination ↑ NBS, THF



Oxo1

Iodination ↓ $I_2/(CF_3COO)_2IC_6H_5$, $CHCl_3$/pyridine

mono-iodo oxochlorins + di-iodo oxochlorins

Oxo1-I15 22% **Oxo1-I7,15** 5%

Oxo1-I20 14%

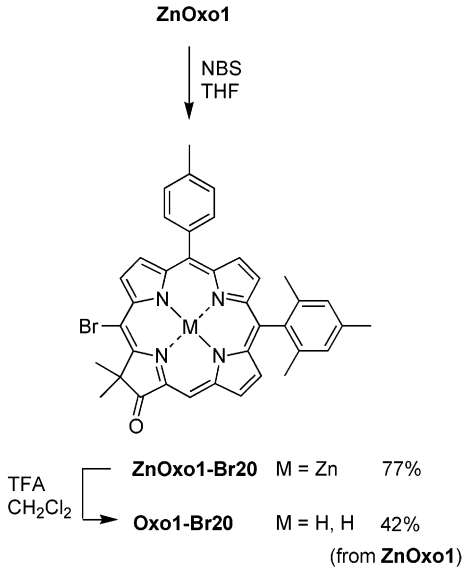
+

other iodo oxochlorins

with recovery of starting material. Purification of the desired 15-halo-substituted free base chlorins was straightforward (chromatography), while the 15-halo-substituted zinc chlorins required lengthy column chromatography for purification. Selective halogenation at the 15-position rather than the 20-position can be ascribed to steric hindrance due to the geminal dimethyl group at the 18-position.

The analogous halogenation of free base oxochlorin **Oxo1** was slower than that of the chlorins, and a significant amount of starting material remained after 3 h. After 24 h, the presence of several brominated components indicated the low selectivity of the bromination process. Extensive chromatography led to isolation of the 20-bromo (**Oxo1-Br20**, 13%), 7-bromo (**Oxo1-Br7**, 12%), 7,20-dibromo (**Oxo1-Br7,20**, 7%), 15-bromo (**Oxo1-Br15**, 4%), 15,20-dibromo (**Oxo1-Br15,20**, 2%), and 7,15-dibromo (**Oxo1-Br7,15**, 1%) products (Scheme 2). The substitution pattern of each bromooxochlorin was identified by ^1H NMR spectroscopy as shown in the Supporting Information. The ^1H NMR spectra of the bromo-substituted oxochlorins exhibit the disappearance of the resonance from the site of bromination and a downfield shift of the resonance from the nearest-neighbor proton. It is noteworthy that the β-pyrrolic position (7-position) was halogenated while deuteriation of the β-pyrrolic position was not observed. In fact, the predominant component present in TFA solution is the diprotonated chlorin/oxo chlorin dication; thus, the results of deuteriation and halogenation are not directly comparable.

SCHEME 3

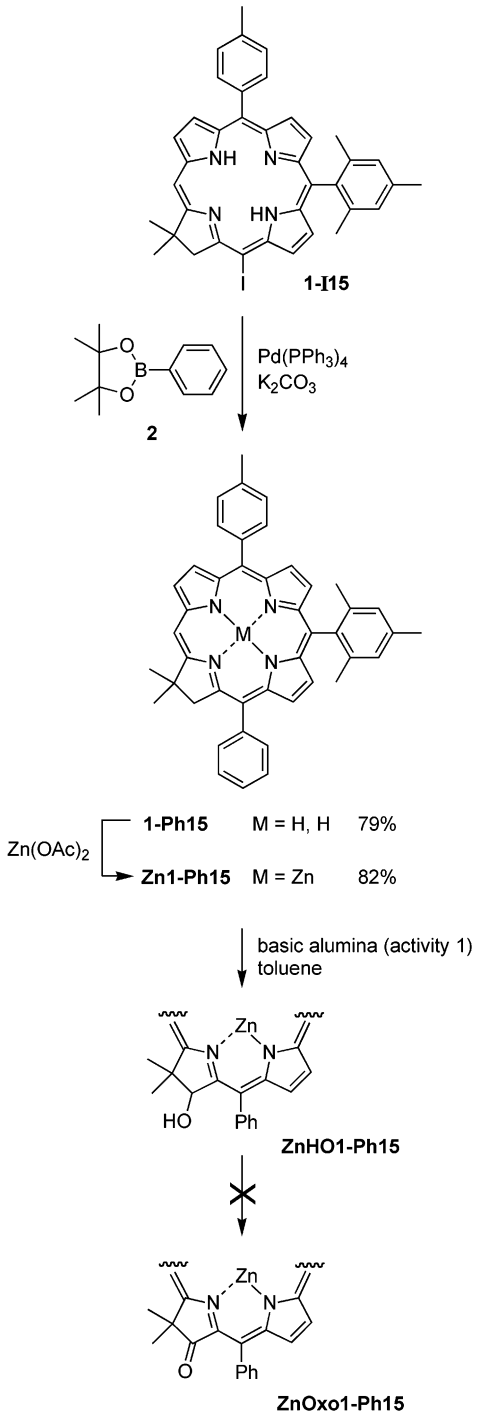


The iodination of free base oxochlorin **Oxo1** gave similar poor selectivity, affording the 15-iodooxochlorin (**Oxo1-I15**, 22%), 20-iodooxochlorin (**Oxo1-I20**, 14%), and the 7,15-diiodo-substituted oxochlorin (Scheme 2). The 15-position was slightly preferred for iodination while the 20-position was preferred in bromination.

By contrast to the poor selectivity in halogenation of the free base oxochlorin, treatment of the zinc oxochlorin **ZnOxo1** with NBS gave the 20-bromo-substituted chlorin **ZnOxo1-Br20** in a quite selective manner (77% yield) (Scheme 3) with only small quantities of dibromo-substituted oxochlorins and recovered starting material. This surprising result is entirely distinct from the result obtained upon halogenation of free base oxochlorin **Oxo1** described above. Free base oxochlorin **Oxo1-Br20** was obtained by demetalation of **ZnOxo1-Br20** with TFA. The facile introduction of a halo substituent at the 20-position provides facile access to 5,10,20-trisubstituted oxochlorins. It is noteworthy that the greater reactivity of the 20-position (versus the 5, 10, and 15-positions) was observed in an oxochlorin derived from zinc octaethylporphyrin.[30]

III. Introduction of a Third Aryl Substituent. With 15-halo-substituted chlorins in hand, the synthesis of 5,10,15-triaryl-substituted chlorins was pursued via Pd-mediated coupling reactions. For benchmark studies, the phenyl group was chosen as the third aryl substituent to be introduced. Suzuki coupling of **1-I15** with 4,4,5,5-tetramethyl-2-phenyl[1,3,2]dioxaborolane[31] (**2**) under conditions for use with porphyrins[13,14,32−34] gave 5,10,15-triaryl-substituted chlorin **1-Ph15** in 79% yield. Subsequent zincation of **1-Ph15** gave **Zn1-Ph15** in 82% yield (Scheme 4). This route provides facile and regioselective introduction of an aryl substituent in two steps from the 5,10-diaryl-substituted chlorin.

SCHEME 4



The formation of a triaryl-substituted oxochlorin from a 5,10-diaryl-substituted chlorin involves three steps: (1) meso-halogenation, (2) halogen replacement upon metal-mediated coupling, and (3) oxidation of the 17-position (conversion of the chlorin via the hydroxychlorin to the oxochlorin). There are three possible permutations of these steps, including route A, (1)→ (2) → (3); route B, (1) → (3) → (2); and route C, (3) → (1) → (2). We investigated each route.

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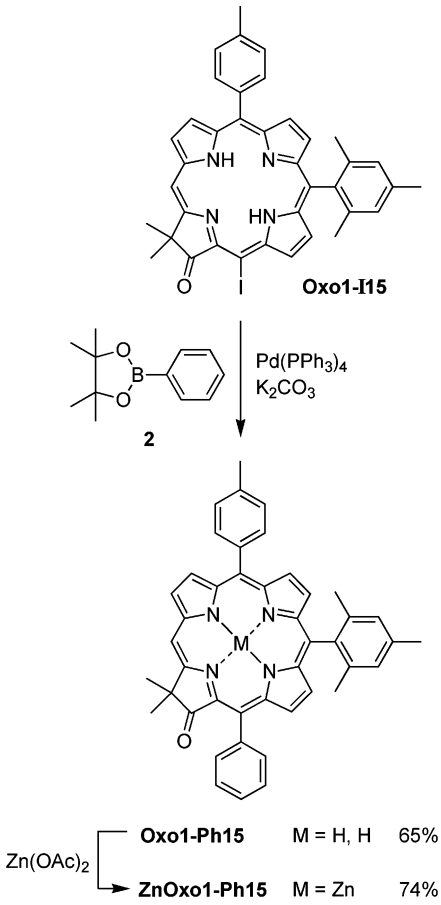
(31) Murata, M.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 6458−6459.
(32) (a) Zhou, X.; Zhou, Z.-Y.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2519−2520. (b) Zhou, X.; Chan, K. S. *J. Org. Chem.* **1998**, *63*, 99−104. (c) Tse, M. K.; Zhou, Z.-Y.; Mak, T. C. W.; Chan, K. S. *Tetrahedron* **2000**, *56*, 7779−7783.
(33) Deng, Y.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1066−1068.
(34) Yu, L.; Lindsey, J. S. *Tetrahedron* **2001**, *57*, 9285−9298.

SCHEME 5

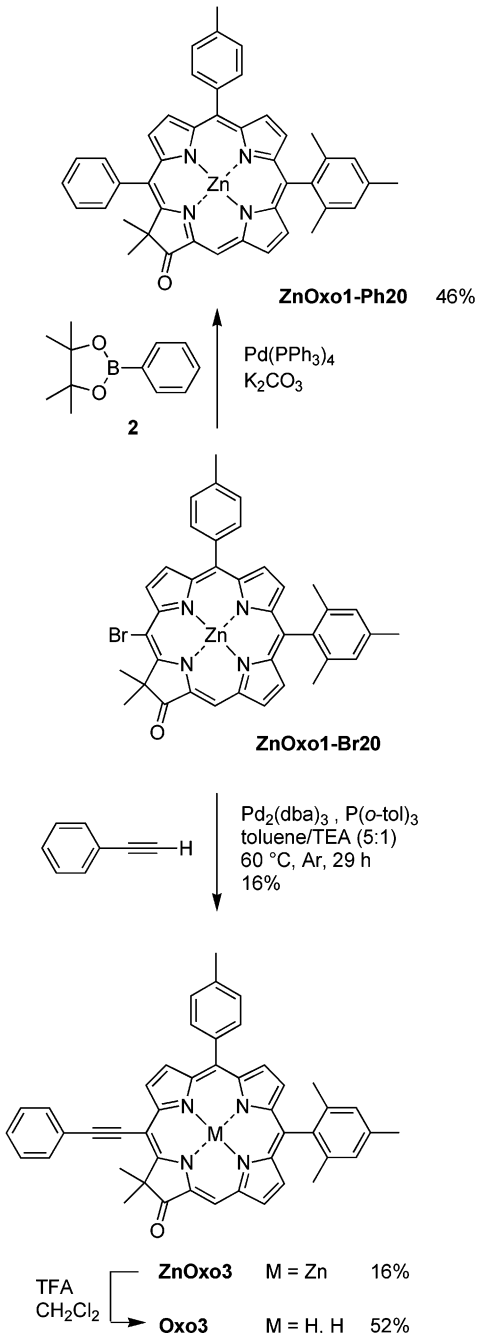


Route A. Treatment of triaryl-substituted chlorin **Zn1-Ph15** to the standard oxidation procedure (alumina/DDQ) to form the oxochlorin[9] gave the expected intermediate hydroxychlorin **ZnHO1-Ph15**, but the subsequent reaction with DDQ gave decomposition rather than the desired **ZnOxo1-Ph15**. (Note that free base chlorins are resistant to oxidation on alumina.) Attempted oxidation of **ZnHO1**−**Ph15** with a wide variety of oxidizing agents proved ineffective (Scheme 4).

Route B. Treatment of 15-halo-substituted chlorin **Zn1-Br15** or **Zn1-I15** to the oxochlorin-forming process gave the intermediate hydroxychlorin **ZnHO1-Br15** or **ZnHO1-I15** (a trace amount of **ZnOxo1-Br15** or **ZnOxo1-I15** was observed by TLC and UV−vis spectroscopy). However, exposure of the hydroxychlorin to DDQ gave no detectable oxochlorin but instead resulted in decomposition. The resistance of the 15-substituted hydroxychlorins to undergo further oxidation is attributed to steric factors.

Route C. Several Pd-mediated coupling reactions were carried out using the halooxochlorins. Suzuki coupling of 15-iodo-substituted oxochlorin **Oxo1-I15** with **2** gave 5,10,15-triaryl-substituted oxochlorin **Oxo1-Ph15** in 65% yield. Zincation of the latter gave **ZnOxo1-Ph15** in 74% yield (Scheme 5). Although this route is attractive for the preparation of a 10,15,20-triaryl-substituted oxochlorin, lack of selectivity in the halogenation of the free base oxochlorin limits the efficiency of the overall synthesis. On the other hand, the 20-halo-substituted oxochlorin **ZnOxo1-Br20** is readily available. Suzuki coupling of 20-halo-substituted oxochlorin **ZnOxo1-Br20** with **2** gave

SCHEME 6



5,10,20-triaryl-substituted oxochlorin **ZnOxo1-Ph20** in 46% yield (Scheme 6) together with a significant amount of debrominated oxochlorin **ZnOxo1**. Debromination of porphyrinic compounds in Suzuki reactions has been reported.[34] The Sonogashira coupling reaction of **ZnOxo1-Br20** with phenylacetylene was performed under copper-free conditions developed for porphyrins, which entail use of $Pd_2(dba)_3$ and P(*o*-tol)$_3$ in toluene/triethylamine (5:1) at 60 °C.[35] The phenylethyne-linked oxochlorin **ZnOxo3** was obtained in 16% yield. Subsequent demetalation with TFA in CH_2Cl_2 gave phenylethyne-linked oxochlorin **Oxo3** in 52% yield.

(35) (a) Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974−2983. (b) Loewe, R. S.; Lammi, R. K.; Diers, J. R.; Kirmaier, C.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 1530−1552.

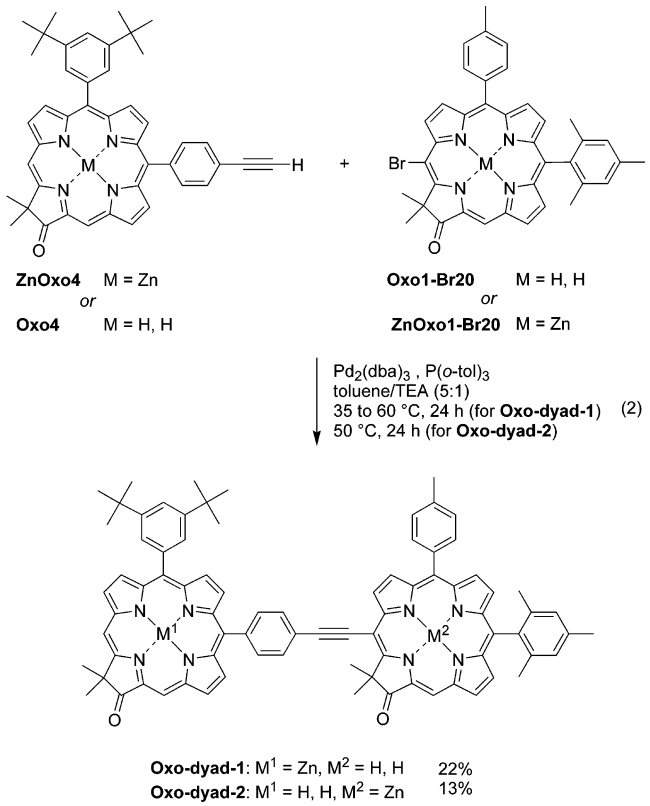
TABLE 3. Absorption Spectral Properties of Chlorins[a]

chlorins	λ_{max} (nm), B	λ_{max} (nm), Q_y	B/Q_y intensity ratio
Zn1	412	608	4.9
Zn1-Ph15	416	613	5.4
ZnOxo1	423	609	5.2
ZnOxo1-Ph15	425	612	4.3
ZnOxo1-Ph20	427	614	6.4
Chlorophyll *a*[b]	430	662	1.3
Chlorophyll *b*[b]	455	644	2.8

[a] In toluene at room temperature. [b] In diethyl ether.[1]

The absorption spectra of triaryl-substituted chlorins/oxochlorins are summarized in Table 3. Both the B and Q_y bands of triaryl-substituted chlorins/oxochlorins underwent a slight red shift compared to that of diaryl-substituted chlorins/oxochlorins. In comparison, introduction of a methyl group at the 20-position in a naturally occurring chlorin (conversion of bacteriochlorophyll *d* → bacteriochlorophyll *c*) caused a more substantial red shift (20 nm).[36] Although increased intensity of the Q_y band is attractive for many applications, the ratio of the intensity of the B/Q_y bands was relatively unchanged upon introduction of the additional aryl or methyl substituent group in the synthetic chlorins or the naturally occurring chlorin,[36] respectively.

IV. Synthesis of Phenylethyne-Linked Oxochlorin−Oxochlorin Dyads. A number of covalently linked dyads containing chlorins or oxochlorins have been prepared. The majority have been designed as models of the photosynthetic special pair,[37] whereas relatively few have served as models for studies of light-harvesting and excited-state energy transfer.[38,39] The dyads that we prepared for the latter studies incorporated a zinc chlorin and a free base chlorin, or a zinc oxochlorin and a free base oxochlorin, with a diphenylethyne linker joining the respective macrocycles at the 10 and 10′ positions.[39] The availability of **Oxo1-Br20** (or **ZnOxo1-Br20**) and the success of the Sonogashira coupling reaction made possible the synthesis of phenylethyne-linked oxochlorin−oxochlorin dyads in distinct metalation states. Thus, the Pd-coupling of the ethynylphenyl-substituted zinc oxochlorin **ZnOxo4**[9] and the bromo-substituted free base oxochlorin **Oxo1-Br20** was carried out using the conditions that have been developed for use with porphyrins.[35] The reaction was performed using equimolar amounts of ethyne and bromo species in dilute solution (2.5 mM each). The reaction was monitored by analytical size exclusion chromatography (SEC). High molecular weight material and monomer species were removed by preparative SEC, affording **Oxo-dyad-1** in 22% yield (eq 2). A similar coupling of **Oxo4** and **ZnOxo1-Br20** gave **Oxo-dyad-2** in 13% yield. Although the coupling reaction to give oxochlorin dyads proceeded in low yield, the resulting dyads are quite valuable for studies of excited-state energy transfer.



Oxo-dyad-1 and **Oxo-dyad-2** each contain one zinc oxochlorin and one free base oxochlorin, and each dyad is joined via a phenylethyne linker. The phenylethyne linker joins the 10 and 20′ positions of the two oxochlorins. The two dyads are structural isomers: in **Oxo-dyad-1** the zinc oxochlorin bears the phenyl unit of the phenylethyne linker at the 10-position, while the free base oxochlorin is substituted with the ethynyl unit of the phenylethyne linker at the 20′-position. In **Oxo-dyad-2** the situation is reversed: the 10-phenyl-substituted oxochlorin is the free base while the 20′-ethynyl-substituted oxochlorin is the zinc chelate.

Each dyad was characterized by analytical SEC, laser-desorption mass spectrometry (LD-MS),[40] FAB-MS, ^{1}H NMR spectroscopy, absorption spectroscopy, and fluorescence spectroscopy. Each dyad exhibited a single sharp peak upon analytical SEC (see the Supporting Information). The LD-MS spectrum of **Oxo-dyad-1** or **Oxo-dyad-2** shows a peak that corresponds to the molecule ion. The ^{1}H NMR spectrum of each dyad appears essentially as the sum of the spectra of the component zinc oxochlorin and free base oxochlorin. The new phenylethyne-linked oxochlorin dyads differ from previous diphenylethyne-linked oxochlorin dyads[39] not only in linker length but also in the position of the linker, which spans the 10 and 20′ positions of the oxochlorins whereas the diphenylethyne linker spanned the 10 and 10′ positions. The phenylethyne-linked oxochlorin dyads have been found to undergo excited-state energy transfer from zinc oxochlorin to free base oxochlorin with rate of ∼(20

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ps)$^{-1}$ and efficiency of >98%, to be compared with ~(140 ps)$^{-1}$ and 83% for the diphenylethyne-linked oxochlorin dyads.[41]

Conclusions

The chemistry described herein provides routes to 5,10,15-trisubstituted chlorins and 5,10,15- or 5,10,20-trisubstituted oxochlorins via a simple two-step pathway from the corresponding disubstituted chlorin/oxochlorin. The steps include (1) meso-halogenation and (2) substitution of the meso-halogen group by Pd-mediated coupling (e.g., Suzuki or Sonogashira reaction). The route to the 5,10,20-oxochlorins is considerably more efficient than that for preparing the 5,10,15-oxochlorins, due to the greater selectivity for 20-bromination of the zinc oxochlorin than 15-iodination or bromination of the free-base oxochlorin. Regardless, both routes provide access to valuable oxochlorin building blocks that have heretofore been inaccessible. The ability to introduce substituents onto the chlorin/oxochlorin perimeter should broaden the scope of application of these valuable hydroporphyrins.

Experimental Section

Noncommercial Compounds. The compounds **1**,[7] **Zn1**,[7,8] **Oxo1**,[9] **ZnOxo1**,[9] **2**,[31] **Oxo4**,[9] and **ZnOxo4**[9] were prepared as described in the literature.

Deuteriation Studies. Deuteriation reactions of **1** and **Oxo1** were examined using neat TFA-d_1 in sealed NMR tubes at 50 °C. The extent of deuteriation was measured by integration of the ^{1}H NMR spectrum (absence of tetramethylsilane). The geminal dimethyl group was used as a primary internal integration standard. Pseudo-first-order rate constants were obtained by nonweighted least-squares fitting of the log of the intensity of the resonance versus the elapsed time. See the Supporting Information for the plot from which the pseudo-first-order rate constants were derived.

Bromination of 1. A solution of **1** (27.5 mg, 50.0 μmol) in THF (25 mL) was treated with NBS (8.9 mg, 50 μmol) at room temperature for 2 h. CH_2Cl_2 (100 mL) was added, and the mixture was washed with aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated and the residue was chromatographed [silica, hexanes/CH_2Cl_2 (3:1)], affording the following three compounds:

15-Bromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)porphyrin (**1-Br15**), a dark purple solid (21.9 mg, 70%): ^{1}H NMR δ −1.75 to −1.69 (br, 1H), −1.50 to −1.43 (br, 1H), 1.84 (s, 6H), 2.06 (s, 6H), 2.60 (s, 3H), 2.67 (s, 3H), 4.65 (s, 2H), 7.22−7.24 (m, 2H), 7.49−7.53 (m, 2H), 7.98−8.02 (m, 2H), 8.30−8.33 (m, 1H), 8.40−8.43 (m, 1H), 8.53−8.57 (m, 1H), 8.74−8.79 (m, 2H), 8.76 (s, 1H), 9.07−9.09 (m, 1H); LD-MS obsd 627.6; FAB-MS obsd 626.2056, calcd 626.2045 ($C_{38}H_{35}BrN_4$); λ_{abs} 409, 516, 540, 594, 646 nm.

7,15-Dibromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)porphyrin (**1-Br7,15**), a dark purple solid (1.4 mg, 4%): ^{1}H NMR δ −1.89 to −1.81 (br, 1H), −1.55 to −1.49 (br, 1H), 1.82 (s, 6H), 2.04 (s, 6H), 2.59 (s, 3H), 2.65 (s, 3H), 4.61 (s, 2H), 7.19−7.22 (m, 2H), 7.45−7.51 (m, 2H), 7.81−7.87 (m, 2H), 8.39 (s, 1H), 8.54−8.58 (m, 1H), 8.63−8.67 (m, 1H), 8.73−8.78 (m, 2H), 8.75 (s, 1H), 9.05−9.09 (m, 1H); LD-MS obsd 703.5; FAB-MS obsd 704.1213, calcd 704.1150 ($C_{38}H_{34}Br_2N_4$); λ_{abs} 415, 520, 544, 592, 644 nm.

15,20-Dibromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)porphyrin (**1-Br15,20**), a dark purple solid (2.7 mg, 8%): ^{1}H NMR δ −1.63 to −1.58 (br, 1H), −1.56 to −1.51 (br, 1H), 1.84 (s, 6H), 2.28 (s, 6H), 2.58 (s, 3H), 2.66 (s, 3H), 4.74 (s, 2H), 7.18−7.23 (m, 2H), 7.46−7.52 (m, 2H), 7.91−7.97 (m, 2H), 8.31−8.34 (m, 1H), 8.50−8.54 (m, 1H), 8.64−8.69 (m, 1H), 9.10−9.15 (m, 2H), 9.27−9.30 (m, 1H); LD-MS obsd 704.1; FAB-MS obsd 704.1204, calcd 704.1150 ($C_{38}H_{34}Br_2N_4$); λ_{abs} 414, 429, 527, 533, 602, 655 nm.

Zn(II) 15-Bromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)porphyrin (Zn1-Br15). A solution of **Zn1** (50.0 mg, 81.7 μmol) in THF (50 mL) was treated with NBS (14.5 mg, 81.7 μmol) at room temperature for 3 h. Standard workup and chromatography [silica, hexanes/CH_2Cl_2 (2:1)] gave a dark purple solid (45.8 mg, 81%): ^{1}H NMR δ 1.84 (s, 6H), 2.02 (s, 6H), 2.57 (s, 3H), 2.65 (s, 3H), 4.56 (s, 2H), 7.17−7.20 (m, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 7.6 Hz, 2H), 8.20 (d, J = 4.4 Hz, 1H), 8.31 (d, J = 4.4 Hz, 1H), 8.44 (d, J = 4.4 Hz, 1H), 8.46 (s, 1H), 8.59 (d, J = 4.4 Hz, 1H), 8.64 (d, J = 4.4 Hz, 1H), 8.99 (d, J = 4.4 Hz, 1H); LD-MS obsd 688.3; FAB-MS obsd 688.1177, calcd 688.1180 ($C_{38}H_{33}BrN_4Zn$); λ_{abs} 417, 614 nm.

17,18-Dihydro-15-iodo-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)porphyrin (1-I15). A solution of **1** (51.5 mg, 93.9 μmol) in chloroform (45 mL) was treated with iodine (23.8 mg, 93.9 μmol), pyridine (0.2 mL), and bis(trifluoroacetoxy)-iodobenzene (40.4 mg, 93.9 μmol) at room temperature for 20 min. Standard workup and chromatography [silica, hexanes/CH_2Cl_2 (2:1)] gave a dark pink solid (51.2 mg, 81%): ^{1}H NMR δ −1.61 to −1.53 (br, 1H), −1.37 to −1.29 (br, 1H), 1.83 (s, 6H), 2.04 (s, 6H), 2.59 (s, 3H), 2.65 (s, 3H), 4.67 (s, 2H), 7.20−7.23 (m, 2H), 7.47−7.53 (m, 2H), 7.96−8.01 (m, 2H), 8.28 (d, J = 4.5 Hz, 1H), 8.40 (d, J = 4.5 Hz, 1H), 8.51 (dd, J = 2.1, 1.5 Hz, 1H), 8.71 (s, 1H), 8.74−8.79 (m, 2H), 9.07 (dd, J = 1.5, 2.1 Hz, 1H); LD-MS obsd 674.1; FAB-MS obsd 674.1912, calcd 674.1906 ($C_{38}H_{35}IN_4$); λ_{abs} 415, 518, 543, 597, 647 nm.

Zn(II) 17,18-Dihydro-15-iodo-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)porphyrin (Zn1-I15). Method A. A solution of **Zn1** (20.0 mg, 32.7 μmol) in THF (3 mL) was treated with iodine (16.6 mg, 65.4 μmol) and silver trifluoroacetate (15.9 mg, 71.9 μmol) at room temperature for 20 min. Standard workup and chromatography [silica, hexanes/CH_2Cl_2 (2:1)] gave a dark purple solid (5.3 mg, 22%).

Method B. A solution of **1-I15** (42.5 mg, 63.0 μmol) in CH_2Cl_2 (20 mL) and methanol (2 mL) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (277 mg, 1.26 mmol) at room temperature for 3.5 h. The completion of the metalation was confirmed by UV−vis and TLC analyses. Standard workup and chromatography [silica, CH_2Cl_2] gave a dark purple solid (28.7 mg, 62%): ^{1}H NMR δ 1.84 (s, 6H), 2.01 (s, 6H), 2.57 (s, 3H), 2.65 (s, 3H), 4.61 (s, 2H), 7.17−7.20 (m, 2H), 7.45−7.49 (m, 2H), 7.90−7.94 (m, 2H), 8.18 (d, J = 4.4 Hz, 1H), 8.30 (d, J = 4.4 Hz, 1H), 8.40 (d, J = 4.4 Hz, 1H), 8.41 (s, 1H), 8.58 (d, J = 4.4 Hz, 1H), 8.64 (d, J = 4.4 Hz, 1H), 9.02 (d, J = 4.4 Hz, 1H); LD-MS obsd 736.4; FAB-MS obsd 736.1094, calcd 736.1041 ($C_{38}H_{33}IN_4Zn$); λ_{abs} 419, 615 nm.

Bromination of Oxo1. A solution of **Oxo1** (28.1 mg, 50.0 μmol) in THF (25 mL) was treated with NBS (8.9 mg, 50 μmol) at room temperature for 24 h. Standard workup and chromatography [silica, hexanes/CH_2Cl_2 (3:1)] gave seven components. Purification of each component by chromatography [silica, hexanes/CH_2Cl_2 (5:1)] gave the following compounds:

7-Bromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-Br7**), a dark purple solid (3.8 mg, 12%): ^{1}H NMR δ −2.46 to −2.40 (br, 1H), −2.36 to −2.30 (br, 1H), 1.83 (s, 6H), 2.09 (s, 6H), 2.61 (s, 3H), 2.69 (s, 3H), 7.23−7.27 (m, 2H), 7.49−7.53 (m, 2H), 7.87−7.91 (m, 2H), 8.59 (s, 1H), 8.72−8.75 (m, 1H), 8.82−8.85 (m, 1H), 9.00−9.03 (m, 1H), 9.07−9.10 (m, 1H), 9.18 (s, 1H), 9.76 (s, 1H); LD-MS obsd 640.0; FAB-MS obsd 640.1873, calcd 640.1838 ($C_{38}H_{33}BrN_4O$); λ_{abs} 418, 515, 552, 590, 642 nm.

15-Bromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-Br15**), a dark purple solid (1.4 mg, 4%): ^{1}H NMR δ −1.96 to −1.89 (br, 1H), −1.74 to −1.66 (br, 1H), 1.82 (s, 6H), 2.06 (s, 6H), 2.61 (s, 3H), 2.68 (s, 3H), 7.22−7.25 (m, 2H), 7.51−7.56 (m, 2H), 7.98−8.03 (m,

(41) Hindin, E.; Kirmaier, C.; Diers, J. R.; Tomizaki, K.-Y.; Taniguchi, M.; Lindsey, J. S.; Bocian, D. F.; Holten, D. *J. Phys. Chem. B* **2004**, *108*, 8190−8200.

2H), 8.39−8.43 (m, 1H), 8.47−8.50 (m, 1H), 8.64−8.67 (m, 1H), 8.86−8.90 (m, 1H), 9.00−9.03 (m, 1H), 9.09 (s, 1H), 9.55−9.59 (m, 1H),; LD-MS obsd 639.7; FAB-MS obsd 640.1883, calcd 640.1838 ($C_{38}H_{33}BrN_4O$); λ_{abs} 418, 521, 556, 597, 648 nm.

20-Bromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-Br20**), a dark purple solid (4.3 mg, 13%): ^{1}H NMR δ −2.38 to −2.28 (br, 1H), −1.98 to −1.90 (br, 1H), 1.84 (s, 6H), 2.25 (s, 6H), 2.61 (s, 3H), 2.69 (s, 3H), 7.24−7.27 (m, 2H), 7.51−7.55 (m, 2H), 7.98−8.02 (m, 2H), 8.41−8.44 (m, 1H), 8.50−8.52 (m, 1H), 8.72−8.74 (m, 1H), 8.84−8.87 (m, 1H), 9.09−9.12 (m, 1H), 9.52−9.55 (m, 1H), 9.83 (s, 1H); LD-MS obsd 640.3; FAB-MS obsd 640.1853, calcd 640.1838 ($C_{38}H_{33}BrN_4O$); λ_{abs} 416, 523, 533, 598, 651 nm.

7,15-Dibromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-Br7,15**), a dark purple solid (0.3 mg, 1%): ^{1}H NMR δ −2.09 to −2.03 (br, 1H), −1.83 to −1.77 (br, 1H), 1.81 (s, 6H), 2.06 (s, 6H), 2.61 (s, 3H), 2.67 (s, 3H), 7.21−7.27 (m, 2H), 7.48−7.52 (m, 2H), 7.83−7.88 (m, 2H), 8.51 (s, 1H), 8.66−8.69 (m, 1H), 8.77−8.80 (m, 1H), 8.95−8.98 (m, 1H), 9.09 (s, 1H), 9.53−9.56 (m, 1H); LD-MS obsd 717.8; FAB-MS obsd 718.1006, calcd 718.0943 ($C_{38}H_{32}Br_2N_4O$); λ_{abs} 422, 523, 560, 595, 648 nm.

7,20-Dibromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-Br 7,20**), a dark purple solid (2.8 mg, 7%): ^{1}H NMR δ −2.40 to −2.35 (br, 1H), −2.35 to −2.30 (br, 1H), 1.83 (s, 6H), 2.24 (s, 6H), 2.60 (s, 3H), 2.69 (s, 3H), 7.22−7.26 (m, 2H), 7.49−7.64 (m, 2H), 7.84−7.89 (m, 2H), 8.55 (s, 1H), 8.72−8.75 (m, 1H), 8.77−8.81 (m, 1H), 9.08−9.12 (m, 1H), 9.48−9.52 (m, 1H), 9.79 (s, 1H); LD-MS obsd 718.5; FAB-MS obsd 718.1002, calcd 718.0943 ($C_{38}H_{32}Br_2N_4O$); λ_{abs} 420, 524, 558, 597, 650 nm.

15,20-Dibromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-Br15,20**), a dark purple solid (0.6 mg, 2%): ^{1}H NMR δ −2.09 to −2.04 (br, 1H), −2.02 to −1.97 (br, 1H), 1.83 (s, 6H), 2.25 (s, 6H), 2.60 (s, 3H), 2.68 (s, 3H), 7.22−7.25 (m, 2H), 7.50−7.55 (m, 2H), 7.94−7.99 (m, 2H), 8.34−8.36 (m, 1H), 8.42−8.45 (m, 1H), 8.62−8.65 (m, 1H), 8.80−8.84 (m, 1H), 9.52−9.55 (m, 1H), 9.62−9.65 (m, 1H),; LD-MS obsd 717.9; FAB-MS obsd 718.1005, calcd 718.0943 ($C_{38}H_{32}Br_2N_4O$); λ_{abs} 422, 536, 568, 605, 659 nm.

Iodination of Oxo1. A solution of **Oxo1** (29.2 mg, 51.9 μmol) in $CHCl_3$ (20 mL) was treated with I_2 (13.2 mg, 52.0 μmol), pyridine (70 μL), and bis(trifluoroacetoxy)iodobenzene (22.4 mg, 52.1 μmol) at room temperature for 5 days. TLC analysis [silica, hexanes/CH_2Cl_2 (1:1)] showed seven components. The solution was washed with aqueous $Na_2S_2O_3$, dried ($MgSO_4$), and filtered. The filtrate was concentrated, and the residue was chromatographed [silica, hexanes/ethyl acetate (1:10)] to give two fractions. The second fraction was purified by chromatography [silica, hexanes/CH_2Cl_2 (1:1), three times; the desired component had R_f = 0.51 on TLC], affording the following compounds:

17,18-Dihydro-15-iodo-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-I15**), a dark pink solid (8.0 mg, 22%): ^{1}H NMR δ −1.77 (br s, 1H), −1.56 (br s, 1H), 1.83 (s, 6H), 2.07 (s, 6H), 2.62 (s, 3H), 2.68 (s, 3H), 7.25 (s, 2H), 7.54 (d, J = 7.5 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 8.41 (d, J = 4.2 Hz, 1H), 8.49 (d, J = 4.2 Hz, 1H), 8.64 (dd, J = 2.1, 2.4 Hz, 1H), 8.90 (dd, J = 1.5 Hz, 1H), 9.01 (dd, J = 1.8 Hz, 1H), 9.11 (s, 1H), 9.65 (dd, J = 2.1 Hz, 1H); LD-MS obsd 686.8; FAB-MS obsd 688.1725, calcd 688.1699 ($C_{38}H_{33}IN_4O$); λ_{abs} 422, 649 nm.

17,18-Dihydro-20-iodo-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-I20**), a dark pink solid (5.1 mg, 14%): ^{1}H NMR δ −2.22 to −2.13 (br, 1H), −1.82 to −1.72 (br, 1H), 1.84 (s, 6H), 2.26 (s, 6H), 2.60 (s, 3H), 2.69 (s, 3H), 7.23−7.25 (m, 2H), 7.50−7.54 (m, 2H), 7.96−8.00 (m, 2H), 8.41 (d, J = 4.5 Hz, 1H), 8.48 (d, J = 4.5 Hz, 1H), 8.71−8.74 (m, 1H), 8.80−8.83 (m, 1H), 9.09−9.12 (m, 1H), 9.58 (dd, J = 5.1, 2.1 Hz, 1H), 9,0.83 (s, 1H); LD-MS obsd 687.7; FAB-MS obsd 688.1749, calcd 688.1699 ($C_{38}H_{33}IN_4O$); λ_{abs} 420, 526, 558, 600, 652 nm.

17,18-Dihydro-7,15-diiodo-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (**Oxo1-I7,15**), dark pink solid (2.1 mg, 5%): ^{1}H NMR δ −1.87 to −1.80 (br, 1H), −1.66 to −1.58 (br, 1H), 1.81 (s, 6H), 2.06 (s, 6H), 2.62 (s, 3H), 2.68 (s, 3H), 7.23−7.25 (m, 2H), 7.52−7.56 (m, 2H), 7.84−7.88 (m, 2H), 8.65 (dd, J = 5.1, 2.1 Hz, 1H), 8.76 (s, 1H), 8.88 (dd, J = 5.1, 2.1 Hz, 1H), 8.96 (dd, J = 5.1, 2.1 Hz, 1H), 9.09 (s, 1H), 9.62 (dd, J = 5.1, 2.1 Hz, 1H); FAB-MS obsd 814.0723, calcd 814.0666 ($C_{38}H_{32}I_2N_4O$); λ_{abs} 430, 528, 565, 599, 650 nm.

Zn(II) 20-Bromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (ZnOxo1-Br20). A solution of **ZnOxo1** (10.0 mg, 16.0 μmol) in THF (10 mL) was treated with NBS (2.84 mg, 16.0 μmol) at room temperature for 40 min. CH_2Cl_2 (50 mL) was added, and the mixture was washed with aqueous $NaHCO_3$. Standard workup and chromatography [silica, hexanes/CH_2Cl_2 (3:1)] gave a dark purple solid (8.7 mg, 77%): ^{1}H NMR δ 1.82 (s, 6H), 2.17 (s, 6H), 2.60 (s, 3H), 2.68 (s, 3H), 7.20−7.24 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H), 8.43 (d, J = 4.4 Hz, 1H), 8.51 (d, J = 4.4 Hz, 1H), 8.64 (d, J = 4.4 Hz, 1H), 8.76 (d, J = 4.4 Hz, 1H), 8.91 (d, J = 4.4 Hz, 1H), 9.46 (d, J = 4.4 Hz, 1H), 9.50 (s, 1H); LD-MS obsd 701.0; FAB-MS obsd 702.1009 calcd 702.0973 ($C_{38}H_{31}BrN_4OZn$); λ_{abs} 428, 615 nm.

20-Bromo-17,18-dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxoporphyrin (Oxo1-Br20). A solution of **ZnOxo1** (44.1 mg, 70.4 μmol) in THF (40 mL) was treated with NBS (12.5 mg, 70.4 μmol) at room temperature for 40 min. After standard workup, the crude reaction mixture was treated with TFA (271 μL, 3.52 mmol) in CH_2Cl_2 (20 mL) for 10 min. CH_2Cl_2 (100 mL) was added, and the mixture was washed with aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated, and the residue was chromatographed [silica, hexanes/CH_2Cl_2 (3:1)] to give a dark purple solid (19.0 mg, 42%).

17,18-Dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-15-phenylporphyrin (1-Ph15). Samples of **1-I15** (13.0 mg, 19.3 μmol), **2** (8.0 mg, 39.2 μmol), $Pd(PPh_3)_4$ (6.6 mg, 5.7 μmol, 30 mol %), and K_2CO_3 (21 mg, 0.15 mmol, 8.0 equiv) were weighed into a Schlenk flask, and the flask was pump-purged with argon three times. Toluene and DMF (2:1, 1.3 mL) were added, and the mixture was heated for 17 h at 90 °C. TLC analysis [silica, hexanes/CH_2Cl_2 (2:1)] showed three components. After removal of the solvent, CH_2Cl_2 (50 mL) was added, and the mixture was filtered. The filtrate was concentrated and the residue was purified by column chromatography [silica, hexanes/CH_2Cl_2 (2:1)] affording a dark yellow solid (9.4 mg, 79%): ^{1}H NMR δ −1.72 (br, 1H), −1.48 (br, 1H), 1.84 (s, 6H), 1.97 (s, 6H), 2.58 (s, 3H), 2.67 (, 3H), 4.18 (s, 2H), 7.21 (s, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.70 (m, 3H), 7.92 (m, 2H), 8.03 (d, J = 8.1 Hz, 2H), 8.19 (dd, J = 4.5, 0.9 Hz, 1H), 8.31 (d, J = 4.2 Hz, 1H), 8.45 (d, J = 4.2 Hz, 2H), 8.77 (d, J = 4.5 Hz, 1H), 8.81 (d, J = 4.5 Hz, 1H), 8.84 (s, 1H); LD-MS obsd 624.1; FAB-MS obsd 624.3274, calcd 624.3253 ($C_{44}H_{40}N_4$); λ_{abs} 418, 514, 539, 593, 645 nm.

Zn(II) 17,18-Dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-15-phenylporphyrin (Zn1-Ph15). A solution of **1-Ph15** (25.2 mg, 40.3 μmol) in CH_2Cl_2 (10 mL) was treated with methanolic $Zn(OAc)_2$ (148 mg, 0.807 mmol), and the reaction mixture was stirred at room temperature for 2 h. Standard workup and chromatography [silica, hexanes/CH_2Cl_2 (1:1)] gave a blue solid (22.8 mg, 82%): ^{1}H NMR δ 1.85 (s, 6H), 1.94 (s, 6H), 2.56 (s, 3H), 2.66 (s, 3H), 4.50 (s, 2H), 7.18 (s, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.65 (m, 3H), 7.87 (m, 2H), 7.97 (d, J = 7.8 Hz, 2H), 8.04 (d, J = 4.8 Hz, 1H), 8.22 (d, J = 4.5 Hz, 1H), 8.35 (d, J = 4.8 Hz, 1H), 8.36 (d, J = 4.2 Hz, 1H), 8.55 (s, 1H), 8.64 (d, J = 4.5 Hz, 1H), 8.68 (d, J = 4.5 Hz, 1H); LD-MS obsd 686.3; FAB-MS obsd 686.2377, calcd 686.2388 ($C_{44}H_{38}N_4Zn$); λ_{abs} 416, 613 nm.

17,18-Dihydro-18,18-dimethyl-5-(4-methylphenyl)-10-mesityl-17-oxo-15-phenylporphyrin (Oxo1-Ph15). Samples of **Oxo1-I15** (8.00 mg, 11.6 μmol), **2** (24.0 mg, 0.118 mmol), $Pd(PPh_3)_4$ (6.7 mg, 5.8 μmol, 50 mol %), and K_2CO_3 (12.85 mg, 92.96 μmol, 8.0 equiv) were weighed into a Schlenk flask, and

the flask was pump-purged with argon three times. Toluene and DMF (2:1, 1.2 mL) were added, and the mixture was heated for 20 h at 90 °C. After removal of the solvent, CH_2Cl_2 (50 mL) was added, and the mixture was filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by chromatography [silica, hexanes/CH_2Cl_2 (1:1)] to give a dark pink solid (4.8 mg, 65%): ^{1}H NMR δ −1.97 (br, 1H), −1.87 (br, 1H), 1.83 (s, 6H), 2.00 (s, 6H), 2.60 (s, 3H), 2.69 (s, 3H), 7.24 (s, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.71 (m, 3H), 7.90 (m, 2H), 8.04 (d, J = 7.8 Hz, 2H), 8.45 (d, J = 4.8 Hz, 1H), 8.50 (dd, J = 1.8, 2.1 Hz, 1H), 8.54 (d, J = 4.5 Hz, 1H), 8.56 (dd, J = 1.8 Hz, 1H), 8.92 (d, J = 4.5 Hz, 1H), 9.05 (d, J = 3.9 Hz, 1H), 9.16 (s, 1H); LD-MS obsd 640.7; FAB-MS obsd 638.3052, calcd 638.3046 ($C_{44}H_{38}N_4O$); λ_{abs} 417, 518, 551, 593, 646 nm.

Zn(II) 17,18-Dihydro-18,18-dimethyl-5-(4-methylphenyl)-10-mesityl-17-oxo-15-phenylporphyrin (ZnOxo1-Ph15). A solution of **Oxo1-Ph15** (3.2 mg, 5.0 μmol) in CH_2Cl_2 (8 mL) was treated with methanolic $Zn(OAc)_2$ (18.4 mg, 100 μmol), and the reaction mixture was stirred at room temperature for 22 h. Standard workup and chromatography (silica, CH_2Cl_2) gave a green solid (2.6 mg, 74%): ^{1}H NMR δ 1.83 (s, 6H), 1.97 (s, 6H), 2.58 (s, 3H), 2.68 (s, 3H), 7.01 (s, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.69 (m, 3H), 7.86 (m, 2H), 7.99 (d, J = 7.8 Hz, 2H), 8.35 (d, J = 4.5 Hz, 1H), 8.43 (d, J = 4.2 Hz, 1H), 8.4 8 (d, J = 4.5 Hz, 1H), 8.52 (d, J = 4.2 Hz, 1H), 8.83 (d, J = 4.2 Hz, 1H), 8.89 (d, J = 4.8 Hz, 1H), 8.91 (s, 1H); LD-MS obsd 698.7; FAB-MS obsd 700.2178, calcd 700.2181 ($C_{44}H_{36}N_4Zn$); λ_{abs} 425, 612 nm.

Zn(II) 17,18-Dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-17-oxo-20-phenylporphyrin (ZnOxo1-Ph20). Samples of **ZnOxo1-Br20** (6.8 mg, 9.6 μmol), **2** (9.8 mg, 48 μmol), $Pd(PPh_3)_4$ (3.4 mg, 9.0 μmol, 30 mol %), and K_2CO_3 (11 mg, 77 μmol, 8.0 equiv) were weighed into a Schlenk flask, and the flask was pump-purged with argon three times. Toluene and DMF (2:1, 1 mL) were added, and the mixture was heated for 17 h at 90 °C. TLC analysis [silica, hexanes/CH_2Cl_2 (2:1)] showed two components. After removal of the solvent, CH_2Cl_2 (50 mL) was added, and the mixture was washed with aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated, and the residue was chromatographed [silica, hexanes/CH_2Cl_2 (1:3)] to give a fast-moving component (**ZnOxo1-Ph20**, 3.2 mg, 46%) and a slow-moving component (**ZnOxo1**, 1.3 mg, 21%). Data for **ZnOxo1-Ph20**: ^{1}H NMR δ 1.68 (s, 6H), 1.84 (s, 6H), 2.61 (s, 3H), 2.66 (s, 3H), 7.22−7.25 (m, 2H), 7.46−7.49 (m, 2H), 7.63−7.67 (m, 2H), 7.70−7.74 (m, 1H), 7.91−7.94 (m, 2H), 7.94−7.97 (m, 2H), 8.10−8.12 (m, 2H), 8.11 (d, J = 4.4 Hz, 1H), 8.46 (d, J = 4.4 Hz, 1H), 8.53 (d, J = 4.4 Hz, 1H), 8.62 (d, J = 4.4 Hz, 1H), 8.68 (d, J = 4.4 Hz, 1H), 8.96 (d, J = 4.4 Hz, 1H), 9.65 (s, 1H); LD-MS obsd 699.1; FAB-MS obsd 700.2182, calcd 700.2181 ($C_{44}H_{36}N_4OZn$); λ_{abs} 427, 614 nm.

Zn(II) 17,18-Dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-20-phenylethynyl-17-oxoporphyrin (ZnOxo3). Samples of **ZnOxo1-Br20** (19.4 mg, 27.5 μmol) and phenylacetylene (9.00 μL, 82.5 μmol) were coupled using $Pd_2(dba)_3$ (3.78 mg, 4.13 μmol) and P(*o*-tol)$_3$ (10.0 mg, 33.0 μmol) in toluene/triethylamine (5:1, 11 mL) at 60 °C under argon. After 5 h, phenylacetylene (9.00 μL, 82.5 μmol), $Pd_2(dba)_3$ (3.78 mg, 4.13 μmol), and P(*o*-tol)$_3$ (10.0 mg, 33.0 μmol) were added to the reaction mixture. After 24 h, the mixture was concentrated under reduced pressure. The residue was chromatographed [silica, hexanes/CH_2Cl_2 (1:1)], affording a greenish purple solid (3.2 mg, 16%): ^{1}H NMR δ 1.85 (s, 6H), 2.30 (s, 6H), 2.60 (s, 3H), 2.68 (s, 3H), 7.23 (s, 2H), 7.47−7.59 (m, 5H), 7.91−7.98 (m, 4H), 8.38 (d, J = 4.4 Hz, 1H), 8.45 (d, J = 4.4 Hz, 1H), 8.58 (d, J = 4.4 Hz, 1H), 8.76 (d, J = 4.4 Hz, 1H), 8.86 (d, J = 4.4 Hz, 1H), 9.50 (d, J = 4.4 Hz, 1H), 9.55 (s, 1H); LD-MS obsd 723.8; FAB-MS obsd 724.2008, calcd 724.2181 ($C_{46}H_{36}N_4OZn$); λ_{abs} 443, 532, 575, 626 nm.

17,18-Dihydro-10-mesityl-18,18-dimethyl-5-(4-methylphenyl)-20-phenylethynyl-17-oxoporphyrin (Oxo3). Treatment of a solution of **ZnOxo3** (1.5 mg, 2.1 μmol) in CH_2Cl_2 (2 mL) with TFA (8.0 μL) for 2 h followed by standard workup and chromatography [silica, hexanes/CH_2Cl_2 (2:1)] gave a reddish purple solid (0.72 mg, 52%): ^{1}H NMR δ −1.76 to −1.70 (br, 1H), −1.56 to −1.49 (br, 1H), 1.85 (s, 6H), 2.31 (s, 6H), 2.60 (s, 3H), 2.69 (s, 3H), 7.25 (s, 2H; overlap to $CHCl_3$), 7.49−7.61 (m, 5H), 7.96−8.02 (m 4H), 8.40 (d, J = 4.8 Hz, 1H), 8.46 (d, J = 4.8 Hz, 1H), 8.66 (dd, J = 1.5, 4.9 Hz, 1H), 8.86 (dd, J = 2.0, 4.9 Hz, 1H), 9.05 (dd, J = 2.0, 4.9 Hz, 1H), 9.58 (dd, J = 2.0, 4.5 Hz, 1H), 9.79 (s, 1H); LD-MS obsd 662.0; FAB-MS obsd 662.3103, calcd 662.3046 ($C_{46}H_{38}N_4O$); λ_{abs} 433, 583, 611, 664 nm.

Oxo-dyad-1. Samples of **ZnOxo4** (16.2 mg, 22.9 μmol) and **Oxo1-Br20** (14.7 mg, 22.9 μmol) were coupled using $Pd_2(dba)_3$ (3.15 mg, 3.44 μmol) and P(*o*-tol)$_3$ (8.36 mg, 27.5 μmol) in toluene/triethylamine (5:1, 9 mL) at 35 °C under argon. After 3 h, the temperature was increased to 60 °C; after 5.5 h, $Pd_2(dba)_3$ (3.15 mg, 3.44 μmol) and P(*o*-tol)$_3$ (8.36 mg, 27.5 μmol) were added to the reaction mixture. Analytical SEC showed that the reaction had leveled off after 24 h. Standard workup [(silica, CH_2Cl_2); (SEC, THF); (silica, CH_2Cl_2)] gave a green solid (6.4 mg, 22%): ^{1}H NMR δ −1.60 to −1.50 (br, 1H), −1.38 to −1.28 (br, 1H), 1.88 (s, 6H), 2.10 (s, 6H), 2.46 (s, 6H), 2.61 (s, 3H), 2.70 (s, 3H), 7.25−7.27 (m, 2H), 7.54 (d, J = 7.6 Hz, 2H), 7.79−7.81 (m, 1H), 7.97−7.99 (m, 2H), 8.04 (d, J = 7.6 Hz, 2H), 8.29−8.32 (m, 4H), 8.40 (d, J = 4.4 Hz, 1H), 8.46 (d, J = 4.4 Hz, 1H), 8.66 (d, J = 4.4 Hz, 1H), 8.68 (d, J = 4.4 Hz, 1H), 8.77 (d, J = 4.4 Hz, 1H), 8.89 (d, J = 4.4 Hz, 1H), 8.91−8.92 (m, 1H), 8.94 (d, J = 4.4 Hz, 1H), 8.96 (d, J = 4.4 Hz, 1H), 8.99 (1H, s), 9.04−9.07 (m, 2H), 9.68 (s, 1H), 9.74−9.76 (m, 1H), 9.79 (s, 1H); LD-MS obsd 1265.2; FAB-MS: high-resolution mass spectrometry was carried out on this sample at greater than unit resolution and the expected molecule ion was observed at *m/z* 1264.52 (calcd 1264.51); thus, elemental composition was confirmed as $C_{82}H_{72}N_8O_2Zn$; λ_{abs} 436, 588, 610, 665 nm.

Oxo-dyad-2. Samples of **Oxo4** (17.7 mg, 27.5 μmol) and **ZnOxo1-Br20** (19.4 mg, 27.5 μmol) were coupled using $Pd_2(dba)_3$ (3.78 mg, 4.13 μmol) and P(*o*-tol)$_3$ (10.0 mg, 33.0 μmol) in toluene/triethylamine (5:1, 11 mL) at 50 °C under argon. After 3 h, $Pd_2(dba)_3$ (3.78 mg, 4.13 μmol) and P(*o*-tol)$_3$ (10.0 mg, 33.0 μmol) were added to the reaction mixture. Analytical SEC showed that the reaction had leveled off after 24 h. Standard workup [(silica, CH_2Cl_2); (SEC, THF); (silica, CH_2Cl_2)] gave a green solid (4.5 mg, 13%): ^{1}H NMR δ −2.34 to −2.30 (br, 1H), −2.19 to −2.16 (br, 1H), 1.91 (s, 6H), 2.10 (s, 6H), 2.11 (s, 6H), 2.63 (s, 3H), 2.69 (s, 3H), 7.27−7.29 (m, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.80−7.82 (m, 1H), 8.00 (d, J = 7.6 Hz, 2H), 8.03−8.05 (m, 2H), 8.23−8.32 (m, 4H), 8.50 (d, J = 4.4 Hz, 1H), 8.54 (d, J = 4.4 Hz, 1H), 8.70 (d, J = 4.4 Hz, 1H), 8.77 (d, J = 4.4 Hz, 1H), 8.82 (d, J = 4.4 Hz, 1H), 8.88−8.91 (m, 2H), 8.93 (1H, s), 8.98−9.01 (m, 1H), 9.03−9.06 (m, 1H), 9.10−9.13 (m, 1H), 9.23−9.26 (m, 1H), 9.84 (s, 1H), 10.10 (s, 1H); LD-MS obsd 1267.8; FAB-MS obsd 1264.5070, calcd 1264.5031 ($C_{82}H_{72}N_8O_2Zn$); λ_{abs} 430, 515, 629, 642 nm; λ_{em} 629, 642 nm.

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Supporting Information Available: Characterization data (absorption, ^{1}H NMR, and LD-MS spectra) for all new chlorins and oxochlorins. This material is available free of charge via the Internet at http://pubs.acs.org.

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