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# Synthesis and Physicochemical Properties of Metallobacteriochlorins

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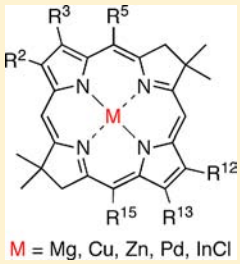
Supporting Information

**ABSTRACT:** Access to metallobacteriochlorins is essential for investigation of a wide variety of fundamental photochemical processes, yet relatively few synthetic metallobacteriochlorins have been prepared. Members of a set of synthetic bacteriochlorins bearing 0−4 carbonyl groups (1, 2, or 4 carboethoxy substituents, or an annulated imide moiety) were examined under two conditions: (i) standard conditions for zincation of porphyrins [$Zn(OAc)_2 \cdot 2H_2O$ in *N*,*N*-dimethylformamide (DMF) at 60−80 °C], and (ii) treatment in tetrahydrofuran (THF) with a strong base [e.g., NaH or lithium diisopropylamide (LDA)] followed by a metal reagent $MX_n$. Zincation of bacteriochlorins that bear 2−4 carbonyl groups proceeded under the former method whereas those with 0−2 carbonyl groups proceeded with NaH or LDA/THF followed by $Zn(OTf)_2$. The scope of metalation (via NaH or LDA in THF) is as follows: (a) for bacteriochlorins that bear two electron-releasing aryl groups, M = Cu, Zn, Pd, and InCl (but not Mg, Al, Ni, Sn, or Au); (b) for bacteriochlorins that bear two carboethoxy groups, M = Ni, Cu, Zn, Pd, Cd, InCl, and Sn (but not Mg, Al, or Au); and (c) a bacteriochlorin with four carboethoxy groups was metalated with Mg (other metals were not examined). Altogether, 15 metallobacteriochlorins were isolated and characterized. Single-crystal X-ray analysis of 8,8,18,18-tetramethylbacteriochlorin reveals the core geometry provided by the four nitrogen atoms is rectangular; the difference in length of the two sides is ∼0.08 Å. Electronic characteristics of (metal-free) bacteriochlorins were probed through electrochemical measurements along with density functional theory calculation of the energies of the frontier molecular orbitals. The photophysical properties (fluorescence yields, triplet yields, singlet and triplet excited-state lifetimes) of the zinc bacteriochlorins are generally similar to those of the metal-free analogues, and to those of the native chromophores bacteriochlorophyll *a* and bacteriopheophytin *a*. The availability of diverse metallobacteriochlorins should prove useful in a variety of fundamental photochemical studies and applications.




## I. INTRODUCTION

Naturally occurring chlorophylls and bacteriochlorophylls are essential constituents in plant and bacterial photosynthesis. Both types of hydroporphyrins contain magnesium as the central metal.[1] The introduction of different metals in tetrapyrrole macrocycles can alter the electronic,[2] axial-ligation,[3] and photophysical[4−6] properties of the coordination complex. The effect of metals can be seen by comparing the properties of metalloporphyrins containing magnesium, zinc, copper, or palladium, each of which is a divalent metal. Magnesium is five or six coordinate, and gives a reasonable yield of fluorescence ($\Phi_f \sim 0.1$), a long-lived excited singlet state ($\tau \sim 10$ ns), and a good yield of intersystem crossing to the triplet state.[4] Zinc is four or five coordinate, and gives a lower yield of fluorescence ($\Phi_f \sim 0.03$), a shorter excited singlet state ($\tau \sim 2$ ns), and a higher yield of intersystem crossing to the triplet state.[4] Copper is four coordinate and gives essentially no detectable fluorescence, a very short-lived nominal excited singlet state, and highly temperature-dependent properties of two excited-states borne from the coupling of the porphyrin triplet with the unpaired metal electron.[5] Palladium is four coordinate and gives no detectable fluorescence, a near unity yield of intersystem crossing, and a short-lived excited triplet state.[6]

A further distinction caused by metals concerns the change in optical properties. The introduction of a metal in a porphyrin typically increases the symmetry (e.g., $D_{2h}$ to $D_{4h}$) and causes the spectral features in the visible region (500−650 nm) to collapse from primarily four bands (due to partially overlapping x and y transitions) to a two-banded spectrum (wherein the x and y transitions are degenerate).[7] The two visible bands are the Q(0,0) and Q(1,0) transitions. (Weaker additional vibronic overtone bands also contribute to the spectra with or without a metal ion.) The resulting absorption of the metalloporphyrin occurs at shorter wavelength than for that of the free base porphyrin. For a chlorin, insertion of a metal does not alter the symmetry but does typically cause a hypsochromic shift in the position of the long-wavelength absorption band. An example is provided by chlorophyll *a* and pheophytin *a* (the free base of chlorophyll *a*) which absorb at 662 and 667 nm, respectively.[1] For a bacteriochlorin, insertion of a metal also does not alter the symmetry but typically causes a bathochromic shift in the position of the long-wavelength absorption band. An example is provided by bacteriochlorophyll *a* (Bchl *a*) and bacteriopheophytin *a* (Bphe *a*), which

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absorb at 772 and 749 nm, respectively.[1] The ability to shift the absorption to longer wavelength upon metalation is quite attractive given the multiple motivations for access to chromophores with strong absorption in the near-infrared (NIR) spectral region. The relatively low energy of photons in the NIR region (1.76−1.23 eV, 700−1000 nm) enables photochemical studies in an energy regime that has been comparatively unexplored versus studies of organic photochemistry in the ultraviolet (6.17−3.09 eV, 200−400 nm) or visible regions (400−700 nm, 3.09−1.76 eV). Applications of NIR-active bacteriochlorins include artificial photosynthetic light-harvesting,[8] optical imaging[9,10] photodynamic therapy[11] of soft tissues, and fluorescent markers in clinical diagnostics.[12] In addition, selected photosynthetic organisms are now known to employ zinc-containing analogues of bacteriochlorophylls (rather than the expected magnesium).[13] For all of these reasons, fundamental studies of diverse metallobacteriochlorins are warranted.

Despite the range of physical behavior that can be elicited with metalloporphyrins, relatively few metallobacteriochlorins have been prepared, and most that have been prepared are derived from Bchl *a*.[14,15] While data from the naturally derived macrocycles are quite valuable, lack of access to diverse synthetic metallobacteriochlorins has precluded wide-ranging studies of effects of peripheral substituents on spectral and photophysical properties, an approach that has been extensively pursued with porphyrins and chlorins. We have been working to develop a rational, de novo synthesis of bacteriochlorins.[16−19] The resulting bacteriochlorins bear a geminal dimethyl group in each reduced, pyrroline ring to resist adventitious oxidants that otherwise could result in dehydrogenation. We recently characterized the photophysical properties of a large set of free base bacteriochlorins[20] derived from this synthetic approach, and also examined several indium(III) chelates thereof,[21] but relatively few metal chelates of the synthetic bacteriochlorins have heretofore been prepared.

The metalation of bacteriochlorins—an ostensibly simple reaction—has proved more difficult than for porphyrins and chlorins. As one illustration, treatment of a chlorin−bacteriochlorin dyad with zinc acetate in $CHCl_3$/methanol at room temperature for 4 h afforded selective metalation of the chlorin; the resulting zinc chlorin-free base bacteriochlorin dyad was isolated in nearly quantitative yield.[9] As a second illustration, conditions that afford smooth zincation of the chlorin pheophytin *a* ($Zn(OTf)_2$ in methanol or acetonitrile at room temperature) upon application to Bphe *a* resulted in decomposition rather than metalation.[22] The origin of the difficulty of metalation of bacteriochlorins remains unclear, but has been attributed to a number of factors. The factors include (1) nucleophilicity, which decreases with increased saturation of the macrocycle (porphyrin > chlorin > bacteriochlorin),[22] and (2) acidity of the N−H protons, which decreases with increasing electron-richness of the ligand (porphyrin > chlorin > bacteriochlorin).[23] A factor that complicates interpretation is that many bacteriochlorins examined in metalation studies to date are derived from natural ligands of somewhat limited stability. In short, the dearth of bacteriochlorins that withstand a broad range of reaction conditions has impeded a thorough investigation of these issues.

In this paper, we first summarize methods that have been used to date for metalation of bacteriochlorins, and identify correlations between methods and structural features of the bacteriochlorins. We then describe the development and application of a new method for metalation of synthetic bacteriochlorins. Finally, we report the spectral and photophysical features of a set of metallobacteriochlorins. While no metalation procedure has yet been developed that is generically applicable to all bacteriochlorins, the present work should expand the availability of a variety of metallobacteriochlorins that have heretofore been inaccessible.

## II. RESULTS AND DISCUSSION

**A. Bacteriochlorin Synthesis.** The metalation studies were carried out on a series of synthetic macrocycles that spanned a range from electron-deficient to electron-rich bacteriochlorins. The most electron-deficient bacteriochlorin (**BC4-MeO**) contains four carboethoxy groups (denoted by "**4**") and a methoxy group at the 5-position (denoted by "**MeO**"), which is followed by the bacteriochlorin-imide **BC3-2E** with three carbonyl groups and two ethyl groups. Bacteriochlorins with two carboethoxy and two alkyl groups **BC2-2E**, **BC2-2H**, and **BC2-2H-MeO** (E = ethyl, H = heptyl) are in the middle of the range, followed by **BC2-2M-MeO** with two carboethoxy and two mesityl groups. The most electron-rich bacteriochlorin (**BC0-2T**) bears electron-donating, *p*-tolyl groups at the 2- and 12-positions. This feature makes **BC0-2T** an appropriate benchmark to gauge the scope of the metalation for electron-rich bacteriochlorins. Additionally, the unsubstituted bacteriochlorin **BC0** lacking any $\beta$-pyrrole substituents provides a benchmark for comparison with diverse substituted bacteriochlorins (Chart 1). The term carbonyl here denotes 1, 2, or 4 carboethoxy substituents and/or the 2 substituted acyl moieties of the annulated imide ring.

The bacteriochlorins thus comprise a far broader range of substituents than has heretofore been examined, and all members of the set differ from the naturally occurring bacteriopheophytins in the following ways: (i) absence of an isocyclic ring (ring E), (ii) presence of a geminal dimethyl group rather than *trans*-dialkyl substituents in each pyrroline ring, and (iii) absence of alkyl ($sp^3$-hybridized) groups on adjacent $\beta$-pyrrole carbons, which could induce nonplanarity. On the other hand, within the set of bacteriochlorins in Chart 1, some are sparsely substituted (i.e., lack 2 or 4 $\beta$-pyrrole substituents); those with mesityl substitutuents are sterically hindered; and the set encompasses molecules with 0−4 carbonyl groups. Collectively, the bacteriochlorins present a rich test of the generality of metalation methods.

The syntheses of bacteriochlorins **BC4-MeO**,[18] **BC3-2E**,[24] **BC2-2E**,[18] **BC0-2T**,[16] and **BC0**[18] have been reported. The syntheses of **BC2-2H**, **BC2-2H-MeO**, and **BC2-2M-MeO** are shown in Scheme 1. The general approach relies on installation of the desired $\beta$-pyrrole substituents at the earliest stage of the synthesis.[18] Thus, treatment of $\alpha,\beta$-unsaturated ester **1H** (R = heptyl) or **1M** (R = mesityl)[25] with *p*-toluenesulfonyl methylisocyanide (TosMIC) via the van Leusen method[26] afforded the corresponding pyrrole **2H** or **2M**. Formylation[27] gave pyrrole-2-carboxaldehyde **3H** or **3M** wherein the formyl group is positioned adjacent to the heptyl or mesityl moiety, respectively. Treatment of **3H** or **3M** to sequential nitroaldol (Henry) condensation[17,28] and reduction[29] gave the nitrovinylpyrrole **4M** (**4H** was not isolated) and 2-(2-nitroethyl)-pyrrole **5H** or **5M**, respectively. Michael addition[30] with the $\alpha,\beta$-unsaturated ketone−acetal **6**[16,19] gave the nitrohexanone−pyrrole **7H** or **7M**, which upon McMurry-type reductive cyclization[17] afforded the dihydrodipyrrin-acetal **8H** or **8M**. Macrocycle formation was carried out by self-condensation at room temperature via two catalytic conditions:[18] TMSOTf/2,6-di-*tert*-butylpyridine


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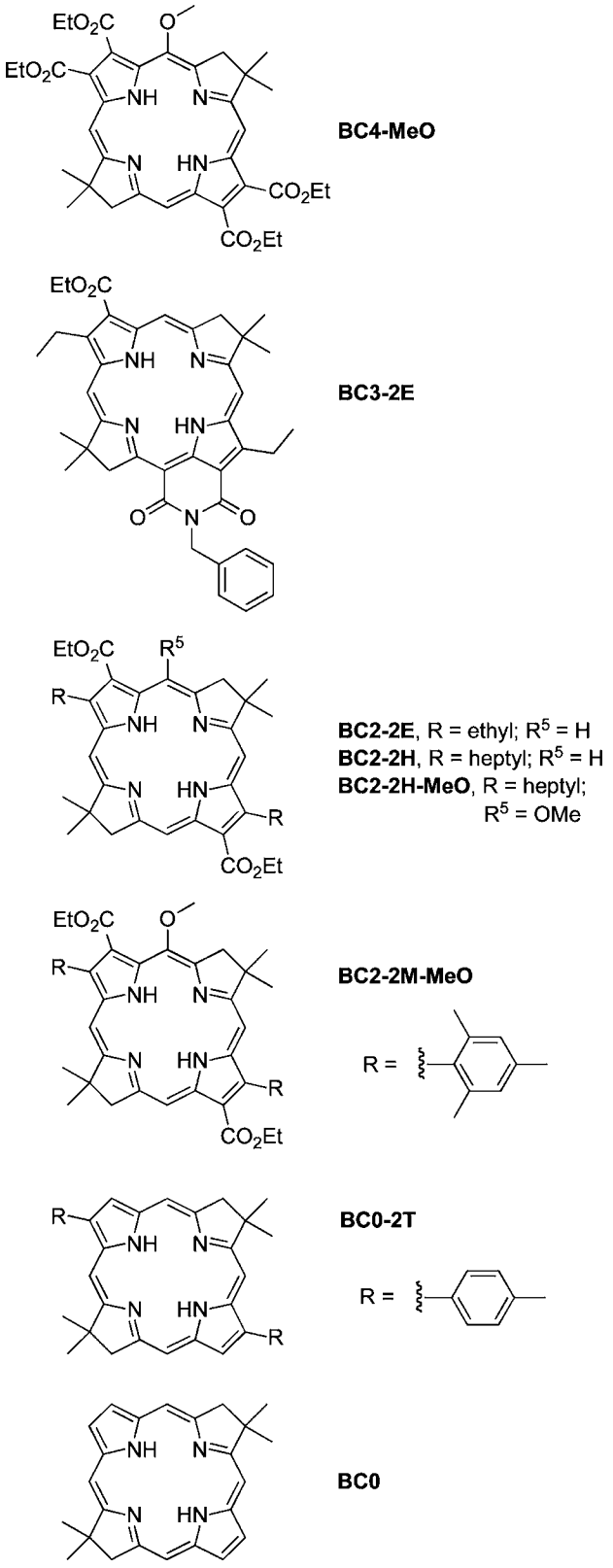
**Chart 1. Synthetic Bacteriochlorins Examined Herein**




(DTBP) in $CH_2Cl_2$ with **8H** or **8M** afforded **BC2-2H-MeO** or **BC2-2M-MeO**, whereas $BF_3{\cdot}OEt_2$ in $CH_3CN$ with **8H** gave **BC2-2H**. The new compounds (**2**, **3**, **5**, **7**, and **8** in the **H** and **M** series) were characterized by melting point, $^1$H NMR spectroscopy, $^{13}$C NMR spectroscopy, and electrospray ionization mass spectrometry (ESI-MS); compounds **2H**, **3H**, **5H**, **7H**, and **8M** also were verified by elemental analysis. Bacteriochlorins **BC2-2H**, **BC2-2H-MeO**, and **BC2-2M-MeO** were characterized by $^1$H NMR spectroscopy, $^{13}$C NMR spectroscopy, absorption spectroscopy, MALDI-MS and ESI-MS.

Bacteriochlorin **BC2-2M-MeO** contains mesityl groups at the 2- and 12-positions. The location of the $\beta$-pyrrole substituents in the macrocycle is set at the stage of formylation of the pyrrole (**2M** → **3M**). It is noteworthy that Vilsmeier formylation[27] of 3-mesitylpyrrole (**S1**), obtained by decarboxylation[31] of pyrrole **2M**, affords the 2-formyl-4-mesitylpyrrole (**S2**) and the isomeric 2-formyl-3-mesitylpyrrole in 4:1 ratio. The availability of **S2** enabled synthesis of a bacteriochlorin that contains mesityl groups at the 3- and 13-positions (**BC0-2M**; see Supporting Information).

**B. Bacteriochlorin Metalation.** *1. Literature Methods for Metal Insertion.* A classic method for metalation of porphyrins entails treatment of the free base macrocycle with a metal acetate (or metal acac) in a somewhat polar solvent at elevated temperature.[32,33] For porphyrins, the use of high temperatures often is acceptable because most porphyrins are stable at high temperature and in solution exposed to air. However, many bacteriochlorins do not survive at high temperatures even if the reactions are run anaerobically.[34] There are two general methods for metalation of bacteriochlorins: (1) direct metalation of a free base bacteriochlorin with a metal salt ($MX_2$) in a solvent at temperatures ranging from room temperature to >100 °C to obtain the Zn(II), Cu(II), Pd(II), Ni(II), or Cd(II) bacteriochlorin (Table 1, entries 1−5);[23,35−48] and (2) transmetalation wherein a Cd(II) chelate of a bacteriochlorin is formed in situ in acetone and then treated with a metal chloride at room temperature to obtain the target metallobacteriochlorin (entry 6).[23,39−41] Strell and Urumow first prepared a variety of metallochlorins via the transmetalation method,[49] which was subsequently applied by Scheer and co-workers[23] to bacteriochlorophylls.

The bacteriochlorins that have been prepared via these methods are displayed in Charts 2 and 3. Examination of structural features of the naturally derived bacteriochlorins (**I**−**VII**) subjected to metalation reveals the presence of at least one if not two carbonyl (ketone, aldehyde, amide, or imide) groups, whereas some of the synthetic bacteriochlorins (**VIII**−**XII**) lack such electron-withdrawing groups. The electron-richness of the macrocycle is believed to be an important feature that affects the rate of metalation and the propensity of the metallobacteriochlorin toward protolytic demetalation.

In addition to the aforementioned general methods, several more specialized procedures have been reported for the preparation of metallobacteriochlorins. (1) Wasielewski employed a hindered Grignard reagent and a non-nucleophilic base to magnesiate Bphe *a* and thereby reconstitute Bchl *a*.[50] (2) Eschenmoser treated octaethylporphyrinogen with nickel acetate in refluxing xylene and obtained nickel octaethylbacteriochlorin; the process entails metalation, tautomerization, and $2e^-/2H^+$ oxidation (converting the hexahydroporphyrin to a tetrahydroporphyrin).[51,52] (3) Stolzenberg applied the method of Arnold (formation and isolation of the dilithium derivative of a tetrapyrrole macrocycle followed by transmetalation with a metal reagent[53,54]) with tetra-*p*-tolylbacteriochlorin to prepare the oxotitanyl chelate.[55] (4) Chen caused a nickel tetrabromoporphyrin to undergo scission of the two $\beta$-pyrrole carbons on opposing rings and thereby form a "bacteriophin," which exhibits an absorption spectrum comparable to that of a bacteriochlorin.[56]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**Scheme 1. Synthesis of Bacteriochlorins Bearing Two Carboethoxy Groups**

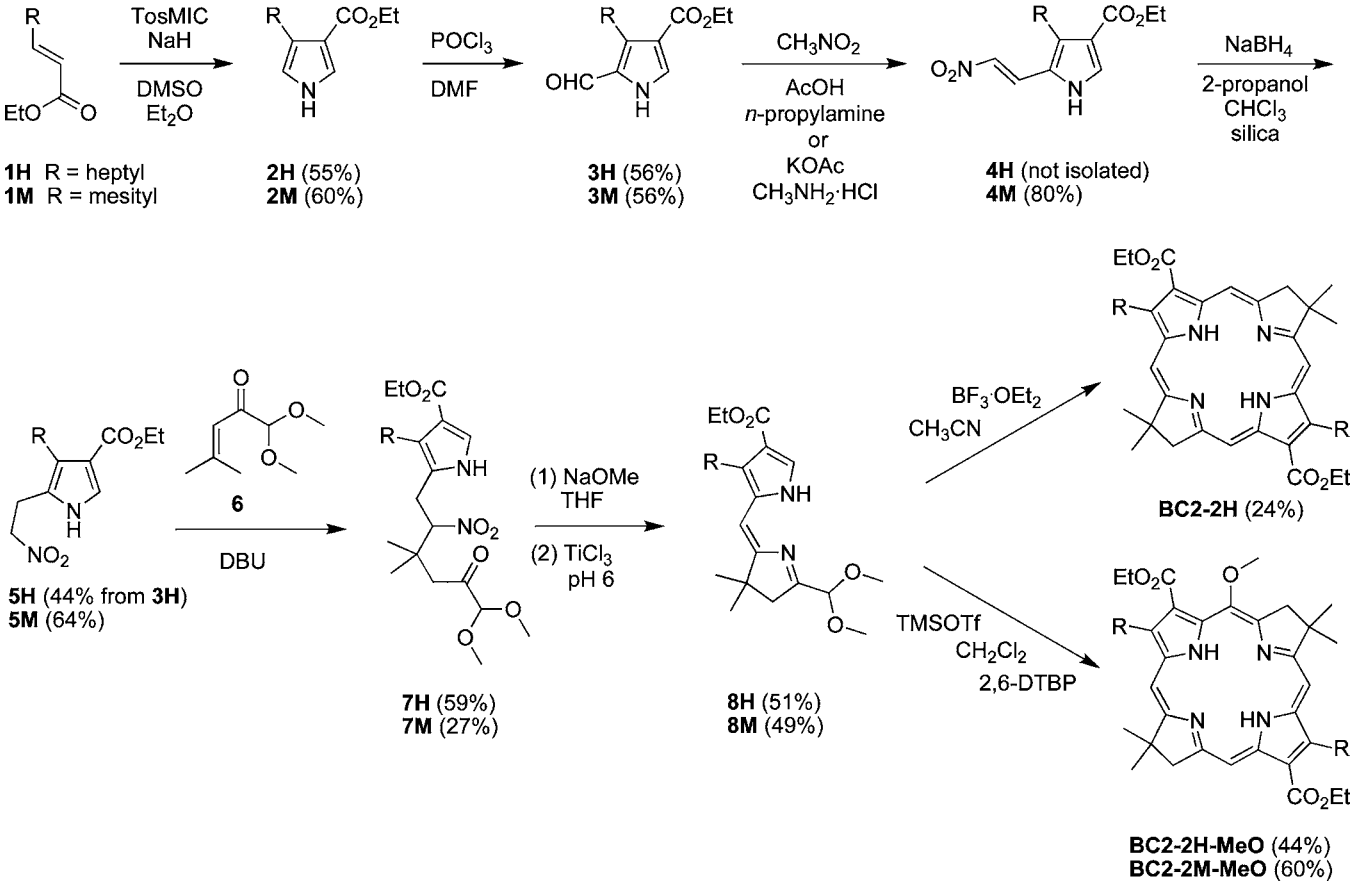


**Table 1. Preparative Methods for Metalation of Bacteriochlorins**

| entry | metal salt | conditions | bacteriochlorin[a] |
|---|---|---|---|
| 1 | $Zn(OAc)_2$ or $Zn(OAc)_2{\cdot}2H_2O$ | reflux in diverse solutions[b] | **I**,[23] **II**,[35,36] **III**,[37] **IV**,[38] **V**,[38] **VI**,[39] **VII**,[40,41] **VIII**,[42] **IX**[43] |
| 2 | $Cu(OAc)_2$ or $CuO_2$ | MeOH or AcOH at rt or reflux; $CHCl_3$/MeOH at reflux | **I**,[23] **II**,[44] **VI**,[39] **IX**[45] |
| 3 | $Pd(OAc)_2$ | MeOH at rt | **I**,[46] **VII**[41] |
| 4 | $NiCl_2{\cdot}6H_2O$[c] or $NiCl_2$ | DMF at reflux | **X**,[47] **XI**,[48] **XII**[48] |
| 5 | $Cd(OAc)_2$ | DMF at reflux | **I**,[23] **VI**,[39] **VII**[40,41] |
| 6[d] | $MnCl_2{\cdot}2H_2O$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $PdCl_2$ | acetone at rt | **I**,[23] **VI**,[39] **VII**[40,41] |

[a]The free base analogue of the structures shown in Charts 2 and 3 were used unless noted otherwise. [b]1,2-Dichloroethane/EtOH, pyridine, AcOH, DMF, $CHCl_3$/MeOH, $CH_2Cl_2$/MeOH, or $CHCl_3$/pyridine (6:1). [c]Incomplete metalation and partial dehydrogenation (to porphyrin) were observed. [d]Transmetalation from the cadmium complex.

An alternative approach to metallobacteriochlorins might be envisaged as the simple hydrogenation of a metalloporphyrin. Whereas tetrahydrogenation of a free base porphyrin affords the free base bacteriochlorin, tetrahydrogenation of a zinc porphyrin affords the zinc isobacteriochlorin rather than the zinc bacteriochlorin.[57]

Through our recent work concerning the de novo synthesis of bacteriochlorins, two reactions were found unexpectedly to yield metallobacteriochlorins: (1) Pd-catalyzed cyanation of a free base 3,13-dibromobacteriochlorin with $Zn(CN)_2$ gave the corresponding zinc(II)-3,13-dicyano-8,8,18,18-tetramethylbacteriochlorin (Chart 4),[58] and (2) self-condensation of a dihydrodipyrrin−acetal in $CH_3CN$ containing $InCl_3$ afforded the corresponding indium bacteriochlorin[21] (Scheme 2). The formation of the zinc chelate in the former case might result from direct metalation of the electron-deficient 3,13-dicyanobacteriochlorin, and the latter case is thus far restricted to indium given that the metal reagent must provide acid catalysis for the condensation and also engender chelation during the course of the reaction. In general, no broadly applicable method for metalating synthetic bacteriochlorins has been developed to date.

*2. Metal Insertion Studies. Survey of Methods for an Electron-Rich Bacteriochlorin.* We examined the metalation of the di-*p*-tolylbacteriochlorin, **BC0-2T**, under four conditions.

(1) Treatment of **BC0-2T** with $Zn(OAc)_2$, $Cu(OAc)_2{\cdot}H_2O$, $Ni(OAc)_2{\cdot}4H_2O$, $Pd(OAc)_2$, $Pd(O_2CCF_3)_2$, or $Co(OAc)_2$ in $CHCl_3$/MeOH at room temperature or reflux did not afford the metal chelate as determined by LD-MS and absorption spectroscopy. More forcing conditions employing elevated temperature in two different solvent systems ($ClCH_2CH_2Cl$/MeOH and DMF) with $Pd(O_2CCF_3)_2$ (used in porphyrin metalation)[59] also showed only starting material.

(2) The standard "acac" conditions[34] with $Zn(acac)_2$ in refluxing benzene did not afford **ZnBC0-2T** (see Supporting Information).

(3) Use of $Cd(OAc)_2$ in DMF at 130 °C, the initial step in the transmetalation method,[23] afforded a byproduct (M + 14; by LD-MS analysis) that was consistent with an analogue of **BC0-2T** wherein one of the pyrroline methylene units is oxidized to form


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**Chart 2. Metal Chelates of Naturally Derived Bacteriochlorins**

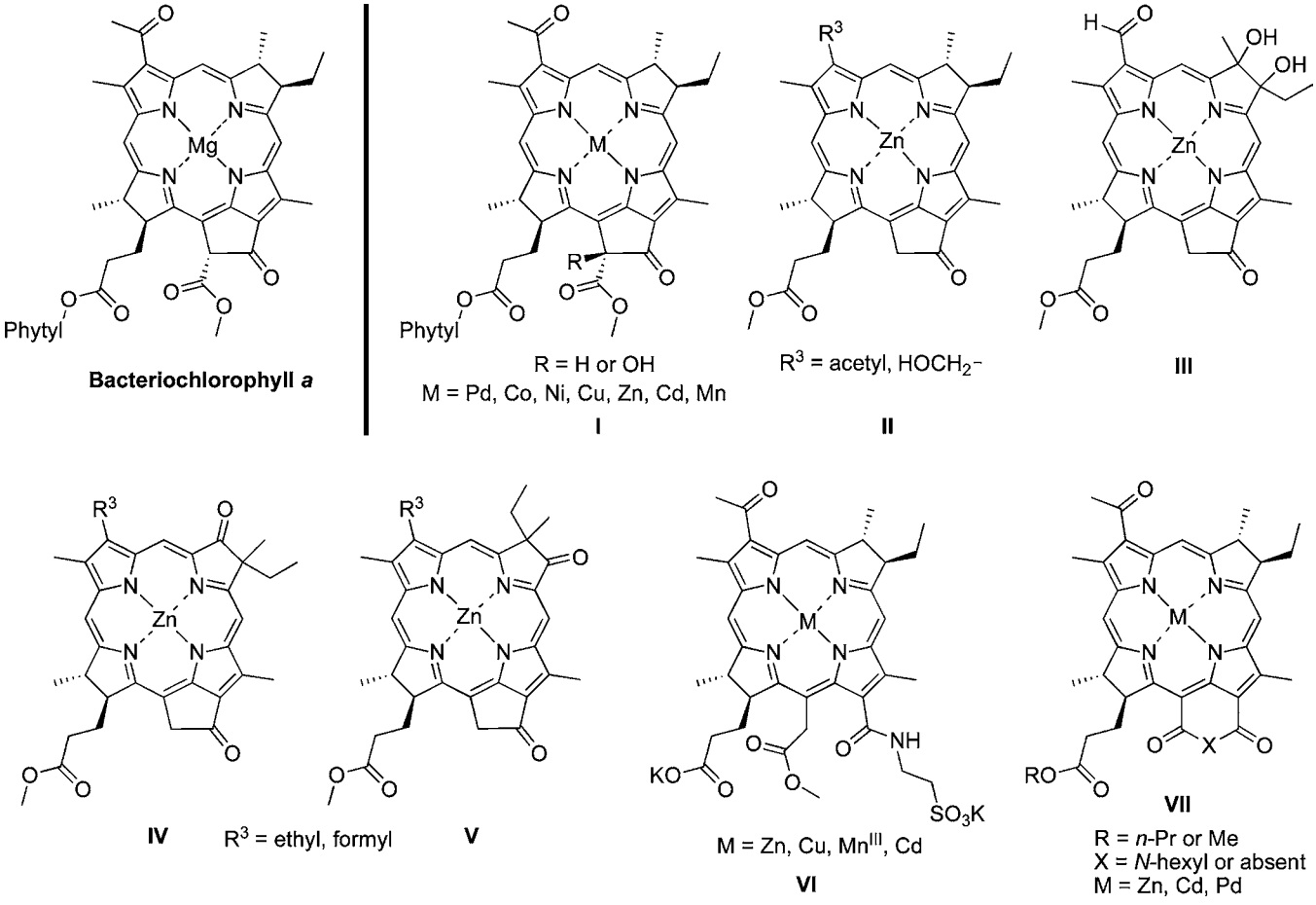
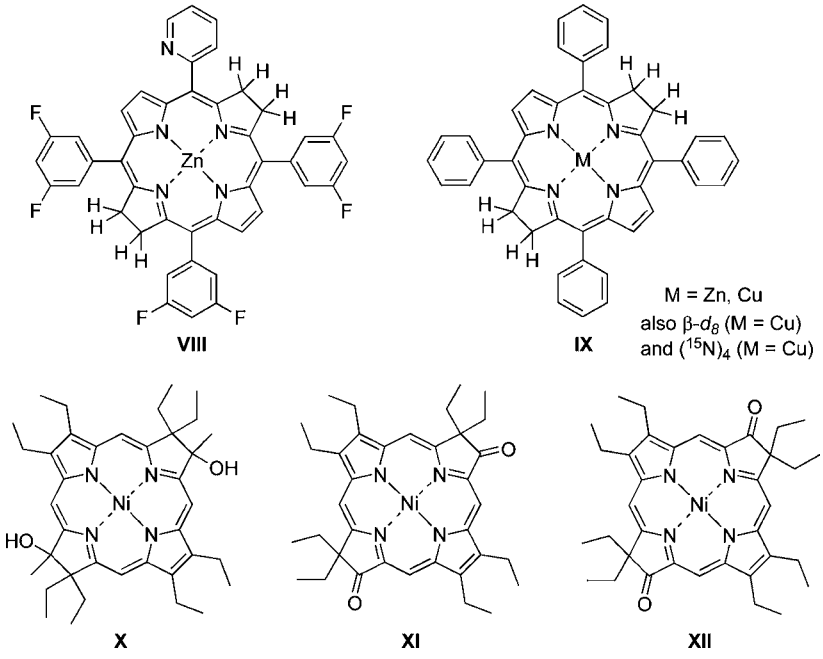



**Chart 3. Metal Chelates of Synthetic Bacteriochlorins**




a ketone (e.g., a putative oxobacteriochlorin). No bacteriochlorin chelate was formed.

(4) A room-temperature method for magnesium insertion into porphyrins employs $MgI_2$ and a noncoordinating base (e.g., diisopropylamine, DIEA) in a noncoordinating solvent (e.g., $CH_2Cl_2$).[60] An extension of this method, using $ZnI_2$ and DIEA in $CH_2Cl_2$ at reflux (~40 °C) for 12 h, afforded **ZnBC0-2T** in 30% yield as determined by absorption spectroscopy.


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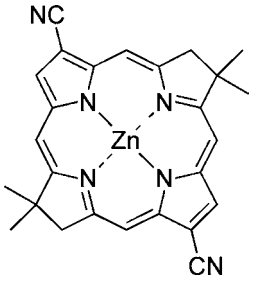
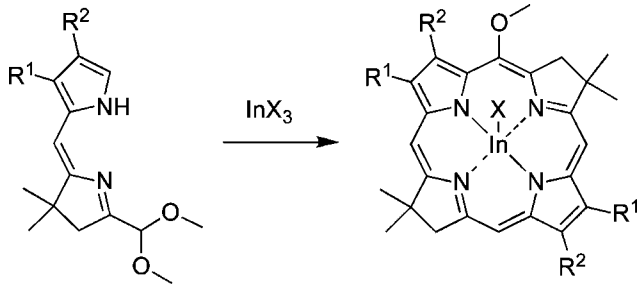
**Chart 4. Zinc Dicyanobacteriochlorin**




**Scheme 2. Metalation during Macrocycle Formation**



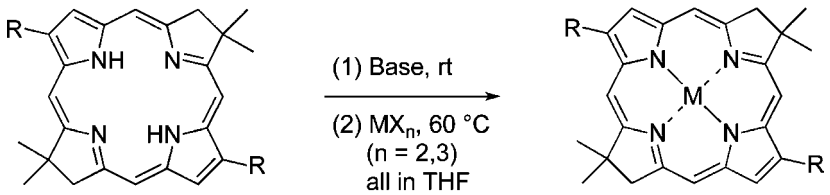

A base may be essential for metalation, to facilitate deprotonation of the bacteriochlorin and/or remove the acid liberated upon metalation (eq 1). We examined a wide variety of bases and metal reagents at slightly elevated temperature. Ultimately we found that treatment of **BC0-2T** with NaH in tetrahydrofuran (THF) at room temperature for 1 h followed by $Zn(OTf)_2$ and heating to 60 °C for 12 h afforded the desired **ZnBC0-2T** (Table 2, entry 1). The development of this method is described in the Supporting Information.

$$H_2BC + MX_2 \rightarrow MBC + 2HX \quad (1)$$

The method was applied to other metal reagents. Thus, use of $PdBr_2$ or $Cu(OAc)_2$ afforded **PdBC0-2T** or **CuBC0-2T**, respectively (entries 2 and 3). The base LDA, which has comparable strength to that of NaH ($pK_a$ of conjugate acid ~35),[61] also was found to be effective. One key difference between NaH and LDA is that typically the former affords a heterogeneous reaction whereas the latter affords a homogeneous reaction. Use of LDA afforded **ZnBC0-2T** and **CuBC0-2T** from the same reagents as with NaH (entries 4 and 5). On the other hand, $InCl_3$ gave no insertion with NaH but did afford the ClIn(III) complex (**ClInBC0-2T**) upon use of LDA (entry 6). For examination of a variety of indium reagents, see the Supporting Information. No metallobacteriochlorins were obtained under any condition explored with metal reagents based on $MgX_2$ (X = Cl, Br, I, OH, OTf), $Al_2O_3$, $AlX_3$ (X = acac, Cl, Br), $NiX_2$ (X = acac, Cl, Br, I), $SnX_2$ (X = OH, OAc, acac, Br, I), or $AuX_3$ (X = Cl, Br, I). In summary, a few metals can be inserted into the electron-rich bacteriochlorin **BC0-2T** with use of NaH or LDA in THF. It warrants consideration that the alkali metal of the base (e.g., Na or Li) is likely not a spectator but instead plays a role in coordination of the deprotonated bacteriochlorin. In this regard, the overall metalation reflects in part a competition between two cations (acids) and two anionic ligands (bases). In-depth study of the nature of reaction intermediates, the role of counterions, and delineation of the kinetics and thermodynamics of reaction are beyond the scope of the present paper.

*Zincation of Bacteriochlorins Bearing 0–4 Carbonyl Substituents.* To better understand the scope of the metalation method ($MX_n$/NaH or LDA), we examined the set of bacteriochlorins shown in Chart 1 and isolated the corresponding metal chelates. For comparison, the standard "porphyrin metalation conditions" of $Zn(OAc)_2{\cdot}2H_2O$ in DMF were also examined. The unsubstituted bacteriochlorin **BC0** afforded **ZnBC0** in 80% isolated yield upon treatment with NaH/THF and $Zn(OTf)_2$ (Table 3, entry 1) whereas no reaction was observed with the standard porphyrin metalation conditions of $Zn(OAc)_2{\cdot}2H_2O$ in DMF (entry 2). Treatment of diester-bacteriochlorin **BC2-2H** with the NaH/THF method for 6 h at 60 °C gave the zinc chelate in 31% yield (entry 3) whereas $Zn(OAc)_2{\cdot}2H_2O$ in DMF at 80 °C for 3 days gave some metalation but extensive byproducts interfered with isolation (entry 4). Essentially identical results were observed with the 5-methoxy analogue, namely, **BC2-2H-MeO** (entries 5 and 6). Treatment of diester-bacteriochlorin **BC2-2M-MeO** with the NaH/THF method for 5 h at 60 °C gave the zinc chelate in 54%

**Table 2. Survey of Metalation (BC0-2T)**




**BC0-2T** R = *p*-tolyl **MBC0-2T**

| entry | base | metal reagent | time[a] | product | yield[b] |
|---|---|---|---|---|---|
| 1 | NaH | $Zn(OTf)_2$ | 12 h | **ZnBC0-2T** | 80% |
| 2 | NaH | $PdBr_2$ | 0.5 h | **PdBC0-2T** | 78% |
| 3 | NaH | $Cu(OAc)_2$ | 3 h | **CuBC0-2T** | 80% |
| 4 | LDA | $Zn(OTf)_2$ | 2 h | **ZnBC0-2T** | quantitative |
| 5 | LDA | $Cu(OAc)_2$ | 0.5 h | **CuBC0-2T** | 56% |
| 6 | LDA | $InCl_3$ | 1 h | **ClInBC0-2T**[c] | 85% |

[a]The reaction conditions entail (1) treatment of **BC0-2T** (1.1 mg, 4.0 mM) in THF at room temperature with NaH (100 equiv = 400 mM) for 1 h or LDA (10 equiv = 40 mM) for 5 min, (2) addition of the metal reagent (30–80 mM, see Supporting Information), and (3) heating at 60 °C for the indicated period. [b]The crude mixtures were monitored by TLC and LD-MS. The yields were determined by absorption spectroscopy.


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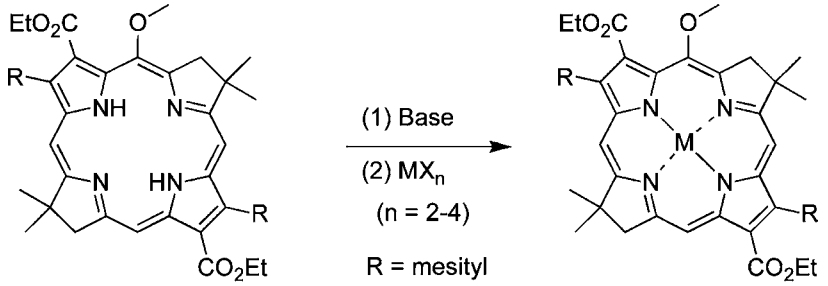
**Table 3. Zinc Metalation of Synthetic Bacteriochlorins**

| entry | substrate | conditions[a] | temp./time | product(s) | isolated yield |
|---|---|---|---|---|---|
| 1 | **BC0** | NaH/THF, $Zn(OTf)_2$ | 60 °C/16 h | **ZnBC0** | 80% |
| 2 | **BC0** | DMF, $Zn(OAc)_2{\cdot}2H_2O$ | 80 °C/24 h | no reaction | |
| 3 | **BC2-2H** | NaH/THF, $Zn(OTf)_2$ | 60 °C/6 h | **ZnBC2-2H** | 31% |
| 4 | **BC2-2H** | DMF, $Zn(OAc)_2{\cdot}2H_2O$ | 80 °C/3 days | **ZnBC2-2H** and byproduct | |
| 5 | **BC2-2H-MeO** | NaH/THF, $Zn(OTf)_2$ | 60 °C/6 h | **ZnBC2-2H-MeO** | 50% |
| 6 | **BC2-2H-MeO** | DMF, $Zn(OAc)_2{\cdot}2H_2O$ | 80 °C/3 days | **ZnBC2-2H-MeO** and byproduct | |
| 7 | **BC2-2M-MeO** | NaH/THF, $Zn(OTf)_2$ | 60 °C/5 h | **ZnBC2-2M-MeO** | 54% |
| 8 | **BC2-2M-MeO** | LDA/THF, $Zn(OTf)_2$ | 60 °C/3 h | **ZnBC2-2M-MeO** | quantitative[b] |
| 9 | **BC2-2E** | DMF, $Zn(OAc)_2{\cdot}2H_2O$ | 80 °C/24 h[c] | **ZnBC2-2E** | 86% |
| 10 | **BC3-2E** | DMF, $Zn(OAc)_2{\cdot}2H_2O$ | 80 °C/7 h[c] | **ZnBC3-2E** | 54% |
| 11 | **BC4-MeO** | DMF, $Zn(OAc)_2{\cdot}2H_2O$ | 80 °C/3 h[c] | **ZnBC4-MeO** | 97% |

[a]The reaction conditions entail: (a) treatment of bacteriochlorin (4 mM) in THF at room temperature with NaH (150 equiv = 600 mM) for 1 h or LDA (10 equiv = 40 mM) for 5 min, followed by $Zn(OTf)_2$ (30 equiv) and heating as indicated; or (b) treatment of bacteriochlorin (4 mM) in DMF with $Zn(OAc)_2{\cdot}2H_2O$ (30 equiv) and heating as indicated. [b]Yield determined by absorption spectroscopy. [c]After an initial period of 60 °C for 16 h.

**Table 4. Survey of Metalation of Bacteriochlorin BC2-2M-MeO**




**BC2-2M-MeO** **MBC2-2M-MeO**

| entry | base | metal reagent | time[a] | product | yield[b] |
|---|---|---|---|---|---|
| 1 | NaH | $Cu(OAc)_2$ | 8 h | **CuBC2-2M-MeO** | 39% |
| 2 | NaH | $PdBr_2$ | 2 h | **BC2-2M** | 29%[c] |
| 3 | LDA | $Cu(OAc)_2$ | 20 h | **CuBC2-2M-MeO** | 42% |
| 4 | LDA | $InCl_3$ | 28 h | **ClInBC2-2M-MeO** | 59% |
| 5 | LDA | $PdBr_2$ | 3 h | **PdBC2-2M-MeO** | 71% |
| 6 | NaH | $NiCl_2$ | 3 h | **NiBC2-2M-MeO** | 78% |
| 7 | NaH | $CdCl_2$ | 3 h | **CdBC2-2M-MeO** | 78% |
| 8 | NaH | $SnCl_2$ | 1 h | **$Cl_2$SnBC2-2M-MeO** | 53%[d] |
| 9 | NaH | $SnCl_4$ | 2 h | **$Cl_2$SnBC2-2M-MeO** | 31%[e] |

[a]The reaction conditions (0.60 mg of **BC2-2M-MeO**) entail (1) treatment of **BC2-2M-MeO** (4.0 mM) in THF at room temperature with NaH (600 mM) for 1 h or LDA (40 mM) for 5 min, followed by (2) addition of the metal reagent and heating at 60 °C for the indicated period. [b]The crude mixtures were monitored by TLC and MALDI-MS. The yields were determined by absorption spectroscopy (assuming equal molar absorptivity of the respective free base and metallobacteriochlorins at the $Q_y(0,0)$ band). [c]Isolated yield based on 7.8 mg of **BC2-2M-MeO**. [d]The free base bacteriochlorin also was present (24% yield). [e]The free base bacteriochlorin also was present (69% yield).

yield (entry 7) whereas use of LDA/THF for 3 h at 60 °C gave **ZnBC2-2M-MeO** in quantitative yield (entry 8).

The remaining bacteriochlorins with 2−4 carbonyl groups (**BC2-2E**, **BC3-2E**, **BC4-MeO**) were each treated to the standard porphyrin zincation conditions [$Zn(OAc)_2{\cdot}2H_2O$ in DMF] at 60 °C for 16 h, and examined for metalation (by absorption spectroscopy and MALDI-MS). If metalation was less than quantitative, the reaction mixture was then heated at elevated temperature. Thus, **BC2-2E**, **BC3-2E**, and **BC4-MeO** were successfully metalated upon subsequent heating at 80 °C for 24, 7, and 3 h, respectively (entries 9−11). The differences in yield are attributed to purification procedures, given that each reaction appeared to go to completion.

In summary, bacteriochlorins bearing three or four carbonyl groups undergo zincation upon standard porphyrin metalation conditions, whereas those with no such electron-withdrawing groups do not, and instead require use of a strong base (NaH or LDA). Bacteriochlorins bearing two carboethoxy substituents undergo metalation via both the NaH or LDA/THF method and the DMF method, the cleanliness and ease of isolation depending on the nature of the set of bacteriochlorin substituents.

*Scope of Metalation of Diester-Bacteriochlorins.* The diester-bacteriochlorin **BC2-2M-MeO** was readily zincated upon treatment with NaH or LDA in THF followed by $Zn(OTf)_2$ (Table 3, entries 7 and 8). We sought to examine the range of metal chelates that could be prepared with this substrate versus that lacking ester substituents (i.e., **BC0-2T**) as examined in Table 1. Thus, metalation of **BC2-2M-MeO** was monitored by TLC, absorption spectroscopy, and MALDI-MS. Metal reagents that provided the best yield in the metalation of **BC0-2T** were examined for **BC2-2M-MeO** and also gave reasonable yields (Table 4, entries 1−5). In addition to insertion of Zn(II), Cu(II),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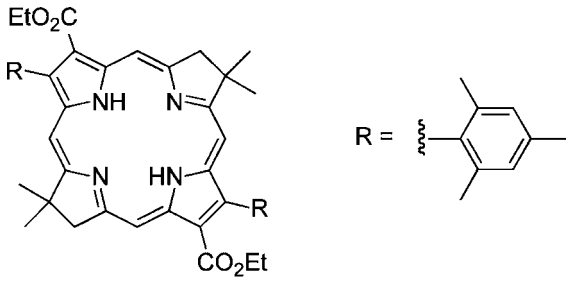
Pd(II), and In(III), treatment with $NiCl_2$, $CdCl_2$, and $SnCl_2$ also gave the corresponding metal chelates (Table 4, entries 6–8). For insertion of $SnCl_2$ as well as $SnCl_4$, only partial metalation was observed despite supplemental reagents or prolonged reaction time (entries 8 and 9). Here, the reaction failed with $Mg(OTf)_2$ $Al(OTf)_2$, and $AuCl_3$.

Surprisingly, when **BC2-2M-MeO** was treated with NaH and $PdBr_2$, the reaction mixture showed a peak at [M − 30] in comparison to the starting material by MALDI-MS (Table 4, entry 2). The absorption spectrum showed a hypsochromically shifted $Q_x$ band and a bathochromically shifted $Q_y$ band; the positions of the resulting bands were typical for the absence of a methoxy group.[16,20] The reaction at the multimilligram scale afforded a product that upon isolation and characterization (by $^1$H NMR spectroscopy, absorption spectroscopy, MALDI-MS and ESI-MS) proved indeed to be the free base bacteriochlorin that lacks the 5-methoxy group (**BC2-2M**, Chart 5).

**Chart 5. Demethoxylated Byproduct upon Attempted Palladiation**




**BC2-2M**

A Ni-catalyzed process for reductive cleavage of aryl methyl ethers has recently been reported.[62] An in-depth scrutiny of the Pd-mediated cleavage observed herein is beyond the scope of the present paper.

*Magnesiation of Ester-Bacteriochlorins.* Magnesium tetrapyrroles (e.g., chlorophylls, bacteriochlorophylls) are ubiquitous, a fact thrown into sharp relief given the historical difficulties that have surrounded the chemical insertion of magnesium into the free base macrocycles.[60] The biosynthetic incorporation of magnesium (into protoporphyrin IX) is endergonic.[63] Magnesium porphyrins are class IV metalloporphyrins[32] and as such readily demetalate upon exposure to weak acids such as silica gel and acetic acid. Failure to magnesiate **BC2-2M-MeO** with $Mg(OTf)_2$ and NaH in THF, while not unexpected, also pointed toward the use of other reaction conditions and/or more electron-deficient bacteriochlorins. As stated above, porphyrins (and many chlorins) can be magnesiated upon use of $MgX_2$ (X = Br or I) under noncoordinating slightly basic conditions (e.g., in $CH_2Cl_2$ containing triethylamine (TEA)).[60]

Application of the condition for magnesiation of porphyrins[60] ($MgI_2$ in $CH_2Cl_2$ containing TEA) to the tetraester-bacteriochlorin **BC4-MeO** did not yield any magnesium chelate after 16 h (Table 5, entry 1). A large excess of magnesium reagent only resulted in the decomposition of **BC4-MeO** (Table 5, entry 2). Returning to the conditions identified for zincation in Table 2, **BC4-MeO** in THF was treated with NaH followed by $MgI_2$ (Table 5, entries 3 and 4). After heating at 60 °C for 24 h, the $Q_x$ band was found at 612 nm (versus 548 nm for **BC4-MeO**; all in $CH_2Cl_2$) and a peak at [M + 22] was found upon MALDI-MS,

**Table 5. Survey of Magnesiation of Bacteriochlorins[a]**

| entry | substrate | condition | base[b] | metal reagent | result[c] |
|---|---|---|---|---|---|
| 1 | **BC4-MeO** | 40 °C, 16 h | [TEA] = 80 mM | 40 mM | no reaction |
| 2 | **BC4-MeO** | 40 °C, 5 h | [TEA] = 80 mM | 120 mM | decomposition |
| 3 | **BC4-MeO** | 60 °C, 24 h | [NaH] = 0.6 M | 120 mM | **MgBC4-MeO** and byproducts |
| 4 | **BC4-MeO** | 60 °C, 3 h | [NaH] = 1.2 M | 120 mM | **MgBC4-MeO** |
| 5 | **BC3-2E** | 60 °C, 40 h | [NaH] = 1.2 M | 120 mM | no reaction |
| 6 | **BC2-2E** | 60 °C, 30 h | [NaH] = 0.6 M | 120 mM | no reaction |

[a]The reaction procedure entails treatment of substrate (4 mM) in $CH_2Cl_2$ (with TEA) or THF (with NaH) followed by $MgI_2$ at the indicated temperature for the indicated time. [b]The quantity is given in concentration units for ease of comparison even though not all material may be dissolved. [c]The crude mixture was checked by TLC, absorption spectroscopy, and MALDI-MS.

indicating formation of the magnesium chelate. However, the crude mixture contained a significant amount of unknown impurities as examined by TLC and absorption spectroscopy. Increasing the amount of NaH to 300 equivalents considerably reduced the impurities and the reaction was completed within 3 h. The magnesium chelate was found to be quite unstable, decomposing in $CH_2Cl_2$ solution within 2 h at room temperature, but could be handled by avoiding chlorinated solvents and by performing chromatography on basic alumina. Although the tetraester-bacteriochlorin **BC4-MeO** was successfully magnesiated, **BC3-2E** and **BC2-2E** each gave no reaction under similar conditions (entries 5 and 6).

A summary of our observations concerning metalation of synthetic bacteriochlorins is shown in Figure 1. The chief results are as follows: (1) Bacteriochlorins lacking any electron-withdrawing groups, including unsubstituted **BC0**, afford a limited set of metal chelates upon treatment with a strong base (NaH or LDA) in THF. (2) The same strong-base conditions accommodate a broader scope of metal chelates upon application to a bacteriochlorin bearing two carboethoxy substituents. (3) Bacteriochlorins bearing 2–4 carbonyl (carboethoxy, imide) substituents can be zincated with the standard "porphyrin metalation conditions" of $Zn(OAc)_2{\cdot}2H_2O$ in hot DMF. (4) Where direct comparisons were made for the bacteriochlorins bearing two carboethoxy substituents, treatment with a strong base (NaH or LDA) afforded more rapid and cleaner metalation than use of $Zn(OAc)_2{\cdot}2H_2O$ in hot DMF. (5) A bacteriochlorin bearing 4 carboethoxy substituents could be magnesiated under the strong base conditions, but the resulting magnesium chelate exhibited limited stability. (6) *Ortho*-aryl substituents are known to slow substantially the rate of metalation of *meso*-tetraarylporphyrins,[64] yet no adverse effect was observed upon application of the preparative procedures with the dimesitylbacteriochlorin (**BC2-2M-MeO**).

*Isolation and Characterization of Metallobacteriochlorins.* A number of reactions were carried out at the multimilligram scale to obtain sufficient metallobacteriochlorin for physicochemical studies. Thus, eight zinc bacteriochlorins (Tables 2 and 3), three copper chelates (**CuBC2-2M-MeO**, **CuBC0-2T**, **CuBC0**), two palladium chelates (**PdBC2-2M-MeO**, **PdBC0-2T**), and one indium chelate (**ClInBC0-2T**) were isolated and characterized. Upon purification, the metallobacteriochlorins were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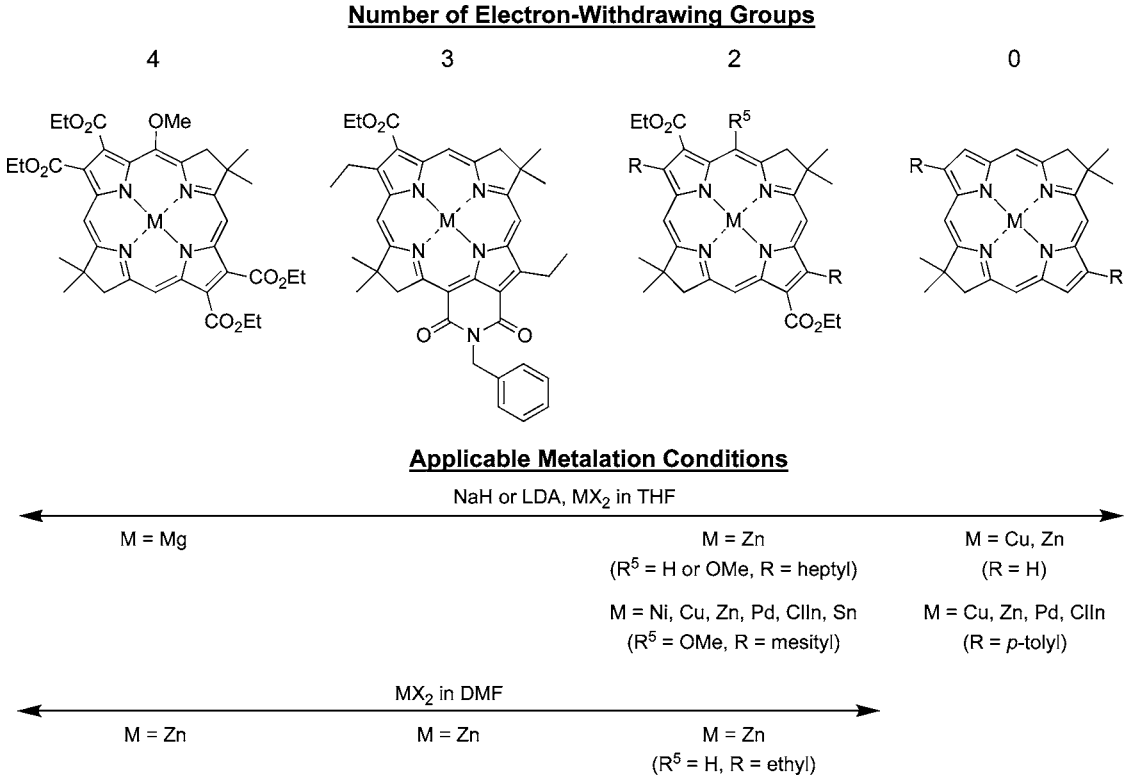


**Figure 1.** Summary of metalation of synthetic bacteriochlorins.

stable under dry conditions in the absence of light for an extended period. Each metallobacteriochlorin was characterized by $^1$H NMR spectroscopy (except for Cu bacteriochlorins), absorption spectroscopy, MALDI-MS or LD-MS, and ESI-MS. The magnesium chelate (**MgBC4-MeO**) was only partially characterized owing to limited stability. The availability of these various metallobacteriochlorins enabled the physicochemical studies described in the following sections.

**C. Structural and Physicochemical Characteristics.** *1. Structural Analysis.* The single-crystal X-ray structures of bacteriochlorins **BC0**, **BC0-2M**, and **CuBC0-2T** are shown in Figure 2. Note that **BC0-2M** contains 3,13-dimesityl groups whereas **CuBC0-2T** contains 2,12-di-*p*-tolyl groups. While a sizable number of photosynthetic proteins containing bacteriochlorophylls have been examined by X-ray crystallography, relatively few single-crystal X-ray studies have been carried out of bacteriochlorins. These include synthetic free base bacteriochlorins,[65] synthetic metallobacteriochlorins,[42,52,66] and naturally derived (free base) bacteriopheophorbides.[67]

The core shape of porphyrin (**porphine**), chlorin (**FbC**), and bacteriochlorin (**BC0**) macrocycles are shown in Figure 3. The core shape of porphine is close to square,[68] while that of chlorin **FbC** is slightly kite-shaped because of the presence of one pyrroline ring (D) and three pyrrole rings (A, B, and C).[69,70] The core shape of bacteriochlorin **BC0** is slightly rectangular. The two pyrrole rings and two pyrroline rings that constitute a bacteriochlorin alternate upon circumambulating the macrocycle; thus, the two pyrroline rings occupy opposite corners, as do the two pyrrole rings. The core size can be evaluated by the comparison of the average distances between each of the nitrogen atoms and their centroid.[71] The order of average nitrogen-centroid distances is porphine (2.055 Å) < chlorin (2.074 Å) < bacteriochlorin (2.096 Å).

The core shape of the copper bacteriochlorin **CuBC0-2T** is shown in the Supporting Information, Figure S1. Copper bacteriochlorin **CuBC0-2T** is fairly planar, with the copper atom located on the least-squares plane defined by the four nitrogen atoms. The average copper−centroid distance is 2.005 Å, which is shorter than that of free base bacteriochlorins **BC0** and **BC0-2M** (~2.095 Å).

*2. Spectral Properties.* The ground-state electronic absorption spectra of the metallobacteriochlorins and the free base bacteriochlorins in toluene are shown in Figure 4 (**Zn** series) and Figure 5 (**BC0-2T** series). The spectral data including the position, intensity, and full-width at half-maximum (fwhm) of the long-wavelength absorption band ($Q_y$); the shift ($\Delta\lambda$) in the position of the $Q_y$ band with respect to the free base bacteriochlorins; and intensity ratios of the $Q_y$ to $B_y$ bands ($I_{Q_y}/I_{B_y}$ ratio) are listed in Table 6. Table 6 also gives spectral data for the native bacteriochlorins. In general, the absorption spectra of the synthetic metallobacteriochlorins resemble that of Bchl *a*, just as the spectra of the synthetic free base bacteriochlorins resemble that of the native free-base (Mg-less) analogue Bphe *a*.

The spectrum of each bacteriochlorin exhibits four absorption bands generally categorized as $B_y(0,0)$, $B_x(0,0)$, $Q_x(0,0)$, and $Q_y(0,0)$ from short to long wavelength. ($B_y(0,0)$ and $B_x(0,0)$ may reverse positions depending on the bacteriochlorin and have mixed *x* and *y* polarizations.) In general, the B bands of all bacteriochlorins examined herein fall in the region 330 to 419 nm. The Q bands of the **BC0-2T** series including the free base and all metal chelates lie at shorter wavelength ($Q_x$ 499 to 536 nm; $Q_y$ 737 to 763 nm) versus those of the **BC2-2M-MeO** series ($Q_x$ 524 to 556 nm; $Q_y$ 758 to 779 nm). For the **Zn** series, the Q bands are located at longer wavelength compared to the corresponding free base bacteriochlorins. The shifts in $Q_x$ bands (19−34 nm) are generally more significant than those of $Q_y$ bands (12−16 nm). The $Q_y$ bands of the


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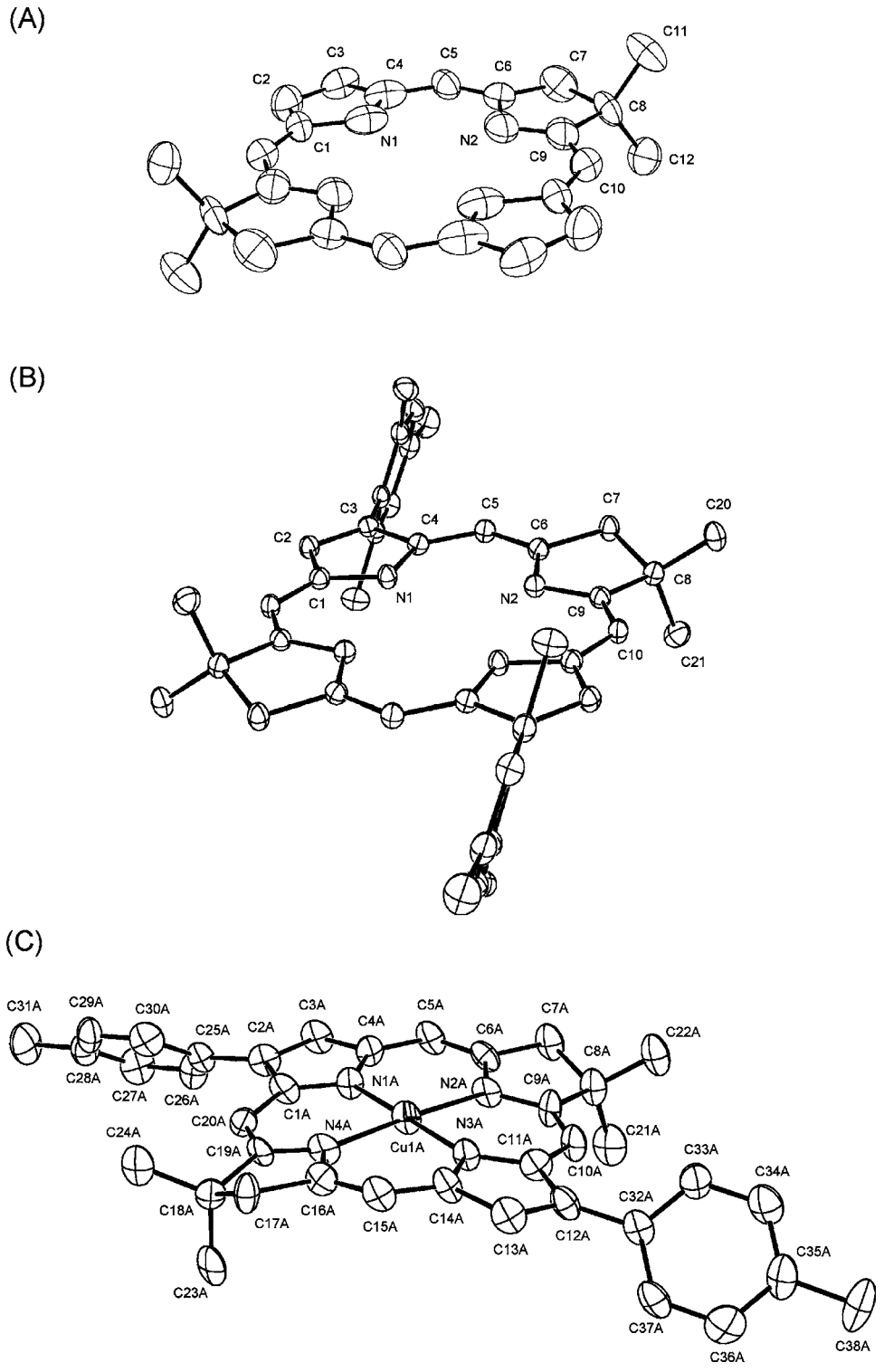


**Figure 2.** ORTEP drawing of (A) free base bacteriochlorin **BC0**, (B) free base bacteriochlorin **BC0-2M**, and (C) copper bacteriochlorin **CuBC0-2T** (one molecule from the unit cell). Ellipsoids are displayed at the 50% probability level and hydrogen atoms are omitted for clarity. The large spherical ellipsoids of **BC0** result from the high R factor value due to the weakly diffracting crystal.

synthetic bacteriochlorins are quite intense. For **BC0-2T**, the long-wavelength maximum (732 nm) has a molar absorptivity of ~120,000 $M^{-1}$ $cm^{-1}$.[16]

Within the same bacteriochlorin series, the extent of the $Q_x$ band shift increases in order of Pd < Cu < Zn (<ClIn) chelates, while that of $Q_y$ increases in order of Pd < Zn < Cu (<ClIn). Each bacteriochlorin features a sharp $Q_y$ band with fwhm in the range of 20−24 nm, except for the Cu chelates which exhibit broadened $Q_y$ band in the range of 29−40 nm. The intensity ratios of the $Q_y$ to $B_y$ bands of the metallobacteriochlorins increase inversely with the increase of the wavelength shift ($\Delta\lambda$) with respect to the free base bacteriochlorins in order of (ClIn) < Cu < Zn < Pd. For the **Zn** series, the intensity ratios of the $Q_y$ to $B_y$ bands fall in the range of 1.3−1.9.


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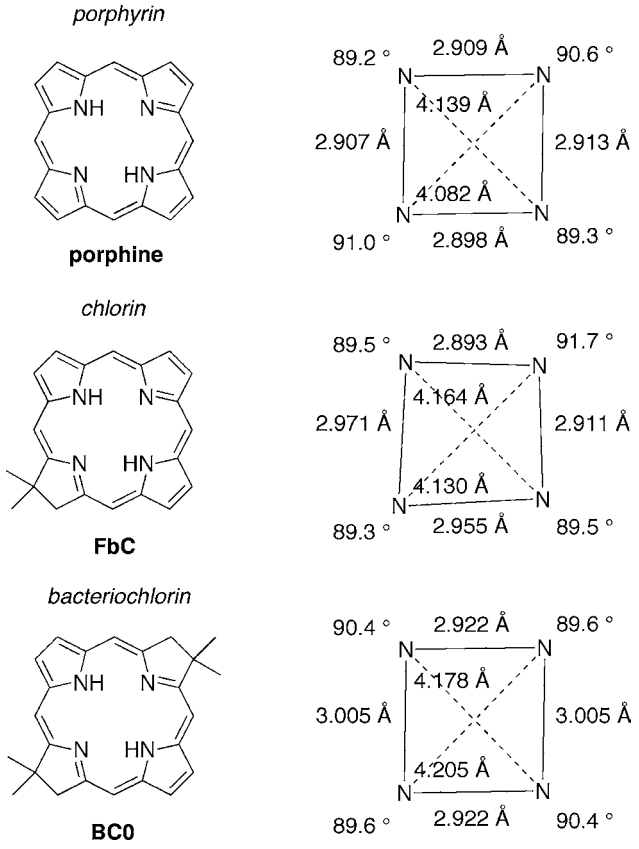


**Figure 3.** Comparison of core structural parameters across porphyrin, chlorin, and bacteriochlorin macrocycles.

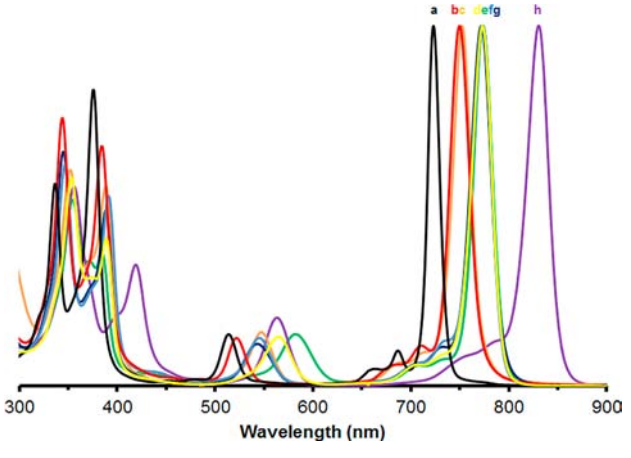


**Figure 4.** Absorption spectra in toluene at room temperature of bacteriochlorins (normalized at the $Q_y$ bands). The labels in the graph are as follows: (a) **ZnBC0** (black), (b) **ZnBC0-2T** (red), (c) **ZnBC2-2H-MeO** (orange), (d) **ZnBC2-2M-MeO** (yellow), (e) **ZnBC4-MeO** (green), (f) **ZnBC2-2E** (blue), (g) **ZnBC2-2H** (dark blue), and (h) **ZnBC3-2E** (purple).

The fluorescence spectrum of each zinc bacteriochlorin is dominated by a $Q_y(0,0)$ band that is only modestly (5−10 nm) shifted to longer wavelength than the $Q_y(0,0)$ absorption band and has a comparable spectral width (Table 6). This behavior is analogous to that observed for free base bacteriochlorins (Table 6 and ref 20). Similar fluorescence spectra are found for the indium chelates, as we have reported previously,[21] and for the palladium bacteriochlorins. However, compared to the zinc and

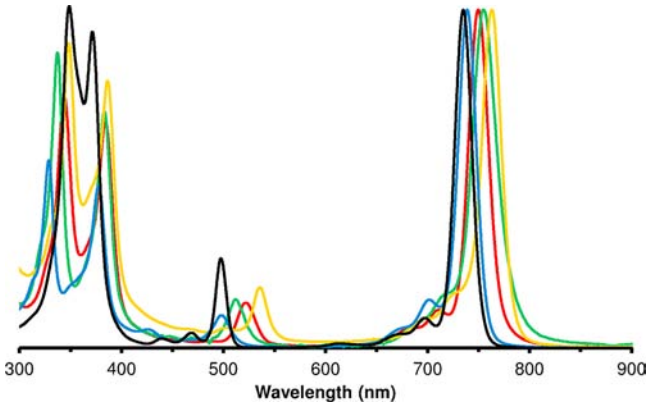


**Figure 5.** Absorption spectra in toluene at room temperature of bacteriochlorins (normalized at the $Q_y$ bands). The labels in the graph are as follows: (a) **BC0-2T** (black), (b) **PdBC0-2T** (blue), (c) **ZnBC0-2T** (red), (d) **CuBC0-2T** (green), and (e) **ClInBC0-2T** (orange).

free base bacteriochorins, the fluorescence intensities are much weaker for the indium complexes and weaker still for the palladium complexes as described in the following.

*3. Photophysical Properties.* Table 7 lists the photophysical properities of the zinc and palladium bacteriochlorins, along with representative data for the free base and indium analogues. The table also gives data for the native chromophores Bchl *a* and Bphe *a* in toluene. In comparing exact values of the photophysical characteristics of the zinc and free base bacteriochlorins, one must take into account that some of the zinc chelates may be axially ligated because they, like a few Fb complexes, were studied in THF rather than toluene for greater solubility (as indicated in Table 7 footnotes).

The zinc bacteriochlorins exhibit fluorescence quantum yields ($\Phi_f$) generally in the range 0.08−0.20 with an average value of 0.13 that is comparable to that (0.15) for the free base analogues studied here or previously.[20] The exception is $\Phi_f = 0.033$ for the bacteriochlorin−imide **ZnBC3-2E**, which like that (0.040)[20] for the free base analogue is reduced because of the lower energy ($Q_y$ > 800 nm; Table 6) of the singlet excited state resulting in more facile nonradiative internal conversion. The lifetimes ($\tau_S$) of the singlet excited state for the zinc bacteriochlorins are in the range 2.2−4.4 ns, with an average value of 3.3 ns. These lifetimes are also similar to those for the free base analogues (3.3−4.4 ns; average 3.8 ns). The typical yield of intersystem crossing to the triplet excited state ($\Phi_{isc}$) for the zinc bacteriochlorins is ∼0.7, which is somewhat greater than the average value of ∼0.5 for the free base analogues because of a modest effect of the metal ion on spin−orbit coupling. The typical $\Phi_f$ and $\tau_S$ values for the indium chelates (0.02 and ∼0.3 ns)[21] are reduced and the $\Phi_{isc}$ values (∼0.9) increased from those for the zinc chelates because of greater heavy metal enhancement of spin−orbit coupling.

The heavy metal effect (and potential d-orbital contribution) is greater still for the palladium bacteriochlorins, resulting in essentially quantitative singlet-to-triplet intersystem crossing. The consequence for **PdBC2-2M-MeO** is a very low fluorescence yield ($\Phi_f$ = 0.006) and singlet lifetime ($\tau_S$ = 15 ps). The two values are somewhat greater for **PdBC0-2T** for reasons that are not clear. Enhanced spin−orbit coupling also results in a progressive shortening of the lifetime of the lowest triplet excited state ($\tau_T$) from a typical value of ∼100 $\mu$s for the zinc and free base bacteriochlorins to ∼30 $\mu$s for the indium chelates and to ∼10 $\mu$s for the palladium chelates.


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**Table 6. Spectral Properties of Bacteriochlorins**[a]

| compound | $B_y(0,0)$[b] abs $\lambda$ (nm) | $B_x(0,0)$[b] abs $\lambda$ (nm) | $Q_x(0,0)$ abs $\lambda$ (nm) | $Q_y(0,0)$ abs $\lambda$ (nm) | $Q_y(0,0)$ abs fwhm (nm) | $Q_y(0,0)$ em $\lambda$ (nm) | $Q_y(0,0)$ em fwhm (nm) | $\Delta Q_x$[c] $\Delta\lambda$ (nm) | $\Delta Q_y$[c] $\Delta\lambda$ (nm) | $I_{Qy}/I_{By}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| *Zn-BCs* | | | | | | | | | | |
| **ZnBC0-2T** | 344 | 384 | 521 | 749 | 23 | 756 | 26 | 22 | 13 | 1.3 |
| **ZnBC2-2M-MeO** | 353 | 389 | 565 | 773 | 25 | 780 | 26 | 27 | 15 | 1.6 |
| **ZnBC4-MeO** | 354 | 385 | 581 | 774 | 22 | 782 | 27 | 31 | 15 | 2.0 |
| **ZnBC3-2E** | 356 | 419 | 564 | 830 | 27 | 835 | 23 | 20 | 12 | 1.7 |
| **ZnBC2-2E** | 347 | 391 | 546 | 773 | 24 | 778 | 25 | 25 | 12 | 1.6 |
| **ZnBC2-2H** | 347 | 391 | 547 | 775 | 23 | 780 | 24 | 26 | 13 | 1.2 |
| **ZnBC2-2H-MeO** | 353 | 389 | 548 | 750 | 26 | 758 | 26 | 26 | 10 | 1.3 |
| **ZnBC0** | 336 | 375 | 514 | 723 | 14 | 725 | 18 | 25 | 10 | 1.7 |
| *Pd-BCs* | | | | | | | | | | |
| **PdBC0-2T** | 330 | 379 | 499 | 739 | 21 | 745 | 25 | 0 | 3 | 1.7 |
| **PdBC2-2M-MeO** | 337 | 382 | 538 | 758 | 20 | 765 | 23 | 0 | 0 | 2.8 |
| *Cu-BCs* | | | | | | | | | | |
| **CuBC0-2T** | 337 | 383 | 512 | 755 | 29 | | | 13 | 18 | 1.2 |
| **CuBC2-2M-MeO** | 348 | 390 | 556 | 780 | 37 | | | 18 | 22 | 1.5 |
| **CuBC0** | 332 | 378 | 507 | 728 | 19 | | | 18 | 15 | 1.7 |
| *FbBCs* | | | | | | | | | | |
| **BC0-2T** | 351 | 374 | 499 | 736 | 20 | 742 | 23 | 0 | 0 | 1.0 |
| **BC2-2M-MeO** | 361 | 383 | 538 | 758 | 22 | 765 | 23 | 0 | 0 | 1.0 |
| **BC4-MeO**[d] | 361 | 368 | 550 | 759 | 20 | 763 | 23 | 0 | 0 | 1.2 |
| **BC3-2E**[d] | 358 | 408 | 544 | 818 | 24 | 823 | 24 | 0 | 0 | 1.3 |
| **BC2-2E**[d] | 354 | 383 | 521 | 761 | 20 | 764 | 21 | 0 | 0 | 0.9 |
| **BC2-2H** | 354 | 383 | 521 | 762 | 20 | 766 | 21 | 0 | 0 | 0.9 |
| **BC2-2H-MeO** | 357 | 379 | 522 | 740 | 18 | 746 | 21 | 0 | 0 | 1.1 |
| **BC0**[d] | 340 | 365 | 489 | 713 | 12 | 716 | 16 | 0 | 0 | 0.9 |
| *In-ClBCs* | | | | | | | | | | |
| **ClInBC0-2T**[e] | 350 | 388 | 539 | 763 | 23 | 769 | 31 | 40 | 27 | 1.1 |
| *MgBCs* | | | | | | | | | | |
| **MgBC4-MeO** | 360 | 380 | 599 | 776 | 31 | 780 | 33 | 49 | 17 | 0.9 |
| *Native BCs* | | | | | | | | | | |
| BChl *a* | 363 | 396 | 581 | 781 | 28 | 789 | 29 | 49 | 21 | 1.4 |
| BPhe *a*[d] | 362 | 389 | 532 | 758 | 31 | 768 | 27 | 0 | 0 | 0.7 |

[a]In toluene at room temperature. [b]The nominal $B_x(0,0)$ and $B_y(0,0)$ absorption bands may alternate order with compound and have mixed *x* and *y* polarization. [c]The shift of the band relative to that of the free base analogue. [d]Data from ref 20. [e]Data from ref 21.

In the case of copper bacteriochlorins (**CuBC0**, **CuBC0-2T**, **CuBC2-2M-MeO**), interactions involving the unpaired metal electron associated with the $d^9$ configuration of Cu(II) transform the macrocycle singlet excited state into a "singdoublet" and split the macrocycle triplet excited state into "tripdoublet" and "quartet" excited states that are close in energy, in analogy to copper porphyrins.[7] Normal fluorescence is not expected (and none is found in the case of **CuBC2-2M-MeO**). Transient absorption studies of **CuBC0**, **CuBC0-2T**, and **CuBC2-2M-MeO** indicate essentially complete decay to the ground state with time constants of 0.3, 0.5, and 1.7 ns in THF. This time evolution likely represents deactivation of the tripdoublet/quartet excited-state manifold via a ring-to-metal charge-transfer state that has been implicated in the excited-state dynamics of copper porphyrins,[72] but which now lies at lower energy in the corresponding bacteriochlorins because of the greater ease of macrocycle oxidation.

Zinc tetrapyrroles (generally porphyrins and chlorins until the present) are often exploited in photophysical and photochemical applications compared to the corresponding magnesium complexes because of a reduced propensity for demetalation. In the case of porphyrins, a sacrifice is a shorter singlet excited-state lifetime (e.g., ~2 versus ~6 ns) and fluorescence yield (~0.03 versus ~0.13). Here we have found that the zinc bacteriochlorin **ZnBC4-MeO** has $\Phi_f$, $\tau_S$, $\Phi_{isc}$, and $\tau_T$ values comparable to those of the corresponding magnesium bacteriochorin **MgBC4-MeO**. In this regard, compared to the native magnesium bacteriochlorin, Bchl *a* (Table 6),[73−75] the zinc bacteriochlorins generally have similar $\Phi_f$, comparable or greater $\tau_S$, comparable $\Phi_{isc}$, and longer $\tau_T$ values. This comparison is similar to that for the free base bacteriochlorins relative to the native metal-free bacteriochlorin Bphe *a* (Table 6).[20] In summary, the synthetic zinc bacteriochlorins (and the indium and palladium analogues), like the free base bacteriochlorins, exhibit photophysical characteristics suitable for a range of applications in solar-energy conversion and photomedicine.

*4. Electrochemical and Molecular Orbital Characteristics.* The redox properties (reduction potentials) and energies of the frontier molecular orbitals (MOs) of the bacteriochlorins are listed in Table 7. Only the potentials for the first oxidation ($E_{ox}$) and reduction ($E_{red}$) (which are both reversible) are presented in the table, as these are most germane for the discussion below. It should be noted, however, that the molecules also exhibit redox processes corresponding to second oxidations and reductions. Differences in the $E_{ox}$ and $E_{red}$ values among the different metallobacteriochlorins and free base analogues generally parallel those for porphyrin systems.[2] In prior work on a large number of chlorins,[76] good correlations were found between the $E_{ox}$ and the highest occupied molecular orbital (HOMO) energy and between the $E_{red}$ and the lowest unoccupied molecular orbital (LUMO) energy. Such a correlation is generally found in


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**Table 7. Photophysical, Redox, and Molecular-Orbital Properties of Bacteriochlorins[a]**

| compound | $\tau_S$ (ns) | $\Phi_f$ | $\Phi_{isc}$ | $\tau_T$[c] ($\mu$s) | $E_{ox}$[b] (V) | $E_{red}$[b] (V) | HOMO (eV) | LUMO (eV) |
|---|---|---|---|---|---|---|---|---|
| *Zn-BCs* | | | | | | | | |
| **ZnBC0-2T** | 2.9 | 0.11 | 0.83 | 161 | −0.04 | −1.60 | −4.26 | −2.20 |
| **ZnBC2-2M-MeO** | 2.9 | 0.12 | 0.71 | 120 | +0.45 | −1.38 | −4.55 | −2.51 |
| **ZnBC4-MeO** | 4.4 | 0.13 | 0.80 | 38 | +0.16 | −1.10 | −4.87 | −2.92 |
| **ZnBC3-2E** | 2.2 | 0.033 | 0.28 | 94 | +0.02 | −1.12 | −4.78 | −2.94 |
| **ZnBC2-2E** | 2.6 | 0.08 | 0.71 | 149 | −0.12 | −1.42 | −4.48 | −2.53 |
| **ZnBC2-2H** | 3.5 | 0.14 | 0.60 | 191 | 0.00 | −1.42 | −4.47 | −2.52 |
| **ZnBC2-2H-MeO** | 4.3 | 0.20 | 0.70 | 187 | −0.14 | −1.47 | −4.48 | −2.46 |
| **ZnBC0** | 3.4 | 0.10 | 0.67 | 151 | −0.12 | −1.68 | −4.30 | −2.16 |
| *Pd-BCs* | | | | | | | | |
| **PdBC0-2T** | 0.35 | 0.020 | >0.99 | 12 | +0.43 | −1.14 | −4.36 | −2.26 |
| **PdBC2-2M-MeO** | 0.015 | 0.006 | >0.99 | 5.8 | +0.29 | −1.29 | −4.63 | −2.54 |
| *Cu-BCs* | | | | | | | | |
| **CuBC0-2T** | | | | 0.5 ns[c] | −0.04 | −1.53 | −4.25 | −2.25 |
| **CuBC2-2M-MeO** | | | | 1.7 ns[c] | +0.18 | −1.32 | −4.53 | −2.55 |
| **CuBC0** | | | | 0.3 ns[c] | −0.04 | −1.60 | −4.27 | −2.18 |
| *FbBCs* | | | | | | | | |
| **BC0-2T**[d] | 3.3 | 0.18 | 0.55 | 163 | +0.21 | −1.49 | −4.40 | −2.22 |
| **BC2-2M-MeO** | 3.9 | 0.15 | 0.35 | 52 | +0.38 | −1.29 | −4.65 | −2.48 |
| **BC4-MeO**[d] | 4.3 | 0.16 | 0.24 | 46 | +0.57 | −1.05 | −5.00 | −2.95 |
| **BC3−2E**[d] | 1.9 | 0.04 | 0.51 | 85 | +0.45 | −0.98 | −4.91 | −2.99 |
| **BC2-2E**[d] | 3.3 | 0.14 | 0.55 | 110 | +0.29 | −1.32 | −4.68 | −2.58 |
| **BC2-2H** | 3.3 | 0.10 | 0.45 | 110 | +0.29 | −1.33 | −4.59 | −2.52 |
| **BC2-2H-MeO** | 4.4 | 0.17 | 0.49 | 86 | +0.28 | −1.43 | −4.60 | −2.45 |
| **BC0**[d] | 3.9 | 0.14 | 0.24 | 169 | +0.45 | −0.99 | −4.46 | −2.20 |
| *In-ClBCs* | | | | | | | | |
| **ClInBC0-2T**[e] | 0.21 | 0.016 | 0.9 | 44 | +0.31 | −1.25 | −4.52 | −2.52 |
| *MgBCs* | | | | | | | | |
| **MgBC4-MeO** | 5.4 | 0.16 | 0.60 | 90 | | | −4.86 | −2.94 |
| *Native BCs* | | | | | | | | |
| BChl *a* | 3.1 | 0.12 | 0.30 | 50 | | | −4.75 | −2.86 |
| BPhe *a*[d] | 2.7 | 0.10 | 0.57 | 25 | | | −4.87 | −2.84 |

[a]In toluene at room temperature except as follows: the $\tau_T$ values for all compounds and the $\Phi_f$, $\Phi_{isc}$, and $\tau_S$ values for **BC2-2H**, **BC2-2H-MeO**, **ZnBC0**, **ZnBC2-2H**, **ZnBC2-2H-MeO**, and **MgBC4-MeO** were determined in tetrahydrofuran. [b]First oxidation ($E_{ox}$) and first reduction ($E_{red}$) potentials measured in 0.1 M tetrabutylammonium hexafluorophosphate in which the ferrocene couple has an $E_{1/2}$ of 0.19 V. [c]Decay of the tripdoublet/quartet excited-state manifold in nanoseconds. [d]Data from ref 20. [e]Data from ref 21.

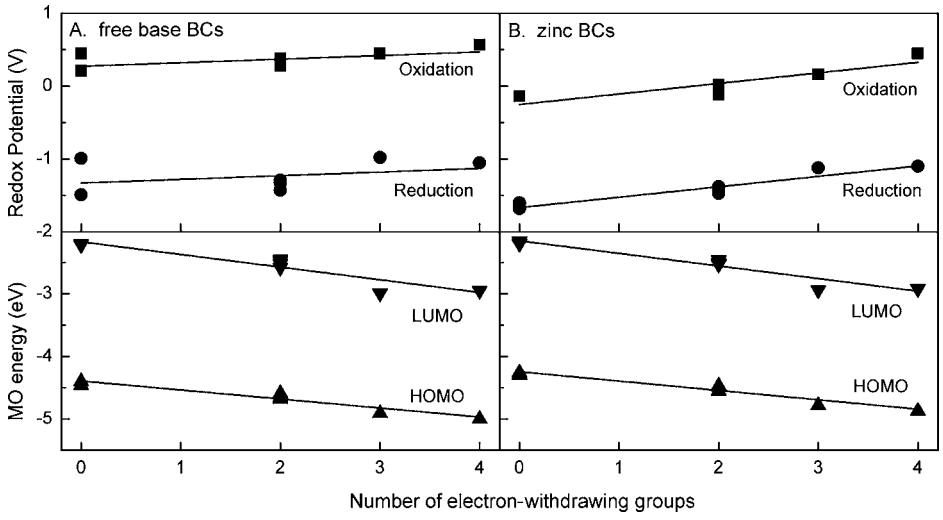


**Figure 6.** Effect of the number of electron-withdrawing (carbonyl) groups on the redox potentials and frontier MO energies.

Table 7 and in Figure 6, which plots the redox potentials and MO energies versus the number of electron-withdrawing groups on the bacteriochlorin.

Comparison of HOMO and LUMO energies of compounds **BC0**, **BC0-2T**, and **BC3-2E** listed in Table 7 with the values for their counterparts studied previously[20] that contain a 5-methoxy


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group shows that the 5-methoxy group shifts the MO energies by a relatively small amount ($\leq$0.08 eV). When there is a shift in the MO energies, the shift is to slightly more negative values, indicating that the compound should be slightly harder to oxidize and easier to reduce. The data in Table 7 and Figure 6 further show that an increasing number of electron-withdrawing groups on the bacteriochlorin (affording greater ease of metalation) is reflected in a more positive $E_{ox}$ (harder to oxidize) and a less negative $E_{red}$ (more difficult to reduce). The one compound that is an outlier is **BC0**. Along the same set of compounds, an increasing number of electron-withdrawing groups is reflected in shifts in the HOMO energy to more negative values (harder to oxidize) and the LUMO energy to more negative values (easier to reduce). Here, compound **BC0** is not an outlier and has essentially the same MO energies as compound **BC0-2T**. Thus, the fact that **BC0** is an outlier in the redox data may be in part a solvation (electrolyte) effect.

As expected, an increasing number of electron-withdrawing groups shifts the redox potentials and MO energies so as to make it harder to remove an electron (or electron density) and easier to add an electron (or electron density). Because metalation involves replacing two protons of the free base with a divalent metal ion, and a pair of protons is typically more electropositive than the metal ion, metalation effectively involves a net addition of electron density to the macrocycle. This property results in the correlation between the ease of metalation and the redox and MO energies.

The above comparisons are made for a set of bacteriochlorins that differ in the number and types of substituents at the same macrocycle positions. These changes cause shifts in the energies and electron densities of the HOMO and LUMO, but do not alter the identities of these two orbitals. The finding of such correlations, or even the interpretation if they are found, may be more difficult if the set of molecules differ in the sites of macrocycle substitution, and particularly if different macrocycles are involved. For example, depending on the substituent pattern, in progressing from porphyrin to chlorin (and then to bacteriochlorin), the HOMO may change from the $a_{2u}(\pi)$ orbital that has substantial electron density at the central nitrogens (and metal ion once incorporated) to the $a_{1u}(\pi)$-like orbital that has far less electron density or even nodes at these positions. Such a switch would need to be taken into account in assessing relationships between the ease (kinetics and thermodynamics) of metalation versus the MO and redox properties.

## III. CONCLUSIONS AND OUTLOOK

The ability to prepare synthetic metallobacteriochlorins is essential for biomimetic studies pertaining to the roles of bacteriochlorophylls in bacterial photosynthesis and to probe the electronic interplay of peripheral substituents and central metal on photophysical properties. In this regard, the metalation of bacteriochlorins over the years has in some cases proceeded uneventfully and in other cases proved extremely difficult. In general, the reaction course for metalation of tetrapyrrole macrocycles has been interpreted in terms of a variety of parameters, including macrocycle conformation, molecular rigidity (ability to distort from a planar conformation to accommodate the incoming metal ion), nucleophilicity of the nitrogens toward the incoming metal ion, and solvent interactions that entail deprotonation of the pyrrolic NH bonds as well as coordination to the metal ion.[22] Related to the ease of preparing a metal chelate is the stability of the resulting metal chelate toward demetalation. The difficulty of metalation upon moving to hydroporphyrins (porphyrin < chlorin < bacteriochlorin) has been attributed to the diminution of ligand nucleophilicity that accompanies saturation of the pyrrole rings.[22] On the other hand, a careful study by Saga et al. of identically substituted macrocycles revealed that the ease of zinc demetalation decreased along the series porphyrin $\gtrsim$ chlorin $\gg$ bacteriochlorin.[77] In contrast to porphyrins, where the availability of collections of diverse macrocycles in ample quantities have enabled systematic studies of metalation and demetalation chemistry, comparable studies with bacteriochlorins to assess kinetics and thermodynamics have largely remained out of reach.

A de novo route to bacteriochlorins has provided a suite of macrocycles that differ in number and type of substituents. The macrocycles provide the foundation for initiation of systematic studies of metalation methods. While a full matrix defined by metalation conditions, metal types, metal ligands, and bacteriochlorin substrates has not been performed, attempts to metalate the set of synthetic bacteriochlorins examined herein has led to the following observations:

- The difficulty of metalation of tetrapyrrole macrocycles decreases for bacteriochlorins with increasing number of electron-withdrawing groups.
- Metalation of a bacteriochlorin occurs upon treatment with a strong base (e.g., NaH or LDA) in THF followed by $MX_n$: (a) for bacteriochlorins that bear electron-releasing groups, M = Cu, Zn, Pd, and InCl; (b) for bacteriochlorins that bear two carboethoxy (electron-withdrawing) groups, M = Ni, Cu, Zn, Pd, Cd, InCl, and Sn (but not Al or Au); and (c) a bacteriochlorin with four carboethoxy groups was metalated with Mg.
- Bacteriochlorins that bear $\geq$2 carbonyl groups typically can be zincated by standard porphyrin metalation conditions [$Zn(OAc)_2 \cdot 2H_2O$ in DMF at 60−80 °C].

Scheer has suggested that the rate-determining step of bacteriochlorin metalation consists of deprotonation of the pyrrole N−H protons.[23] The use of a very strong base overcomes this limitation, and resembles the method developed by Arnold for preparing early transition metal chelates of porphyrins. The Arnold method entails formation and isolation of the dilithium derivative of the porphyrin as the reactive species for transmetalation upon treatment with a metal reagent.[53,54] Such method has been applied by Stolzenberg with tetra-*p*-tolylbacteriochlorin to prepare the oxotitanyl chelate.[55] The deprotonation of the N−H protons would be facilitated with increasing number of electron-withdrawing groups located on the pyrrole units, as observed here.

In comparing the above results with other types of tetrapyrrole macrocycles, it warrants emphasis that the (up to four) carbonyl groups were located exclusively in the pyrrole (rings A and C) and not in the pyrroline (rings B and D) units of the bacteriochlorins. By contrast, studies of chlorins can incorporate groups in the pyrrole (rings A and C), pyrrolenine (ring B), and pyrroline (ring D) units. In porphyrins, both pyrrole and pyrrolenine groups are present yet facile tautomerization typically precludes localization of a substituent in a particular heterocycle.

The studies reported herein concerning metalation of diverse synthetic bacteriochlorins—an ostensibly simple reaction—provide access to a number of the corresponding metallobacteriochlorins. One area of particular interest is the examination of dyadic (and larger) arrays composed of free base and metallobacteriochlorins. In this regard, a review of all covalently linked arrays that contain one or more bacteriochlorins


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reveals only ~20 dyads prepared to date, and most of the bacteriochlorins incorporated therein have been free base species.[8] Thus, the study of heterometalated arrays, an approach that has been widely used to probe photosynthetic-like mechanisms in synthetic multipigment architectures,[78] has largely resided outside the scope of experimentation for bacteriochlorins (but has been accessible via computational means[79]). The straightforward access described herein should open the door to the study of fundamental properties, tuning NIR spectral properties, and pursuit of a range of photochemical applications of synthetic metallobacteriochlorins.

## IV. EXPERIMENTAL SECTION

**A. General Methods.** $^1$H NMR (400 MHz) spectra and $^{13}$C NMR spectra (100 MHz) were collected at room temperature in $CDCl_3$ unless noted otherwise. Absorption spectra were collected in toluene at room temperature. NaH (60% dispersion in mineral oil) and LDA (2.0 M solution in heptanes/THF/ethylbenzene) were provided by Aldrich. Bacteriochlorins were analyzed by laser desorption mass spectrometry in the absence of a matrix (LD-MS) (e.g., the **BC0-2T** series) or in the presence of the matrix POPOP (MALDI-MS).[80] Silica gel (40 $\mu$m average particle size) was used for column chromatography. All solvents were reagent grade and were used as received unless noted otherwise. THF was freshly distilled from sodium/benzophenone ketyl. Anhydrous MeOH was reagent grade and was used as received. Electrospray ionization mass spectrometry (ESI-MS) and fast atom bombardment mass spectrometry (FAB-MS) data are reported for the molecular ion or protonated molecular ion. The concentration of bases and metal reagents is typically given in mM quantities for clarity although not all material may be dissolved.

**B. Survey of Metalation.** Each reaction was carried out in a conical microreaction vial equipped with a conical stir bar and fitted with a Teflon septum. A bulk solution of the bacteriochlorin was prepared (~6 mg of bacteriochlorin in ~10 mL of THF) and divided without dilution into the microreaction vials. The concentration of the bulk solution was determined by 1000-fold dilution into an absorption cuvette, relying on the known molar absorption coefficient of representative bacteriochlorins (**BC0-2T** has $\lambda_{737\ nm}$ = 130,000 $M^{-1}$ $cm^{-1}$;[16] **BC2-2M-MeO** has $\lambda_{758\ nm}$ = 120,000 $M^{-1}$ $cm^{-1}$) in toluene.

The reaction mixtures were checked by TLC and absorption spectroscopy, the latter again by 1000-fold dilution into an absorption cuvette. The yield was determined spectroscopically assuming equal absorptivity in the $Q_y$ band for both the free base bacteriochlorin and the metallobacteriochlorin. If the metalation was found to go to completion, the reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ solution and extraction with $CH_2Cl_2$ or ethyl acetate. The resulting mixture was concentrated and checked by LD-MS or MALDI-MS. The results are reported in Tables 2, 4, and 5, and in the Supporting Information.

**C. Noncommercial Compounds.** Compounds **1M**,[25] **6**,[16,19] **BC0**,[18] **BC4-MeO**,[18] **BC3-2E**,[24] **BC2-2E**,[18] and **BC0-2T**[16] were prepared as described in the literature.

**D. Purification.** The NaH was received as a 60% dispersion in mineral oil. The reaction could be carried out with the NaH as received, without a prewash with hexanes to remove the mineral oil, in which case the mineral oil would be removed from the metallobacteriochlorin upon column chromatography or crystallization. In general, however, it was preferable to remove the mineral oil from NaH, under argon, by washing with hexanes, prior to treatment with the free base bacteriochlorin.

Typically the crude reaction mixture upon metalation is relatively clean, the dominant impurities consisting of hydrocarbons (e.g., derived from NaH) and any unwanted free base bacteriochlorin. Initially, we attempted purification by flash chromatography on silica gel. During the course of elution, an intense colored band gradually split into multiple colored bands, which reflected the decomposition of the macrocycles. Absorption spectroscopy analysis of each collected band indicated the fastest eluting band was usually the desired metallobacteriochlorin whereas the slower eluting bands consisted of impurities. Chromatography with longer retention times afforded an increase in impurities. A basicified eluant [hexanes/$CH_2Cl_2$ (1:1 to 3:1) containing 1−2% of TEA] and passage over a short column (ca. 10 cm length, 2 cm diameter) diminished the decomposition but at the expense of resolution. The poor resolution impeded removal of hydrocarbons and unreacted free base bacteriochlorin. Attempts to perform purification on alumina columns or the very traditional sugar columns (widely employed for chlorophyll isolation)[81] also gave the same issue of balance between retention time and purity.

Greater success at purification was achieved by forcing the reaction to completion with prolonged reaction time, thereby affording a mixture that contains only a small amount of the free base bacteriochlorin. The crude mixture was then subjected to chromatography on silica gel [hexanes/$CH_2Cl_2$ (1:1) to $CH_2Cl_2$] to remove impurities. At small scale, the chromatography could be performed in a Pasteur pipet. The resulting product was concentrated to dryness. The method of subsequent purification of the resulting solid depended on the solubility of the free base bacteriochlorin and metallobacteriochlorin.

For the **BC4-MeO**, **BC3-2E**, **BC2-2E**, **BC0-2T**, and **BC0** series, free base bacteriochlorins were soluble in hexanes whereas the metallobacteriochlorins derived therefrom were insoluble in hexanes. Accordingly, the crude solid was treated with hexanes, sonicated in a benchtop sonication bath, centrifuged, and the supernatant discarded. Repetition once or twice resulted in a solid product that consisted of the metallobacteriochlorin in pure form.

For the **BC2-2E**, **BC2-2E-MeO**, and **BC2-2M-MeO** series, both free base bacteriochlorins and the metallobacteriochlorins derived therefrom were soluble in hexanes. Accordingly, the crude solid was dissolved in methanol and treated with hexanes. Two intensely colored phases typically form, and can be separated with the aide of illumination to identify the interface. Thus, the hexanes phase (upper layer) was removed as this phase was highly enriched in free base bacteriochlorins yet also contained some metallobacteriochlorin. The methanol phase typically contained the desired metallobacteriochlorin in pure form.

The zinc bacteriochlorins, except those that contain ≥3 electron-withdrawing substituents (**ZnBC4-MeO** and **ZnBC3-2E**) tend to demetalate if exposed to prolonged chromatography on silica gel. In most cases, the workup entailed a short column chromatography or washing the solid metallobacteriochlorin product with hexanes to remove hydrocarbons (derived from NaH) or other impurities. In the case of palladium metalation with LDA, an isopropylamine-like byproduct was always found in the crude mixture by $^1$H NMR spectroscopy; in the case of **BC2-2M-MeO** such impurity could be removed by size-exclusion chromatography.

**E. X-ray Crystallographic Data Collection and Processing.** The samples were mounted on a nylon loop with a small amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 CCD diffractometer at a temperature of 173 K (**BC0** and **CuBC0-2T**) or 110 K (**BC0-2M**). The frame integration was performed using SAINT+.[82] The resulting raw data were scaled and absorption-corrected by multiscan averaging of symmetry equivalent data using SADABS.[83] The data are shown in Table 8.

**F. X-ray Crystallographic Structure Solution and Refinement.** The structures were solved by direct methods using SIR92.[84] All non-hydrogen atoms were obtained from the initial E-map. The hydrogen atom positions were placed at idealized positions and were allowed to ride on the parent carbon atom. The structural model was fit to the data using full matrix least-squares based on $F^2$. The model required 100 restraints to keep the anisotropic displacement parameters from going nonpositive definite. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the XL program from the SHELXTL package,[85] and graphic plots were produced using the version of ORTEP included in the NRCVAX crystallographic program suite.[86]

**G. Optical and Photophysical Characterization.** Static absorption (Varian Cary 100 or Shimadzu UV-1800) and fluorescence (Spex Fluorolog Tau 2 or PTI Quantamaster 40) measurements were performed at room temperature, as were all other studies. The fluorescence quantum yield ($\Phi_f$), singlet excited-state lifetime ($\tau_S$) and triplet yield ($\Phi_T$) measurements utilized dilute ($\mu$M) Ar-purged toluene and methanol


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**Table 8. Summary of Crystal Data for BC0, BC0-2M, and CuBC0-2T**

| | BC0 | BC0-2M | CuBC0-2T |
|---|---|---|---|
| formula | $C_{24}H_{26}N_4$ | $C_{42}H_{46}N_4$ | $C_{38}H_{36}CuN_4$ |
| formula weight (g/mol) | 370.49 | 606.85 | 612.25 |
| crystal dimensions (mm) | 0.12 × 0.10 × 0.02 | 0.30 × 0.26 × 0.10 | 0.20 × 0.16 × 0.10 |
| crystal color and habit | green prism | dark green prism | red plate |
| crystal system | rhombohedral | triclinic | monoclinic |
| space group | $R\bar{3}$ | $P\bar{1}$ | $P2_1/c$ |
| temperature, K | 173 | 110 | 173 |
| $a$, Å | 20.4174(6) | 7.2455(3) | 17.3789(11) |
| $b$, Å | 20.4174 | 10.4695(3) | 35.432(2) |
| $c$, Å | 12.4782(4) | 12.0705(5) | 16.9880(12) |
| $\alpha$, deg | 90.00 | 71.0943(16) | 90.0 |
| $\beta$, deg | 90.00 | 85.586(2) | 90.017(5) |
| $\gamma$, deg | 120.00 | 74.8557(17) | 90.0 |
| $V$, Å$^3$ | 4504.9(2) | 836.12(5) | 10460.8(12) |
| $Z$ | 9 | 1 | 14 |
| $\mu$, (cm$^{-1}$) | 0.074 | 0.07 | 0.765 |
| 2Φmax (deg) | 44.04 | 61.28 | 41.3 |
| no. of reflections measured | 20677 | 31993 | 47168 |
| unique reflections measured | 1237 | 4362 | 10634 |
| $R_1$[a] | 0.1146 | 0.065 | 0.0662 |
| $wR_2$[b] | 0.3003 | 0.056 | 0.1533 |
| $R_1$ (all data)[a] | 0.1434 | 0.067 | 0.1344 |
| $wR_2$ (all data)[b] | 0.3304 | 0.066 | 0.1930 |
| GOF | 0.095 | 1.96 | 1.126 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

solutions. The triplet lifetime ($\tau_T$) measurements utilized Ar-purged 2-methyltetrahydrofuran (2-MeTHF) solutions. Samples for $\Phi_f$ measurements had an absorbance ≤0.1 at the excitation wavelength to minimize front-face effects and similarly low absorbance in the $Q_y(0,0)$ band to minimize inner-filter effects.

Static emission measurements employed 2−4 nm excitation- and detection-monochromator bandwidths and 0.2-nm data intervals. Emission spectra were corrected for detection-system spectral response. Fluorescence quantum yields were determined relative to several different standards. These standards are (i) chlorophyll *a* in deoxygenated toluene ($\Phi_f = 0.325$),[87] which is the value measured in benzene;[88] (ii) free base *meso*-tetraphenylporphyrin (**FbTPP**) in nondegassed toluene, for which $\Phi_f = 0.070$ was established with respect to the zinc chelate **ZnTPP** in nondegassed toluene ($\Phi_f = 0.030$),[89] consistent with prior results on **FbTPP**;[90] and (iii) 8,8,18,18-tetramethylbacteriochlorin[91] in Ar-purged toluene, for which $\Phi_f = 0.14$ was established with respect to chlorophyll *a* in benzene and **FbTPP** in toluene.

Fluorescence lifetimes were obtained using time-correlated-single-photon-counting detection on an apparatus with an approximately Gaussian instrument response function with a full-width-at-half-maximum of ∼1 ns (Photon Technology International LaserStrobe TM-3). Samples were excited in the Soret or Q regions using excitation pulses at 337 nm from a nitrogen laser or in the blue to green spectral regions from a dye laser pumped by the nitrogen laser.

The $\Phi_{isc}$ values (triplet yields) were obtained using transient absorption spectroscopy. The extent of bleaching of the ground-state $Q_x$ bands due to the formation of the lowest singlet excited state was measured immediately following a 130 fs flash in the $Q_y(0,0)$ band and compared with that due to the formation of the lowest triplet excited state at the asymptote of the singlet excited-state decay.[20,92]

**H. Electrochemistry.** The electrochemical studies were performed in butyronitrile (Burdick and Jackson) using previously described instrumentation.[93] The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich; recrystallized three times from methanol and dried at 110 °C in vacuo). The electrochemical cell was housed in a Vacuum Atmospheres glovebox (Model HE-93) equipped with a Dri-Train (Model 493). The $E_{1/2}$ values were obtained with square wave voltammetry (frequency 10 Hz) under conditions where the ferrocene couple has a potential of +0.19 V.

**I. Density Functional Theory Calculations.** Calculations were performed with Spartan '08 for Windows version 1.2.0 in parallel mode[94] on a PC equipped with an Intel i7-975 CPU, 24 Gb ram, and three 300 Gb, 10k rpm hard drives. The calculations employed the hybrid B3LYP functional and 6-31G* basis set. The equilibrium geometries were fully optimized using the default parameters of the Spartan program.

**J. Synthesis Procedures.** *3-(Ethoxycarbonyl)-4-heptylpyrrole (**2H**).* Following the van Leusen method,[26] a solution of $\alpha,\beta$-unsaturated ester **1H** (12.3 g, 58.0 mmol) and TosMIC (12.6 g, 64.5 mmol) in diethyl ether/DMSO (300 mL, 2:1) was slowly added via an addition funnel to a suspension of NaH (5.0 g, 60% in oil suspension, 0.12 mol) in 100 mL of diethyl ether. The resulting exotherm caused the mixture to reflux. The reaction mixture was stirred at room temperature for 16 h. Water was added carefully, and the mixture was extracted with diethyl ether. The organic layer was concentrated and dried ($Na_2SO_4$). Column chromatography (silica, $CH_2Cl_2$) afforded a light yellow solid (8.3 g, 55%): mp 54−56 °C; $^1$H NMR (300 MHz) $\delta$ 0.88 (t, $J$ = 6.6 Hz, 3H), 1.26−1.35 (m, 9H), 1.33 (t, $J$ = 7.2 Hz, 2H), 1.58 (m, 2H), 2.71 (t, $J$ = 7.2 Hz, 2H), 4.27 (q, $J$ = 7.2 Hz, 2H), 6.52 (m, 1H), 7.37 (m, 1H), 8.78 (brs, 1H); $^{13}$C NMR (75 MHz) $\delta$ 14.1, 14.5, 22.7, 26.3, 29.3, 29.7, 30.6, 32.0, 59.4, 114.1, 116.8, 124.6, 126.4, 165.8; ESI-MS obsd 260.1614, calcd 260.1621 [(M + Na)$^+$, M = $C_{14}H_{23}NO_2$]; Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.90; H, 9.81; N, 5.48.

*4-(Ethoxycarbonyl)-2-formyl-3-heptylpyrrole (**3H**).* Following a general procedure,[27] the Vilsmeier reagent was prepared by treatment of dry DMF (30 mL) with $POCl_3$ (4.6 mL, 49 mmol) at 0 °C and stirring of the resulting mixture for 10 min. In a separate flask, a solution of **2H** (10.7 g, 45.1 mmol) in DMF (150 mL) was treated with the freshly prepared Vilsmeier reagent at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and then 2 h at room temperature. The reaction mixture was treated with a mixture of saturated aqueous sodium acetate/$CH_2Cl_2$ [400 mL, 1:1 (v/v)] and stirred for 1 h. The water phase was separated and extracted with $CH_2Cl_2$. The combined organic phase was washed with saturated NaCl, dried ($Na_2SO_4$), and concentrated. Column chromatography (silica, $CH_2Cl_2$) afforded a light brown solid (6.7 g, 56%): mp 45−47 °C; $^1$H NMR (300 MHz) $\delta$ 0.88 (t, $J$ = 6.4 Hz, 3H), 1.27−1.37 (m, 9H), 1.36 (t, $J$ = 7.2 Hz, 2H), 1.66 (m, 2H), 3.04 (t, $J$ = 7.2 Hz, 2H), 4.31 (q, $J$ = 7.6 Hz, 2H), 7.63 (m, 1H), 9.60 (brs, 1H), 9.69 (s, 1H); $^{13}$C NMR $\delta$ 14.1, 14.4, 22.7, 24.3, 29.2, 29.6, 31.9, 32.3, 60.0, 116.5, 130.4, 131.5, 140.1, 164.1, 178.8; ESI-MS obsd 266.1746, calcd 266.1751 [(M + H)$^+$, M = $C_{15}H_{23}NO_3$]; Anal. Calcd for $C_{15}H_{23}NO_3$: C, 67.90; H, 8.74; N, 5.28. Found: C, 67.86; H, 8.76; N, 5.17.

*4-(Ethoxycarbonyl)-3-heptyl-2-(2-nitroethyl)pyrrole (**5H**).* Following a general procedure,[17] a stirred mixture of **3H** (5.8 g, 22 mmol), potassium acetate (1.7 g, 18 mmol), and methylamine hydrochloride (1.2 g, 18 mmol) in absolute ethanol (8 mL) was treated with nitromethane (3.0 mL, 55 mmol). The mixture was stirred for 2 h, whereupon water was added. The reaction mixture was filtered, and the filtered material was washed with water and a small amount of cold ethanol. The filtered material was dried under high vacuum to afford a yellow solid, which was used directly in the next step. The crude solid material was dissolved in $CHCl_3$/2-propanol (3:1, 250 mL). Silica (24 g) and $NaBH_4$ (1.5 g, 40 mmol) were added,[29] and the mixture was stirred at room temperature under argon for 2 h. The reaction mixture was filtered, and the filtrate was concentrated. The resulting crude solid was dissolved in $CH_2Cl_2$. The organic solution was washed (water, brine), dried ($Na_2SO_4$), and concentrated to afford a pale brown solid (3.0 g, 44%): mp 93−95 °C; $^1$H NMR (300 MHz) $\delta$ 0.88 (t, $J$ = 6.4 Hz, 3H), 1.28−1.35 (m, 9H), 1.33 (t, $J$ = 7.2 Hz, 2H), 1.49 (m, 2H), 2.63 (t, $J$ = 7.8 Hz, 2H), 3.25 (t, $J$ = 6.3 Hz, 2H), 4.27 (q, $J$ = 7.2 Hz, 2H), 4.54 (t, $J$ = 6.3 Hz, 2H), 7.31 (d, $J$ = 3.0 Hz, 1H), 8.39 (brs, 1H); $^{13}$C NMR $\delta$ 14.2, 14.5, 22.8, 23.4, 25.0, 29.4, 30.0, 31.9, 32.1, 59.6, 75.3, 114.8, 123.5, 123.7, 124.2, 165.5; ESI-MS obsd 311.1951, calcd 311.1965 [(M + H)$^+$,


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M = $C_{16}H_{26}N_2O_4$]; Anal. Calcd for $C_{16}H_{26}N_2O_4$: C, 61.91; H, 8.44; N, 9.03. Found: C, 62.52; H, 8.48; N, 8.81.

*6-(4-(Ethoxycarbonyl)-3-heptylpyrrol-2-yl)-1,1-dimethoxy-4,4-dimethyl-5-nitrohexan-2-one (**7H**).* Following a general procedure,[30] a mixture of **5H** (2.8 g, 9.0 mmol) and **6** (4.2 g, 27 mmol, 3 equiv) was treated with DBU (4.2 mL, 27 mmol). The reaction mixture was stirred under argon at room temperature for 16 h. A saturated solution of cold aqueous $NH_4Cl$ was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine, dried ($Na_2SO_4$), and concentrated. Column chromatography [silica, $CH_2Cl_2$/ethyl acetate (9:1)] afforded a pale brown solid (2.5 g, 59%): mp 78−82 °C; $^1$H NMR (300 MHz) $\delta$ 0.88 (t, $J$ = 6.8 Hz, 3H), 1.15 (s, 3H), 1.25 (s, 3H), 1.28−1.33 (m, 9H), 1.32 (t, $J$ = 7.2 Hz, 2H), 1.51 (m, 2H), 2.61 (m, 2H), 2.60, 2.75 (AB, $J$ = 18.7 Hz, 2H), 3.00 (ABX, $^3J$ = 2.3 Hz, $^2J$ = 15.5 Hz, 1H), 3.27 (ABX, $^3J$ = 11.7 Hz, $^2J$ = 15.5 Hz, 1H), 3.43 (s, 3H), 3.44 (s, 3H), 4.25 (q, $J$ = 7.2 Hz, 2H), 4.36 (s, 1H), 5.11 (ABX, $^3J$ = 2.3 Hz, $^3J$ = 11.7 Hz, 1H), 7.26 (d, $J$ = 8.8 Hz, 1H), 8.46 (brs, 1H); $^{13}$C NMR (75 MHz) $\delta$ 14.2, 14.5, 22.8, 24.2, 24.3, 24.6, 25.0, 29.4, 30.0, 31.8, 32.1, 36.6, 45.0, 55.3, 59.4, 94.7, 104.9, 114.7, 123.5, 123.7, 124.1, 165.2, 203.7; ESI-MS obsd 469.2893, calcd 469.2908 [(M + H)$^+$, M = $C_{24}H_{40}N_2O_7$]; Anal. Calcd for $C_{24}H_{40}N_2O_7$: C, 61.52; H, 8.60; N, 5.98. Found: C, 61.84; H, 8.68; N, 5.82.

*8-(Ethoxycarbonyl)-2,3-dihydro-1-(1,1-dimethoxymethyl)-7-heptyl-3,3-dimethyldipyrrin (**8H**).* Following a general procedure,[17] in a first flask a solution of **7H** (2.2 g, 4.7 mmol) in freshly distilled THF (13 mL) at 0 °C was treated with NaOMe (7.6 g, 24 mmol). The mixture was stirred and degassed by bubbling argon through the solution for 45 min. In a second flask purged with argon, $TiCl_3$ (20 mL, 20 wt % in 3% HCl solution, 34 mmol), THF (70 mL), and $NH_4OAc$ (20.0 g, 261 mmol) were combined under argon, and the mixture was degassed by bubbling with argon for 45 min. Then, the first flask mixture was transferred via cannula to the buffered $TiCl_3$ mixture. The resulting mixture was stirred under argon at room temperature for 16 h. The mixture was extracted with ethyl acetate. The organic extract was washed (saturated aqueous $NaHCO_3$), dried ($Na_2SO_4$) and concentrated. Column chromatography (silica, $CH_2Cl_2$) afforded a yellow oil (1.0 g, 51%): $^1$H NMR (300 MHz) $\delta$ 0.87 (t, $J$ = 6.4 Hz, 3H), 1.23 (s, 6H), 1.23−1.36 (m, 11H), 1.50−1.58 (m, 2H), 2.63 (s, 2H), 2.77 (q, $J$ = 7.2 Hz, 2H), 3.44 (s, 6H), 4.25 (q, $J$ = 7.2 Hz, 2H), 5.03 (s, 1H), 5.86 (s, 1H), 7.42 (d, $J$ = 3.0 Hz, 1H), 10.84 (brs, 1H); $^{13}$C NMR $\delta$ 14.1, 14.4, 22.6, 24.6, 29.14, 29.20, 29.5, 31.7, 31.9, 40.2, 48.2, 54.5, 59.1, 102.5, 104.6, 114.2, 124.6, 125.2, 128.6, 159.8, 165.4, 174.6; ESI-MS obsd 419.2884, calcd 419.2904 [(M + H)$^+$, M = $C_{24}H_{38}N_2O_4$].

*3-(Ethoxycarbonyl)-4-mesitylpyrrole (**2M**).* Following the van Leusen method,[26] a suspension of TosMIC (12.0 g, 61.5 mmol) and the known $\alpha,\beta$-unsaturated ester **1M**[25] (12.8 g, 58.6 mmol) in anhydrous $Et_2O$/DMSO (2:1) (281 mL) was added dropwise under argon into a stirred suspension of NaH (3.07 g, 60% dispersion in mineral oil, 76.8 mmol) in anhydrous THF (118 mL). After stirring for 2.5 h, water (260 mL) was carefully added. The mixture was extracted with diethyl ether and $CH_2Cl_2$. The combined extract was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated to afford a yellow oil. Chromatography [silica, ethyl acetate/hexanes (1:9 → 1:3)] gave a white solid (9.13 g, 60%): mp 164−165 °C; $^1$H NMR (300 MHz) $\delta$ 1.08 (t, $J$ = 7.2 Hz, 3H), 2.03 (s, 6H), 2.30 (s, 3H), 4.07 (q, $J$ = 7.2 Hz, 2H), 6.54−6.56 (m, 1H), 6.89 (s, 2H), 7.53−7.55 (m, 1H), 8.47 (br, 1H); $^{13}$C NMR (75 MHz) $\delta$ 14.3, 21.0, 21.3, 59.5, 117.9, 124.6, 127.7, 129.7, 130.6, 132.3, 136.3, 137.7, 165.2; FAB-MS obsd 257.1414, calcd 257.1416 ($C_{16}H_{19}NO_2$).

*4-(Ethoxycarbonyl)-2-formyl-3-mesitylpyrrole (**3M**).* Following a general procedure,[27] a solution of **2M** (19.8 g, 77.0 mmol) in DMF (24.6 mL) and $CH_2Cl_2$ (400 mL) at 0 °C under argon was treated dropwise with freshly distilled $POCl_3$ (8.50 mL, 92.7 mmol). After 1 h, the ice bath was removed. The flask was allowed to warm to room temperature with stirring for 18 h. The reaction mixture was cooled to 0 °C, whereupon 2.5 M aqueous NaOH (350 mL) was added. The mixture was extracted with $CH_2Cl_2$. The organic phase was washed [10% (w/w) aqueous acetic acid and saturated brine], dried ($Na_2SO_4$), and concentrated. The residue was triturated with hexanes and filtered to afford a pale yellow solid (11.2 g, 56%): mp 214−216 °C; $^1$H NMR $\delta$ 1.06 (t, $J$ = 7.2 Hz, 3H), 2.00 (s, 6H), 2.30 (s, 3H), 4.14 (q, $J$ = 7.2 Hz, 2H), 6.84−6.86 (m, 1H), 6.91 (s, 2H), 9.64−9.92 (br, 1H), 10.25 (s, 1H); $^{13}$C NMR $\delta$ 13.7, 20.7, 21.0, 60.3, 121.2, 123.8, 127.6, 130.4, 133.4, 136.8, 137.1, 163.5, 182.2; ESI-MS obsd 286.1439, calcd 286.1438 [(M + H)$^+$, M = $C_{17}H_{19}NO_3$].

*4-(Ethoxycarbonyl)-3-mesityl-2-(2-nitrovinyl)pyrrole (**4M**).* Following a general procedure,[28] a stirred solution of acetic acid (0.69 mL, 13 mmol) in methanol (1.75 mL) under argon at 0 °C was treated dropwise with *n*-propylamine (0.95 mL, 12 mmol). The resulting *n*-propylammonium acetate solution was stirred at 0 °C for 5 min, then added dropwise to a stirred solution of **3M** (5.90 g, 20.7 mmol) in nitromethane (3.38 mL, 90.0 mmol) and freshly distilled THF (20 mL) at 0 °C. The resulting mixture was stirred at 0 °C. After 15 min, the cooling bath was removed, and stirring was continued at room temperature. The color changed from yellow to dark red during the course of reaction. After 3 h, $CH_2Cl_2$ (100 mL) was added, and the organic phase was washed with water and brine. The organic layer was dried ($Na_2SO_4$) and concentrated to afford a dark viscous mixture. Filtration through a silica pad (ethyl acetate) afforded a dark brown solid (5.44 g, 80%): mp 68−70 °C; $^1$H NMR $\delta$ 1.03 (t, $J$ = 7.2 Hz, 3H), 2.01 (s, 6H), 2.30 (s, 3H), 4.11 (q, $J$ = 7.2 Hz, 2H), 6.81 (d, $J$ = 2.8 Hz, 1H), 6.89 (s, 2H), 7.56 (d, $J$ = 14.0 Hz, 1H), 8.71 (d, $J$ = 14.0 Hz, 1H), 8.91−9.07 (br, 1H); $^{13}$C NMR $\delta$ 13.4, 20.7, 21.0, 60.5, 120.1, 123.2, 126.4, 127.6, 128.2, 128.4, 130.8, 134.2, 136.8, 136.9, 164.1; ESI-MS obsd 329.1501, calcd 329.1501 [(M + H)$^+$, M = $C_{18}H_{20}N_2O_4$].

*4-(Ethoxycarbonyl)-3-mesityl-2-(2-nitroethyl)pyrrole (**5M**).* Following a general procedure,[29] a solution of **4M** (5.42 g, 16.5 mmol) in $CHCl_3$ (150 mL) and isopropanol (50 mL) was treated with silica (19.8 g). The resulting suspension was treated in one portion with $NaBH_4$ (1.25 g, 33.0 mmol) under vigorous stirring. After 20 min, a further portion of $NaBH_4$ (355 mg, 9.38 mmol) was added in one batch. After 20 min, TLC analysis showed complete consumption of the vinylpyrrole. The mixture was filtered, and the filter cake was washed with $CH_2Cl_2$. The filtrate was concentrated, and the resulting dark oil was filtered through a bed of silica (hexanes/ethyl acetate, 3:1) to afford a brown solid (3.48 g, 64%): mp 108−110 °C; $^1$H NMR $\delta$ 0.91 (t, $J$ = 7.2 Hz, 3H), 1.99 (s, 6H), 2.29 (s, 3H), 3.63 (t, $J$ = 6.1 Hz, 2H), 3.98 (q, $J$ = 7.2 Hz, 2H), 4.77 (t, $J$ = 6.1 Hz, 2H), 6.42 (d, $J$ = 2.5 Hz, 1H), 6.86 (s, 2H), 8.52 (br, 1H); $^{13}$C NMR $\delta$ 13.6, 20.7, 21.0, 25.8, 59.2, 74.7, 111.5, 116.0, 124.7, 127.3, 132.4, 133.2, 136.0, 137.2, 165.2; ESI-MS obsd 331.1651, calcd 331.1652 [(M + H)$^+$, M = $C_{18}H_{22}N_2O_4$].

*6-[4-(Ethoxycarbonyl)-3-mesitylpyrrol-2-yl]-1,1-dimethoxy-4,4-dimethyl-5-nitro-2-hexanone (**7M**).* Following a general procedure,[30] a mixture of **5M** (3.48 g, 10.5 mmol) and **6** (4.99 g, 31.3 mmol) was treated with DBU (4.49 mL, 30.0 mmol). $CH_2Cl_2$ (5 mL) was added to the reaction mixture to dissolve completely the nitroethylpyrrole compound **5M**. The reaction mixture was stirred at room temperature for 7 h, diluted with ethyl acetate (100 mL), and washed with aqueous $NH_4Cl$ solution and brine. The organic layer was dried ($Na_2SO_4$) and concentrated. The resulting oil was chromatographed [silica, ethyl acetate/hexanes (1:2)] to afford a brown solid (1.37 g, 27%): mp 131−134 °C; $^1$H NMR $\delta$ 0.90 (t, $J$ = 7.2 Hz, 3H), 1.22 (s, 3H), 1.33 (s, 3H), 1.94 (s, 3H), 1.99 (s, 3H), 2.28 (s, 3H), 2.67, 2.76 (AB, $^2J$ = 18.6 Hz, 2H), 3.34 (ABX, $^3J$ = 11.8 Hz, $^2J$ = 14.6 Hz, 1H), 3.83 (ABX, $^3J$ = 2.5 Hz, $^2J$ = 14.6 Hz, 1H), 3.42 (s, 3H), 3.43 (s, 3H), 3.94−4.07 (m, 2H), 4.41 (s, 1H), 5.22 (ABX, $^3J$ = 2.5 Hz, $^3J$ = 11.8 Hz, 1H), 6.36 (d, $J$ = 2.5 Hz, 1H), 6.85 (s, 2H), 8.23−8.30 (br, 1H); $^{13}$C NMR $\delta$ 13.9, 20.7, 20.9, 21.2, 23.8, 24.2, 27.1, 36.7, 44.7, 55.1, 59.2, 95.2, 104.6, 111.8, 116.2, 124.8, 127.27, 127.39, 132.8, 133.2, 136.0, 137.3, 137.6, 165.2, 203.3; ESI-MS obsd 489.2591, calcd 489.2595 [(M + H)$^+$, M = $C_{26}H_{36}N_2O_7$].

*8-(Ethoxycarbonyl)-1-(1,1-dimethoxymethyl)-3,3-dimethyl-7-mesityl-2,3-dihydrodipyrrin (**8M**).* Following a general procedure,[17] a solution of **7M** (1.37 g, 2.81 mmol) in anhydrous THF (12.0 mL) under argon was treated with NaOMe (0.45 g, 8.3 mmol). The reaction mixture was bubbled with argon for 15 min and then stirred for 1 h at room temperature (first flask). In a second flask, $TiCl_3$ [8.6 wt % $TiCl_3$ in 28 wt % HCl, 13.3 mL, 9.7 mmol] and THF (27 mL) were combined. The mixture was bubbled with argon for 30 min. Then, $NH_4OAc$ (11.2 g, 145 mmol) was slowly added under argon bubbling to buffer the mixture to pH 6.0 (pH paper). The mixture in the first flask containing


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the nitronate anion of **7M** was transferred via a cannula to the buffered $TiCl_3$ mixture in the second flask. The resulting mixture was stirred overnight at room temperature. Then the mixture was poured into a vigorously stirred solution of saturated aqueous $NaHCO_3$ (300 mL). After 10 min, the mixture was extracted with ethyl acetate. The organic layers were combined, washed with water, dried ($Na_2SO_4$), and concentrated. Filtration through a alumina pad (alumina, hexanes/ethyl acetate, 3:1) afforded a dark brown solid (0.60 g, 49%): mp 148−150 °C; $^1$H NMR $\delta$ 0.93 (t, $J$ = 7.2 Hz, 3H), 1.28 (s, 6H), 2.04 (s, 6H), 2.30 (s, 3H), 2.67 (s, 2H), 3.47 (s, 6H), 4.01 (q, $J$ = 7.2 Hz, 2H), 5.05 (s, 1H), 6.56 (d, $J$ = 2.5 Hz, 1H), 6.87 (s, 2H), 6.97 (s, 1H), 11.18−11.31 (br, 1H); $^{13}$C NMR $\delta$ 13.8, 20.9, 21.1, 29.1, 40.7, 48.4, 54.7, 59.0, 102.6, 106.3, 111.5, 117.8, 124.4, 127.3, 133.3, 135.5, 135.8, 137.4, 163.4, 165.6, 176.8; Anal. Calcd for $C_{26}H_{34}N_2O_4$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.46; H, 7.98; N, 6.31.

*3,13-Bis(ethoxycarbonyl)-2,12-diheptyl-8,8,18,18-tetramethylbacteriochlorin (**BC2-2H**).* Following a general procedure,[18] a solution of **8H** (340 mg, 0.81 mmol, 18 mM) in anhydrous $CH_3CN$ (45 mL) was treated with $BF_3{\cdot}O(Et)_2$ (0.80 mL, 6.5 mmol, 140 mM). The reaction mixture was stirred at room temperature for 16 h. Excess TEA (1.2 mL) was added to the reaction mixture. The reaction mixture was concentrated, and the residue was chromatographed (silica, $CH_2Cl_2$). A single purple band was isolated and concentrated to afford the title compound as a purple solid (70 mg, 24%): $^1$H NMR $\delta$ −1.41 (brs, 2H), 0.89−0.92 (m, 6H), 1.31−1.71 (m, 22H), 1.94 (s, 12H), 2.09−2.18 (m, 4H), 4.10 (t, $J$ = 7.8 Hz, 4H), 4.42 (s, 4H), 4.78 (q, $J$ = 7.2 Hz, 4H), 8.64 (s, 2H), 9.66 (s, 2H); $^{13}$C NMR $\delta$ 14.3, 14.8, 22.9, 27.5, 29.5, 30.4, 31.1, 32.1, 33.4, 46.0, 52.0, 60.9, 94.8, 98.7, 119.4, 134.0, 135.1, 140.5, 160.6, 166.7, 171.1; $\lambda_{abs}$ (toluene) 353, 383, 520, 761 nm; $\lambda_{em}$ ($\lambda_{exc}$ 522 nm) 768 nm; MALDI-MS obsd 710.5; ESI-MS obsd 711.4830, calcd 711.4844 [$(M + H)^+$, M = $C_{44}H_{62}N_4O_4$].

*3,13-Bis(ethoxycarbonyl)-2,12-diheptyl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**BC2-2H-MeO**).* Following a general procedure,[18] a solution of **8H** (430 mg, 1.1 mmol, 18 mM) in anhydrous $CH_2Cl_2$ (60 mL) was treated first with 2,6-DTBP (4.70 mL, 21.2 mmol, 360 mM) and second with TMSOTf (0.956 mL, 5.30 mmol, 90 mM). The reaction mixture was stirred at room temperature for 16 h. The reaction mixture was concentrated, and the residue was chromatographed (silica, $CH_2Cl_2$). The second green band was isolated and concentrated to afford the title compound as a purple solid (160 mg, 44%): $^1$H NMR $\delta$ −1.84 (brs, 1H), −1.56 (brs, 1H), 0.87−0.89 (m, 6H) 1.31−1.71 (m, 22H), 1.94 (d, $J$ = 4.0 Hz, 12H), 2.15 (m, 4H), 3.78 (t, $J$ = 7.6 Hz, 2H), 4.12 (t, $J$ = 7.6 Hz, 2H), 4.22 (s, 3H), 4.36 (s, 2H), 4.40 (s, 2H), 4.78 (q, $J$ = 6.8 Hz, 4H), 8.53 (s, 1H), 8.65 (s, 1H), 9.60 (s, 1H); $^{13}$C NMR $\delta$ 14.10, 14.11, 14.59, 14.68, 22.68, 22.70, 26.6, 27.3, 29.23, 29.37, 29.9, 30.2, 30.9, 31.1, 31.81, 31.91, 32.8, 33.3, 45.6, 45.9, 47.9, 51.7, 60.7, 61.7, 64.3, 93.8, 95.5, 97.6, 118.5, 124.6, 127.9, 132.5, 134.31, 134.36, 134.9, 135.2, 140.3, 155.7, 160.5, 166.6, 167.9, 168.9,171.3; $\lambda_{abs}$ (toluene) 358, 379, 522, 740 nm; $\lambda_{em}$ ($\lambda_{exc}$ 521 nm) 744 nm; MALDI-MS obsd 740.1; ESI-MS obsd 741.4938, calcd 741.4949 [$(M + H)^+$, M = $C_{45}H_{64}N_4O_5$].

*3,13-Bis(ethoxycarbonyl)-2,12-dimesityl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**BC2-2M-MeO**).* Following a general procedure,[18] a solution of **8M** (600 mg, 1.24 mmol) in anhydrous $CH_2Cl_2$ (69 mL) was treated first with 2,6-di-*tert*-butylpyridine (4.75 mL, 24.8 mmol) and second with TMSOTf (1.21 mL, 6.21 mmol). The resulting mixture was stirred at room temperature for 19 h. The reaction mixture was concentrated and chromatographed (silica, $CH_2Cl_2$/ethyl acetate, 1:1) to afford a pink greenish solid (290 mg, 60%): $^1$H NMR $\delta$ −1.15 (brs, 1H), −0.90 (brs, 1H), 1.19 (t, $J$ = 7.2 Hz, 3H), 1.25 (t, $J$ = 7.2 Hz, 3H), 1.92 (s, 6H), 1.93 (s, 6H), 2.00 (s, 6H), 2.08 (s, 6H), 2.48 (s, 3H), 2.53 (s, 3H), 3.63 (s, 3H), 4.19 (s, 2H), 4.26 (s, 2H), 4.42 (q, $J$ = 7.2 Hz, 2H), 4.47 (q, $J$ = 7.2 Hz, 2H), 7.72 (s, 2H), 7.78 (s, 2H), 8.12 (s, 1H), 9.61 (s, 1H), 9.63 (s, 1H); $^{13}$C NMR $\delta$ 13.8, 13.9, 21.0, 21.24, 21.34, 21.38, 29.1, 30.9, 31.1, 45.8, 47.4, 51.4, 60.43, 60.49, 62.7, 96.9, 97.3, 97.5, 120.4, 121.5, 127.43, 127.8, 132.1, 134.2, 134.74, 134.80, 135.1, 135.8, 136.2, 136.7, 137.34, 137.47, 137.56, 139.5, 155.7, 162.0, 165.6, 166.2, 171.7; $\lambda_{abs}$ (toluene) 361, 382, 538, 758 nm ($\lambda_{758\ nm}$ = 120,000 $M^{-1}$ $cm^{-1}$); $\lambda_{em}$ ($\lambda_{exc}$ 538 nm) 763 nm; ESI-MS obsd 781.4322, calcd 781.4323 [$(M + H)^+$, M = $C_{49}H_{56}N_4O_5$].

*3,13-Bis(ethoxycarbonyl)-2,12-dimesityl-8,8,18,18-tetramethylbacteriochlorin (**BC2-2M**).* Following Procedure A (see next section), a solution of **BC2-2M-MeO** (7.8 mg, 10 $\mu$mol, 4 mM) in freshly distilled THF (2.5 mL) under argon was treated with NaH (60 mg, 1.5 mmol, 60% dispersion in mineral oil) at room temperature for 30 min. $PdBr_2$ (80 mg, 0.30 mmol) was then added to the mixture, and the flask was heated at 60 °C for 2 h. The reaction was monitored by absorption spectroscopy and TLC [silica, hexanes/ethyl acetate (3:1)]. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated and chromatographed [alumina, hexanes/$CH_2Cl_2$ (2:1) with 1% TEA] to yield a pink solid (2.2 mg, 29%): $^1$H NMR (300 MHz) $\delta$ −1.22 (brs, 2H), 1.25 (t, $J$ = 7.2 Hz, 6H), 1.95 (s, 12H), 1.99 (s, 12H), 2.54 (s, 6H), 4.25 (s, 4H), 4.46 (q, $J$ = 7.2 Hz, 4H), 7.18 (s, 4H), 8.26 (s, 2H), 9.68 (s, 2H); $\lambda_{abs}$ (toluene) 357, 383, 524, 765 nm; $\lambda_{em}$ ($\lambda_{exc}$ 524 nm) 770 nm; MALDI-MS obsd 750.9; ESI-MS obsd 751.4218 calcd 751.4206 [$(M + H)^+$, M = $C_{48}H_{54}N_4O_4$].

**K. Metalation of Bacteriochorins.** *Procedure A (NaH/THF). Zn(II)-8,8,18,18-Tetramethyl-2,12-di-p-tolylbacteriochlorin (**ZnBC0-2T**).* A solution of **BC0-2T** (16.5 mg, 30.0 $\mu$mol, 4 mM) in THF (7.5 mL) under argon was treated with NaH (180 mg, 4.50 mmol) at room temperature for 1 h. The color of the resulting heterogeneous reaction mixture changed from light green to red. Then $Zn(OTf)_2$ (327 mg, 0.900 mmol) was added to the mixture, and the flask was heated to 60 °C for 12 h under argon. TLC analysis [silica, hexanes/$CH_2Cl_2$ (1:1)] showed the disappearance of **BC0-2T** and the presence of only one spot. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated, and the residue was chromatographed on a short column [silica, hexanes/$CH_2Cl_2$/TEA (49:49:2), v/v/v] to afford a black-red solid (16.2 mg). The crude solid was treated with hexanes, sonicated in a benchtop sonication bath, centrifuged, and the supernatant discarded (as this consisted of unreacted **BC0-2T** and hydrocarbon impurities). Repetition twice afforded a black-red powder (12.1 mg, 66%): $^1$H NMR (THF-$d_8$) $\delta$ 1.93 (s, 12H), 2.55 (s, 6H), 4.45 (s, 4H), 7.51 (d, $J$ = 8.0 Hz, 4H), 8.06 (d, $J$ = 8.0 Hz, 4H), 8.62 (s, 2H), 8.63 (s, 2H), 8.76 (s, 2H); $\lambda_{abs}$ (toluene) 344, 385, 523, 750 nm; $\lambda_{em}$ ($\lambda_{exc}$ 523 nm) 760 nm; LD-MS obsd 612.3; FAB-MS obsd 612.2233, calcd 612.2231 ($C_{38}H_{36}N_4Zn$).

**Procedure B (LDA/THF).** *Zn(II)-8,8,18,18-Tetramethyl-2,12-di-p-tolylbacteriochlorin (**ZnBC0-2T**).* A solution of **BC0-2T** (11.0 mg, 20.0 $\mu$mol, 4 mM) in THF (5 mL) under argon was treated with a 2.0 M LDA solution (100 $\mu$L, 200 $\mu$mol) at room temperature for 5 min. The color of the resulting homogeneous reaction mixture rapidly changed from light green to red. Then $Zn(OTf)_2$ (14.1 mg, 40.0 $\mu$mol) was added to the mixture, and the flask was heated to 60 °C for 2−3 h under argon. TLC analysis [silica, hexanes/$CH_2Cl_2$ (1:1)] showed the disappearance of **BC0-2T** and the presence of only one spot, and the absorption spectrum did not show the $Q_x$ band of **BC0-2T**. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated. The resulting solid was treated with hexanes, sonicated in a benchtop sonication bath, centrifuged, and the supernatant discarded (as this consisted of unreacted **BC0-2T** and hydrocarbon impurities). Repetition twice afforded a black-red solid (9.7 mg, 79%) with satisfactory characterization data ($^1$H NMR spectroscopy, absorption spectroscopy, LD-MS and FAB-MS).

**Procedure C ($Zn(OAc)_2{\cdot}2H_2O$/DMF).** *Zn(II)-2,3,12,13-Tetrakis-(ethoxycarbonyl)-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**ZnBC4-MeO**).* A solution of **BC4-MeO** (5.4 mg, 7.8 $\mu$mol, 4 mM) in DMF (2 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (52 mg, 240 $\mu$mol, 30 equiv). The reaction mixture was heated to 60 °C for 16 h and then 80 °C for 3 h. TLC analysis [silica, hexanes/$CH_2Cl_2$ (1:1)] showed the disappearance of **BC4-MeO** and the presence of only one spot. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated. The crude solid was treated with hexanes, sonicated in a benchtop sonication bath, centrifuged, and the supernatant discarded. Repetition twice afforded a dark blue solid (5.7 mg, 97%): $^1$H NMR (300 MHz, THF-$d_8$) $\delta$ 1.51−1.61 (m, 12H), 1.92


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(s, 6H + 6H), 4.13 (s, 3H), 4.33 (s, 2H + 2H), 4.55−4.68 (m, 8H), 8.92 (s, 1H), 9.12 (s, 1H), 9.64 (s, 1H); $\lambda_{abs}$ (toluene) 354, 384, 582, 774 nm; $\lambda_{em}$ ($\lambda_{exc}$ 582 nm) 781 nm; MALDI-MS obsd 750.9; ESI-MS obsd 773.2121, calcd 773.2135 [$(M + Na)^+$, M = $C_{37}H_{42}N_4O_9Zn$].

*Mg(II)-2,3,12,13-Tetrakis(ethoxycarbonyl)-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**MgBC4-MeO**).* Following a modification of Procedure A, a solution of **BC4-MeO** (5.0 mg, 7.3 $\mu$mol, 4 mM) in freshly distilled THF (1.8 mL) was treated with NaH (52 mg, 2.1 mmol, 60% dispersion in mineral oil washed beforehand with hexanes) and $MgI_2$ (60 mg, 0.21 mmol). The reaction mixture was heated at 60 °C for 3 h under argon. The reaction was monitored by absorption spectroscopy and MALDI-MS. The reaction mixture was diluted with ethyl acetate and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated. The crude solid was chromatographed in a Pasteur pipet [basic alumina, ethyl acetate to ethyl acetate/MeOH (95:5)] to afford a blue solid (1.0 mg, 19%): $\lambda_{abs}$ ($CH_2Cl_2$) 360, 612, 764 nm; MALDI-MS obsd 711.2, calcd 710.3 ($C_{37}H_{42}N_4O_9Mg$). Limited stability precluded further analysis.

*Zn(II)-8,8,18,18-Tetramethylbacteriochlorin (**ZnBC0**).* Following Procedure A, a solution of **BC0** (4.6 mg, 12 $\mu$mol, 4 mM) in freshly distilled THF (3 mL) was treated with NaH (46 mg, 1.9 mmol, 60% dispersion in mineral oil washed beforehand with hexanes) and $Zn(OTf)_2$ (131 mg, 0.360 mmol). The reaction mixture was heated at 60 °C for 16 h under argon. The reaction was monitored by absorption spectroscopy and MALDI-MS. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated. The crude solid was treated with hexanes, sonicated in a benchtop sonication bath, centrifuged, and the supernatant discarded. Repetition twice afforded a pink solid (4.3 mg, 80%): $^1$H NMR (300 MHz, THF-$d_8$) $\delta$ 1.97 (s, 12H), 4.46 (s, 4H), 8.60−8.62 (m, 2H), 8.60 (s, 2H), 8.64−8.66 (m, 2H), 8.64 (s, 2H); $\lambda_{abs}$ (toluene) 336, 376, 514, 723 nm; $\lambda_{em}$ ($\lambda_{exc}$ 514 nm) 725 nm; MALDI-MS obsd 432.2; ESI-MS obsd 432.1280, calcd 432.1292 ($C_{24}H_{24}N_4Zn$).

*Zn(II)-3,13-Bis(ethoxycarbonyl)-2,12-dimesityl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**ZnBC2-2M-MeO**).* Following Procedure A, a solution of **BC2-2M-MeO** (9.4 mg, 12 $\mu$mol, 4 mM) in freshly distilled THF (3 mL) was treated with NaH (72 mg, 1.8 mmol, 60% dispersion in mineral oil washed beforehand with hexanes) at room temperature for 30 min. $Zn(OTf)_2$ (131 mg, 0.360 mmol) was added, and the flask was heated at 60 °C for 5 h under argon. The reaction was monitored by absorption spectroscopy and TLC [silica, hexanes/ethyl acetate (3:1)]. The reaction mixture was diluted with ethyl acetate and washed with saturated aqueous $NaHCO_3$. The organic layer was dried ($Na_2SO_4$) and filtered. The crude product was found to contain only hydrocarbon impurities by $^1$H NMR spectroscopy. The crude solid was dissolved in methanol and treated with hexanes. Two intensely colored phases formed. The hexanes phase was removed as this phase was highly enriched in **BC2-2M-MeO** yet also contained some metallobacteriochlorin. The methanol phase, which contained the title metallobacteriochlorin, was collected and concentrated to yield a pink solid (5.5 mg, 54%): $^1$H NMR (300 MHz, THF-$d_8$) $\delta$ 1.14 (t, $J$ = 7.2 Hz, 3H), 1.20 (t, $J$ = 7.2 Hz, 3H), 1.90 (s, 6H), 1.94 (s, 6H), 1.99 (s, 6H), 2.08 (s, 6H), 2.46 (s, 3H), 2.52 (s, 3H), 3.57 (s, 3H), 4.15 (s, 2H), 4.23 (s, 2H), 4.36 (q, $J$ = 7.2 Hz, 2H), 4.40 (q, $J$ = 7.2 Hz, 2H), 7.08 (s, 2H), 7.14 (s, 2H), 8.01 (s, 1H), 9.50 (s, 1H), 9.56 (s, 1H); $\lambda_{abs}$ (toluene) 353, 389, 565, 773 nm; $\lambda_{em}$ ($\lambda_{exc}$ 565 nm) 779 nm; MALDI-MS obsd 842.8; ESI-MS obsd 842.3393, calcd 842.3380 ($C_{49}H_{54}N_4O_5Zn$).

*Zn(II)-3,13-Bis(ethoxycarbonyl)-2,12-diheptyl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**ZnBC2-2H-MeO**).* Following Procedure A, a solution of **BC2-2H-MeO** (5.9 mg, 8.0 $\mu$mol, 4 mM) in THF (2.0 mL) was treated with NaH (48 mg, 1.2 mmol) at room temperature for 1 h. The color of the reaction mixture changed from light green to red. Then $Zn(OTf)_2$ (87 mg, 0.24 mmol) was added to the mixture, and the flask was heated to 60 °C for 6 h under argon. TLC analysis [silica, hexanes/ethyl acetate (3:1)] showed the disappearance of the free base bacteriochlorin and the presence of only one spot. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated, and the residue was chromatographed on a short column [silica, hexanes/ethyl acetate/TEA (74:25:1), v/v/v] to afford a black-red solid (3.2 mg, 50%): $^1$H NMR (300 MHz, THF-$d_8$) $\delta$ 0.86−0.98 (m, 6H) 1.29−1.66 (m, 22H), 1.94 (d, $J$ = 4.0 Hz, 12H), 2.12 (m, 4H), 3.72 (t, $J$ = 7.6 Hz, 2H), 4.10 (t, $J$ = 7.6 Hz, 2H), 4.12 (s, 3H), 4.36 (s, 2H), 4.38 (s, 2H), 4.63 (q, $J$ = 6.8 Hz, 4H), 8.43 (s, 1H), 8.58 (s, 1H), 9.58 (s, 1H); $\lambda_{abs}$ (toluene) 349, 385, 542, 752 nm; $\lambda_{em}$ ($\lambda_{exc}$ 542 nm) 757 nm; MALDI-MS obsd 802.1; ESI-MS obsd 802.3995, calcd 802.4006 ($C_{45}H_{62}N_4O_5Zn$).

*Zn(II)-3,13-Bis(ethoxycarbonyl)-2,12-diheptyl-8,8,18,18-tetramethylbacteriochlorin (**ZnBC2-2H**).* Following Procedure A, a solution of **BC2-2H** (5.7 mg, 8.0 $\mu$mol, 4 mM) in THF (2.0 mL) was treated with NaH (48 mg, 1.2 mmol) at room temperature for 1 h. The color of the reaction mixture changed from light green to red. Then $Zn(OTf)_2$ (87 mg, 0.24 mmol) was added to the mixture, and the flask was heated to 60 °C for 6 h under argon. TLC analysis [silica, hexanes/ethyl acetate (3:1)] showed the disappearance of the free base bacteriochlorin and the presence of only one spot. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated, and the residue was chromatographed on a short column [silica, hexanes/ethyl acetate/TEA (74:25:1), v/v/v] to afford a black-red solid (1.9 mg, 31%): $^1$H NMR (300 MHz, THF-$d_8$) $\delta$ 0.88−0.92 (m, 6H), 1.31−1.66 (m, 22H), 1.94 (s, 12H), 2.12 (m, 4H), 4.12 (t, $J$ = 7.8 Hz, 4H), 4.39 (s, 4H), 4.66 (q, $J$ = 7.2 Hz, 4H), 8.55 (s, 2H), 9.60 (s, 2H); $\lambda_{abs}$ (toluene) 347, 391, 547, 776 nm; $\lambda_{em}$ ($\lambda_{exc}$ 547 nm) 781 nm; MALDI-MS obsd 772.6; ESI-MS obsd 772.3879, calcd 772.3901 ($C_{44}H_{60}N_4O_4Zn$).

*Zn(II)-3,13-Bis(ethoxycarbonyl)-2,12-diethyl-8,8,18,18-tetramethylbacteriochlorin (**ZnBC2-2E**).* Following Procedure C, a solution of **BC2-2E** (5.0 mg, 8.8 $\mu$mol, 4 mM) in DMF (2.2 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (58 mg, 260 $\mu$mol, 30 equiv). The reaction mixture was heated to 60 °C for 16 h and then 80 °C for 24 h under argon. The reaction was monitored by absorption spectroscopy and MALDI-MS. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated. The crude solid was treated with hexanes, sonicated in a benchtop sonication bath, centrifuged, and the supernatant discarded. Repetition twice afforded a dark blue solid (4.8 mg, 86%): $^1$H NMR (THF-$d_8$) $\delta$ 1.64 (t, $J$ = 6.8 Hz, 6H), 1.69 (t, $J$ = 7.6 Hz, 6H), 1.95 (s, 12H), 4.10 (q, $J$ = 7.6 Hz, 4H), 4.39 (s, 4H), 4.66 (q, $J$ = 6.8 Hz, 4H), 8.55 (s, 2H), 9.60 (s, 2H); $\lambda_{abs}$ (toluene) 347, 391, 545, 774 nm; $\lambda_{em}$ ($\lambda_{exc}$ 545 nm) 780 nm; MALDI-MS obsd 631.7; ESI-MS obsd 632.2349, calcd 632.2341 ($C_{34}H_{40}N_4O_4Zn$).

*Zn(II)-15$^2$-N-Benzyl-3-(ethoxycarbonyl)-2,12-diethyl-8,8,18,18-tetramethylbacteriochlorin-13,15-dicarboximide (**ZnBC3-2E**).* Following Procedure C, a solution of **BC3-2E** (6.9 mg, 11 $\mu$mol, 4 mM) in DMF (2.6 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (69 mg, 320 $\mu$mol, 30 equiv). The reaction mixture was heated to 60 °C for 16 h and then 80 °C for 7 h. The reaction was monitored by absorption spectroscopy and MALDI-MS. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated, and the residue was chromatographed on a short column [silica, $CH_2Cl_2$/MeOH (98:2)] to afford a purple solid (4.1 mg, 54%): $^1$H NMR (THF-$d_8$) $\delta$ 1.60−1.69 (m, 9H), 1.90 (s, 6H), 1.92 (s, 6H), 4.03 (q, $J$ = 7.7 Hz, 2H), 4.15 (q, $J$ = 7.3 Hz, 2H), 4.33 (s, 2H), 4.65 (q, $J$ = 7.0 Hz, 2H), 4.74 (s, 2H), 5.55 (s, 2H), 7.18 (t, $J$ = 7.3 Hz, 1H), 7.29 (t, $J$ = 7.5 Hz, 2H), 7.76 (d, $J$ = 7.0 Hz, 2H), 8.47 (s, 1H), 8.62 (s, 1H), 9.51 (s, 1H); $\lambda_{abs}$ (toluene) 356, 419, 563, 831 nm; $\lambda_{em}$ ($\lambda_{exc}$ 563 nm) 834 nm; MALDI-MS obsd 719.9; ESI-MS obsd 720.2501, calcd 720.2523 [$(M + H)^+$, M = $C_{40}H_{41}N_5O_4Zn$].

*Cu(II)-8,8,18,18-Tetramethylbacteriochlorin (**CuBC0**).* Following Procedure A, a solution of **BC0** (5.0 mg, 14 $\mu$mol, 4 mM) in freshly distilled THF (3.4 mL) was treated with NaH (48 mg, 2.0 mmol, 60% dispersion in mineral oil washed beforehand with hexanes) and $Cu(OAc)_2$ (74 mg, 0.41 mmol). The reaction mixture was heated at 60 °C for 16 h under argon. The reaction was monitored by absorption


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spectroscopy and MALDI-MS. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The filtrate was concentrated. The crude solid was treated with hexanes, sonicated in a benchtop sonication bath, centrifuged, and the supernatant discarded. Repetition twice afforded a green solid (2.4 mg, 41%): $\lambda_{abs}$ (toluene) 336, 376, 514, 723 nm; MALDI-MS obsd 431.1; ESI-MS obsd 431.1300, calcd 431.1291 ($C_{24}H_{24}N_4Cu$).

*Cu(II)-8,8,18,18-Tetramethyl-2,12-di-p-tolylbacteriochlorin (**CuBC0-2T**).* Following Procedure B, a solution of **BC0-2T** (16.5 mg, 30.0 μmol, 4 mM) in THF (7.5 mL) was treated with LDA (0.750 mL, 1.50 mmol, 200 mM) at room temperature for 5 min. $Cu(OAc)_2$ (54.5 mg, 300 μmol) was added, and the flask was heated at 70 °C for 30 min under argon. TLC analysis [silica, hexanes/$CH_2Cl_2$ (1:1)] showed the disappearance of **BC0-2T** and the presence of only one spot, and the absorption spectrum did not show the $Q_x$ band of **BC0-2T**. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated brine. The organic layer was treated to the remaining steps of the standard workup procedure to yield a dark powder (10.2 mg, 56%): $\lambda_{abs}$ (toluene) 337, 383, 512, 755 nm; LD-MS obsd 611.3; FAB-MS obsd 611.2238, calcd 611.2336 ($C_{38}H_{36}N_4Cu$).

*Cu(II)-3,13-Bis(ethoxycarbonyl)-2,12-dimesityl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**CuBC2-2M-MeO**).* Following Procedure A, a solution of **BC2-2M-MeO** (6.2 mg, 8 μmol, 4 mM) in freshly distilled THF (2 mL) was treated with NaH (48 mg, 1.2 mmol, 60% dispersion in mineral oil washed beforehand with hexanes) at room temperature for 30 min under argon. $Cu(OAc)_2$ (43 mg, 0.24 mmol) was added, and the flask was heated at 60 °C for 20 h under argon. The reaction was monitored by absorption spectroscopy and TLC [silica, hexanes/ethyl acetate (3:1)]. The standard workup procedure was employed except for the chromatography procedure [silica, hexanes/ethyl acetate (4:1) with 1% TEA], which yielded a pink solid (5.3 mg, 79%): $\lambda_{abs}$ (toluene) 348, 390, 556, 779 nm; MALDI-MS obsd 841.3; ESI-MS obsd 841.3381, calcd 841.3385 ($C_{49}H_{54}N_4O_5Cu$).

*Pd(II)-8,8,18,18-Tetramethyl-2,12-di-p-tolylbacteriochlorin (**PdBC0-2T**).* Following Procedure A, a solution of **BC0-2T** (16.5 mg, 30.0 μmol, 4 mM) in THF (7.5 mL) was treated with NaH (120 mg, 3.00 mmol) at room temperature for 1 h. $PdBr_2$ (240 mg, 90.0 mmol) was then added, and the flask was heated at 60 °C for 0.5 h under argon. TLC analysis [silica, hexanes/$CH_2Cl_2$ (1:1)] showed the disappearance of **BC0-2T** and the presence of only one spot. The standard workup afforded a black-red powder (9.3 mg, 48%): $^1$H NMR $\delta$ 1.87 (s, 12H), 2.59 (s, 6H), 4.43 (s, 4H), 7.54 (d, $J$ = 8.0 Hz, 4H), 8.01 (d, $J$ = 8.0 Hz, 4H), 8.55 (s, 2H), 8.68 (s, 2H), 8.72 (s, 2H); $\lambda_{abs}$ (toluene) 329, 379, 499, 739 nm; $\lambda_{em}$ ($\lambda_{exc}$ 499 nm) 745 nm; LD-MS obsd 653.9; FAB-MS obsd 654.1958, calcd 654.1975 ($C_{38}H_{36}N_4Pd$).

*Pd(II)-3,13-Bis(ethoxycarbonyl)-2,12-dimesityl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (**PdBC2-2M-MeO**).* Following Procedure B, a solution of **BC2-2M-MeO** (7.8 mg, 10 μmol, 4 mM) in freshly distilled THF (2.5 mL) was treated with LDA (50 μL, 0.1 mmol, 0.2 M) at room temperature for 10 min. $PdBr_2$ (80 mg, 0.30 mmol) was then added to the mixture, and the flask was heated at 60 °C for 20 h under argon. The reaction was monitored by absorption spectroscopy and TLC [silica, hexanes/ethyl acetate (3:1)]. The reaction mixture was diluted with ethyl acetate and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried ($Na_2SO_4$) and filtered. The concentrated crude solid was chromatographed [silica, hexanes/ethyl acetate (3:1)], and the only mobile band (pink) was collected. The concentrated mixture was found to contain some amine-like impurity, which was removed by size-exclusion chromatography (toluene, Bio-Beads S-X1, 200−400 mesh). The collected band (pink) was then chromatographed [silica, hexanes/ethyl acetate (3:1)] to afford a purple solid (3.1 mg, 35%): $^1$H NMR (300 MHz) $\delta$ 1.12 (t, $J$ = 7.2 Hz, 3H), 1.18 (t, $J$ = 7.2 Hz, 3H), 1.87 (s, 6H), 1.90 (s, 6H), 2.00 (s, 6H), 2.09 (s, 6H), 2.46 (s, 3H), 2.50 (s, 3H), 3.46 (s, 3H), 4.18 (s, 2H), 4.26 (s, 2H), 4.34 (q, $J$ = 7.2 Hz, 2H), 4.38 (q, $J$ = 7.2 Hz, 2H), 7.07 (s, 2H), 7.13 (s, 2H), 8.04 (s, 1H), 9.55 (s, 1H), 9.61 (s, 1H); $\lambda_{abs}$ (toluene) 337, 382, 538, 758 nm; MALDI-MS obsd 884.5; ESI-MS obsd 884.3228, calcd 884.3202 ($C_{49}H_{54}N_4O_5Pd$).

*In(III)Cl-8,8,18,18-Tetramethyl-2,12-di-p-tolylbacteriochlorin (**InClBC0-2T**).* Following Procedure B, a solution of **BC0-2T** (11.0 mg, 20.0 μmol, 4 mM) in THF (4.5 mL) was treated with LDA in THF (500 μL, 1.00 mmol, 200 mM) at room temperature for 5 min. $InCl_3$ (44.2 mg, 200 μmol) was added, and the flask was heated at 60 °C for 1.5 h under argon. TLC analysis [silica, hexanes/THF (1:1)] showed the disappearance of **BC0-2T** and the presence of only one spot, and the absorption spectrum did not show the $Q_x$ band of **BC0-2T**. The reaction mixture was diluted with $CH_2Cl_2$ and washed with saturated brine. The organic layer was treated to the remaining steps of the standard workup procedure to yield a black-red powder (12.5 mg, 89%): $^1$H NMR (THF-$d_8$) $\delta$ 1.84 (s, 6H), 2.09 (s, 6H), 2.56 (s, 6H), 4.48, 4.71 (AB, $^2J$ = 16.0 Hz, 4H), 7.55 (d, $J$ = 8.0 Hz, 4H), 8.09 (d, $J$ = 8.0 Hz, 4H), 8.78 (s, 2H), 8.82 (s, 2H), 8.87 (s, 2H); $\lambda_{abs}$ (toluene) 350, 389, 539, 764 nm; $\lambda_{em}$ ($\lambda_{exc}$ 539 nm) 772 nm; LD-MS obsd 698.2; FAB-MS obsd 698.1688, calcd 698.1667 ($C_{38}H_{36}ClInN_4$).

## ■ ASSOCIATED CONTENT

### Supporting Information

Development of metalation conditions; further X-ray crystallographic information; and the synthesis and characterization of dimesitylbacteriochlorin **BC0-2M**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

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