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Two Complementary Routes to 7-Substituted Chlorins. Partial Mimics of Chlorophyll *b*

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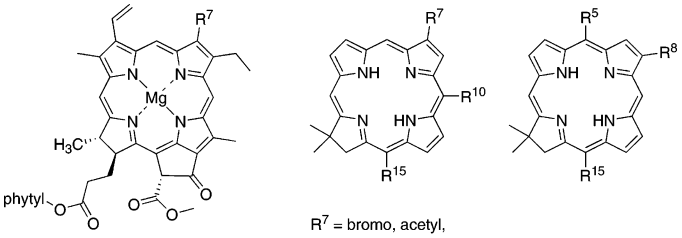

Chlorophyll *a* and chlorophyll *b* exhibit distinct spectra yet differ only in the nature of a single substituent (7-methyl versus 7-formyl, respectively). Two complementary approaches have been developed for the synthesis of 7-substituted chlorins. The first approach is a de novo route wherein 2,9-dibromo-5-*p*-tolyldipyrromethane (Eastern half) and 9-formyl-2,3,4,5-tetrahydro-1,3,3-trimethyldipyrrin (Western half) undergo acid-catalyzed condensation followed by metal-mediated oxidative cyclization. The resulting zinc chlorin is sterically uncongested and bears (1) a geminal dimethyl group in the reduced, pyrroline ring, (2) a bromo substituent at the 7-position, and (3) a *p*-tolyl group at the 10-position. The second approach entails regioselective 7-bromination of a 10,15-diarylchlorin that lacks a substituent at the 5-position. In an extension of this latter approach, a 5,15-diarylchlorin that lacks a substituent at the 10-position undergoes regioselective bromination at the 8-position. The introduction of a TIPS-ethynyl, acetyl, or formyl group at the 7-position was achieved using Pd-catalyzed reactions with the corresponding 7-bromochlorin. In the 10-*p*-tolyl-substituted zinc chlorins, the series of substituents (7-TIPS-ethynyl, 7-acetyl, 7-formyl) progressively causes (1) a bathochromic shift in the absorption maximum of the B band (405 to 426 nm) and (2) a hypsochromic shift in the position of the Q_y band (605 to 598 nm). The trends mirror those for chlorophyll *b* versus chlorophyll *a* but are of lesser magnitude. Taken together, the facile access to chlorins that bear auxochromes at the 7-position enables wavelength tunability and provides the foundation for fundamental spectroscopic studies.

Introduction

Chlorophyll *a* and chlorophyll *b* are the two green pigments that underlie plant photosynthesis. Chlorophylls *a* and *b* each bear a 3-vinyl group, an isocyclic ring spanning the 13−15-positions, and a 7-methyl versus 7-formyl group, respectively, attached to the chlorin macrocycle. The presence of a conjugative substituent at the 3-position (vinyl) and the 13-position (keto group of the isocyclic ring) substantially alters the spectral properties of the chlorin (Figure 1).[1] Chlorophyll *a* exhibits an intense B (Soret) band at 429 nm and a Q_y band at 661 nm of nearly comparable intensity.[2] Chlorophyll *b* exhibits a B band at 453 nm and a Q_y band at 642 nm; the former is more intense than that of chlorophyll *a*, while the latter is less intense.[2] Thus, the presence of the 7-formyl versus 7-methyl group causes a bathochromic shift of the B band but a hypsochromic shift of the Q_y band and also alters the ratio of the B and Q_y band intensities. The profound spectral differences owing to the change of a single substituent render 7-substituted chlorins valuable synthetic targets for fundamental spectroscopic studies

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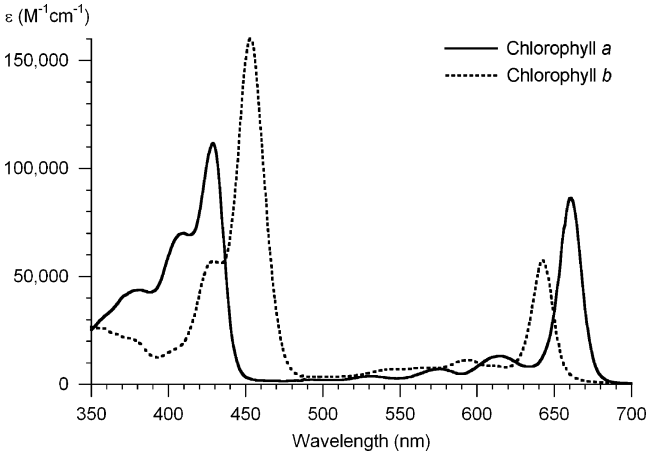
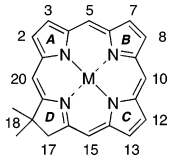


FIGURE 1. The absorption spectra of chlorophyll *a* and chlorophyll *b* in diethyl ether at room temperature.

CHART 1



as well as for potential applications in light harvesting or the life sciences.

In 1994, we began a program to develop rational synthetic routes to stable, tailorable chlorins. To achieve stability, each chlorin (dihydroporphyrin) bears a geminal dimethyl group in the reduced, pyrroline ring to block adventitious dehydrogenation. The program began by building off of prior synthetic routes to naturally occurring non-photosynthetic pigments that also contain a geminal dimethyl group in the pyrroline ring.[3] The ensuing development and application of these routes has now provided access to every peripheral site of the chlorin macrocycle with the exception of the 7-site. The sites include the 2-, 3-, 5-, 8-, 10-, 12-, 13-, 15-, 17-, 18-, and 20-positions (Chart 1).[4−12] An approach for introducing the isocyclic ring, which spans positions 13 and 15, has been established.[13] Streamlined routes to chlorin precursors also are in hand.[14−17] The availability of chlorins bearing substituents at designated sites has enabled a set of fundamental spectroscopic studies.[7,18−26] The objective of the work described herein is to gain access to 7-substituted chlorins and thereby complete this one facet of chlorin chemistry.

The retrosynthetic analyses shown in Scheme 1 constitute two distinct and complementary approaches to 7-substituted chlorins. One strategy introduces the group destined to occupy the chlorin 7-position at an early stage of an established route to chlorins, wherein a Western half and an Eastern half undergo acid-catalyzed condensation followed by metal-mediated oxidation. The groups in the Western and Eastern halves are carried through to the chlorin. In this route, the group destined for the chlorin 7-position must be introduced into the dipyrromethane that constitutes the Eastern half.

A second strategy relies on derivatization of an intact chlorin. The β-positions of ring B (distal to the reduced ring, ring D) are known to be reactive to a variety of reagents. Indeed, reduction (using catalytic hydrogenation,[27] diimide,[28] or sodium isopentoxide[29]) or *vic*-dihydroxylation[30,31] of a chlorin typically affords the bacteriochlorin. Ring B also is susceptible to reagents that characteristically react with isolated double bonds, such as dipolarophiles.[32−34] In this regard, bromination of a *meso*-tetraarylchlorin affords the corresponding 7,8-dibromochlorin.[33]

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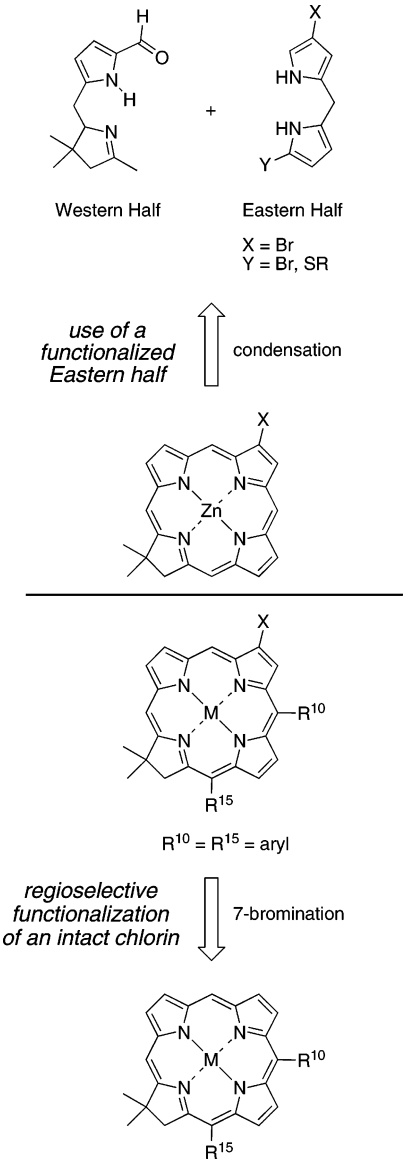
SCHEME 1



In principle, both β-positions (7 and 8) in ring B of a chlorin should have equal reactivity. Our thinking was that the presence of a bulky group at the 10-position might cause substitution to favor the 7- versus 8-position.

In both strategies, the preferred initial substituent was the bromo atom because palladium-mediated coupling reactions can then be utilized to introduce diverse substituents such as aryl, alkyne, amine, and acyl moieties. In addition, the chlorins of initial interest are those that contain few other substituents so that the effects of 7-substituents on spectral properties can be clearly delineated. To our knowledge, routes that enable facile preparation of a variety of 7-substituted chlorins have not previously been described. Jacobi described an elegant synthesis of a series of chlorins that bear 7-alkanoic acids of different lengths, but this route has not been extended to accommodate the distinct types of substituents envisaged herein.[35] Inhoffen described the transformation of the 7-methyl group of chlorin-e_6-trimethyl ester, a relay species derived from chlorophyll *a* or synthesized de novo, to the corresponding 7-formyl group.[36] The chief alternative approach to 7-substituted chlorins entails semisynthesis of naturally occurring pigments. Although semisynthesis has been widely exploited with chlorophyll *a* and analogues,[37−47] less work has been carried out with chlorophyll *b*. Modification of the 7-formyl group of chlorophyll *b* (and pheophorbide analogues) has yielded 7-substituents such as hydroxymethyl,[48] carboxylic acid,[37,41] carbomethoxy,[41] vinyl,[49] hydrazone,[50,51] aminomethyl,[52] and other aldehyde addition products (acetal, oxime, cyanohydrin, and hemithioacetal).[37,39] Modifications also have been carried out on the 7-formyl group in the chlorins bacteriochlorophyll *e*[53] and bacteriochlorophyll *f*.[54] A recent comprehensive review of such modifications is available.[55]

In this paper, we describe the development of the two routes shown in Scheme 1. One of the resulting 7-bromochlorins was derivatized with potential auxochromes such as acetyl, TIPS-ethynyl, and formyl groups. The absorption spectral properties of the corresponding zinc and free base chlorins have been characterized. Taken together, this work provides access to chlorins of interest for a variety of fundamental studies.

Results and Discussion

I. Synthesis of 7-Substituted Chlorins via a Functionalized Eastern Half. A. Synthesis of Eastern Halves. The synthesis of a bromo-substituted dipyrromethane (Eastern half) that is suitable for conversion to the corresponding 7-bromochlorin presented a number of challenges. Two successful routes were developed. The first route, shown in Scheme 2, relies on the use of an α-alkylthio-substituted pyrrole.[56] The α-alkylthio unit

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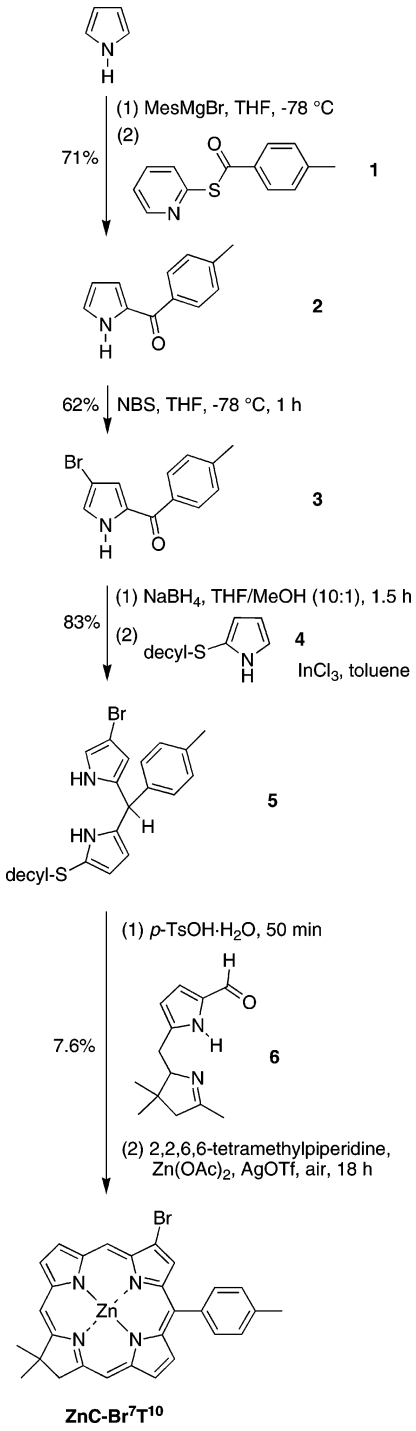
SCHEME 2



directs electrophilic aromatic substitution toward the α′-position and enables the use of a stoichiometric amount of alkylthiopyrrole and pyrrole-carbinol to form the target dipyrromethane.

The synthesis begins by acylation of pyrrole with a Mukaiyama reagent in the standard manner.[57,58] Thus, treatment of pyrrole with MesMgBr at room temperature followed by Mukaiyama reagent **1**[58] at −78 °C gave the known[59] 2-acylpyrrole **2** in 71% yield. The regioselective bromination of **2** was achieved in the presence of NBS following an established procedure[8] to obtain 4-bromo-2-(4-methylbenzoyl)pyrrole (**3**). The regiochemistry of the monobromo-monoacylpyrrole **3** was established by NMR spectroscopy (^{1}H−^{1}H 2D COSY and NOE experiments). Reduction of **3** with $NaBH_4$ gave the corresponding pyrrole-carbinol derivative, which upon condensation with a stoichiometric amount of α-decylthiopyrrole **4**[56] in the presence of $InCl_3$ (10 mol %) afforded dipyrromethane **5** in 83% yield. Attempts to formylate **5** at the α-position adjacent to the *β*-bromo group either with the Vilsmeier reagent or with MesMgBr and phenyl formate[16] afforded a mixture of products. To achieve regioselective formylation, we considered deactivating the decylthio group in **5** by means of oxidation to the sulfone.[56] However, the oxidation of **5** with *m*-CPBA in CH_2Cl_2 at 0 °C for 5 h gave dark polymeric materials, which prompted us to examine the direct use of compound **5** as the Eastern half in the chlorin-forming reaction.

B. Chlorin Formation. The condensation of compound **5** (Eastern half) and 9-formyltetrahydrodipyrrin **6**[17] (Western half) in CH_2Cl_2 containing methanolic *p*-TsOH·H_2O under argon afforded a clear reddish-brown solution over 40−50 min. The reaction mixture was neutralized (with 2,2,6,6-tetramethylpiperidine), concentrated, and treated to metal-mediated oxidative cyclization with $Zn(OAc)_2$ and AgOTf in refluxing CH_3CN exposed to air for 18 h. The 7-bromochlorin **ZnC-Br^{7}T^{10}** was obtained in 7.6% yield after silica column chromatography. The decylthio group was obviously cleaved during the course of macrocycle formation. This route provides direct access to 7-bromochlorins, albeit in low yield. Chlorin **ZnC-Br^{7}T^{10}** was characterized by absorption spectroscopy, ^{1}H NMR spectroscopy, LD-MS, and FAB-MS analyses.

Given the poor leaving ability of the alkylthio group, we explored routes that employed dipyrromethanes other than **5** (see the Supporting Information). The best result was obtained with the desdecylthio analogue of **5**, 2-bromo-5-*p*-tolyldipyrromethane **7**. The synthesis of **7** is shown in Scheme 3. Reduction of **3** with $NaBH_4$ gave the corresponding pyrrole-carbinol species, which upon treatment with excess pyrrole under acidic conditions[5] afforded dipyrromethane **7** in 52% yield after column chromatography. Treatment of **7** with 1.0 molar equiv of NBS at −78 °C gave the crude 2,9-dibromo-5-*p*-tolyldipyrromethane (**7-α-Br**), where bromination occurred at the α-position in the pyrrole ring lacking the *β*-bromo group. This novel dibromodipyrromethane was condensed with Western half **6** under the standard conditions of *p*-TsOH·H_2O catalysis. The putative tetrahydrobiladiene-*ab* formed was subjected to metal-mediated oxidative cyclization (2,2,6,6-tetramethylpiperidine, $Zn(OAc)_2$, and AgOTf) in refluxing acetonitrile in the presence of air for 14 h, affording the zinc chelate of the 7-bromochlorin (**ZnC-Br^{7}T^{10}**) in 41% yield. The **ZnC-Br^{7}T^{10}** prepared in this manner agreed in all respects with the sample of **ZnC-Br^{7}T^{10}** prepared as shown in Scheme 2. The structure of **ZnC-Br^{7}T^{10}** was unambiguously established by X-ray crystallography as well as by 2D NMR spectroscopy (see the Supporting Information).

In summary, the route shown in Scheme 3 provides a concise entrée to 7-bromochlorins and has the following noteworthy features: (i) the dipyrromethane **7** is prepared without use of any protecting group (cf. **5**); (ii) the labile dibromodipyrromethane intermediate **7-α-Br** can be prepared and used

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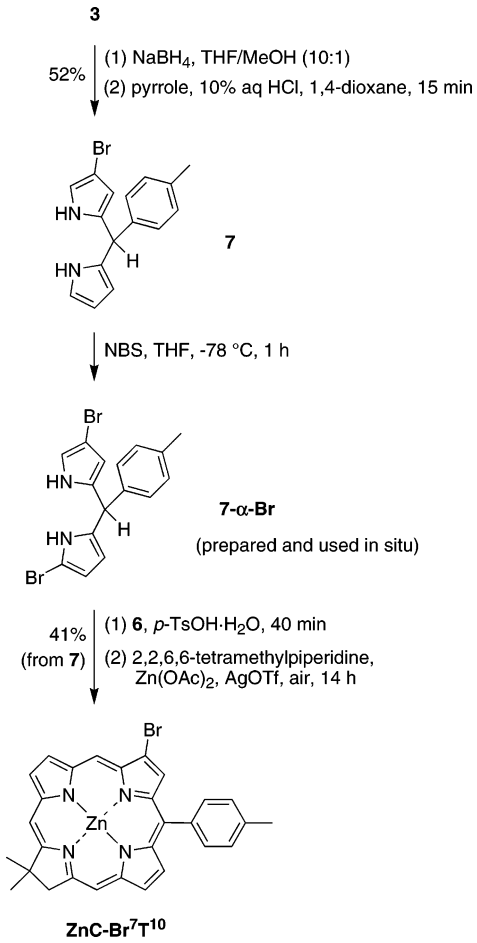
SCHEME 3



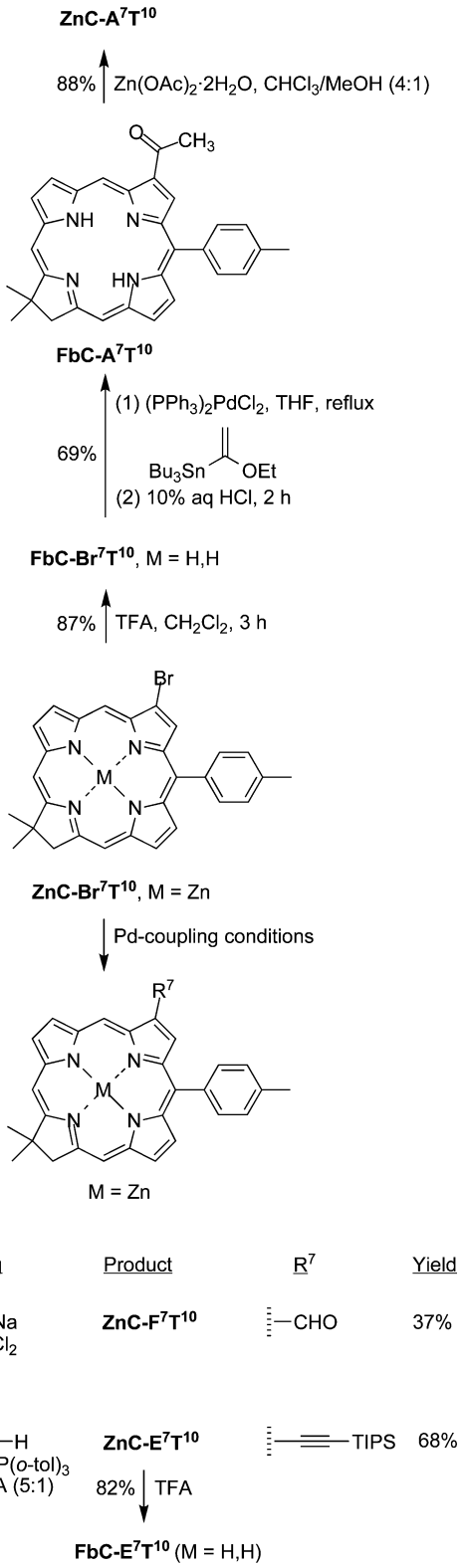
following simple workup; and (iii) the isolated yield of the 7-bromochlorin is several-fold greater than that of the route employing the α-decylthio masking group.

C. Chlorin Derivatization. The 7-bromochlorin was derivatized with three groups (TIPS-ethynyl, acetyl, formyl) to investigate their effects on the absorption spectral properties of chlorins. These groups serve as potent auxochromes upon introduction at the 3- and/or 13-positions of chlorins.[9,12,24] Each derivatization was carried out at small scale and employed palladium-mediated coupling reactions. The palladium-mediated reactions were carried out under copper-free conditions to ensure no unwanted copper transmetalation of zinc chlorins or copper insertion into free base chlorins (Scheme 4).

1. 7-Ethynylation. The synthesis of 7-TIPS-ethynylchlorin **ZnC-E^{7}T^{10}** was carried out by Sonogashira coupling.[9,60] Thus, the reaction of **ZnC-Br^{7}T^{10}** and (triisopropylsilyl)acetylene in the presence of $Pd_2(dba)_3$ and P(*o*-tol)$_3$ gave 7-TIPS-ethynylchlorin **Zn-E^{7}T^{10}** in 68% yield. Demetalation of **ZnC-E^{7}T^{10}** with TFA in CH_2Cl_2 at room temperature gave the free base chlorin **FbC-E^{7}T^{10}** in 82% yield.

2. 7-Acetylation. The synthesis of a 7-acetylchlorin began by treatment of **ZnC-Br^{7}T^{10}** with TFA in CH_2Cl_2 at room temperature to obtain the free base 7-bromochlorin **FbC-Br^{7}T^{10}** in 87% yield. The coupling[9] of **FbC-Br^{7}T^{10}** (15 mM) and tributyl(1-ethoxyvinyl)tin (60 mM) in the presence of 20 mol % of $(PPh_3)_2PdCl_2$ in THF for 20 h followed by hydrolysis with

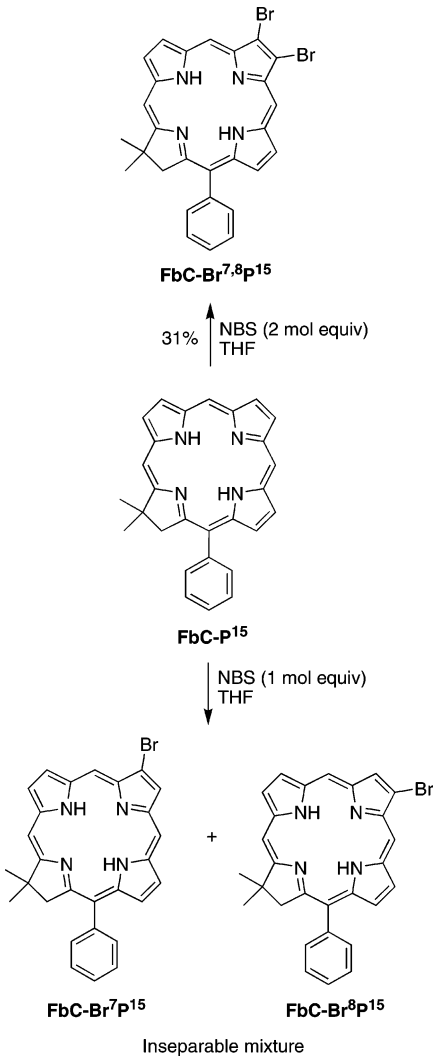
SCHEME 4



10% aqueous HCl gave 7-acetylchlorin **FbC-A^{7}T^{10}** in 69% yield. A streamlined procedure including demetalation, Pd coupling, and acidic workup gave **FbC-A^{7}T^{10}** in 66% yield starting from **ZnC-Br^{7}T^{10}** (not shown). The free base 7-acetylchlorin **FbC-A^{7}T^{10}** was metalated with $Zn(OAc)_2 \cdot 2H_2O$ to obtain **ZnC-A^{7}T^{10}** in 88% yield.

(60) Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974−2983.

SCHEME 5



3. 7-Formylation. The synthesis of a 7-formylchlorin employed reductive carbonylation.[12] Thus, treatment of **ZnC-Br^{7}T^{10}** (10 mM) with sodium formate (25 mM) in the presence of $(PPh_3)_2PdCl_2$ (20 mol %) and PPh_3 (20 mol %) in DMF at 108 °C under an atmosphere of CO afforded the 7-formylchlorin **ZnC-F^{7}T^{10}** in 37% yield.

II. Synthesis of 7-Substituted Chlorins by Regioselective Bromination of an Intact Chlorin. Our previous studies have shown that the electrophilic bromination of a fully unsubstituted chlorin (bearing the 18,18-dimethyl group) proceeds selectively at the 15-position.[8,11] To determine the second-most reactive site in the chlorin macrocycle, we examined the bromination of a chlorin that bears an aryl substituent at the 15-position. Thus, treatment of **FbC-P^{15}** with 1 equiv of NBS in THF at room temperature afforded an inseparable, nearly equimolar mixture of two monobromochlorins (Scheme 5). NMR analysis (^{1}H NMR, NOESY, COSY) showed that one of the components in the mixture was the 7-bromochlorin **FbC-Br^{7}P^{15}** and the second was almost certainly the 8-bromochlorin **FbC-Br^{8}P^{15}**. Treatment of **FbC-P^{15}** with 2 molar equiv of NBS under the same conditions afforded the 7,8-dibromochlorin **FbC-Br^{7,8}P^{15}**. We hypothesized that formation of **FbC-Br^{8}P^{15}** might be suppressed by introduction of a bulky substituent at the 10-position. Thus, we set out to examine the regioselectivity of bromination of chlorins that bear a 15-phenyl group and substituents with various steric bulk (mesityl, *p*-tolyl, pentyl) at the 10-position. In a complementary study, we wanted to examine the bromination of a 5,15-disubstituted, 10-unsubstituted chlorin under analogous conditions.

This strategy required preparation of a series of 10,15-disubstituted (and one 5,15-disubstituted) chlorins. The target 15-substituted chlorins were obtained by bromination of 10- (or 5-) substituted chlorins followed by Suzuki coupling of the resulting 15-bromo derivatives. Note that all transformations (bromination and Suzuki coupling) were performed on the free base rather than corresponding Zn(II) complexes. The free base chlorins are easier to purify than the Zn(II) complexes.

A. Synthesis of 5- or 10-Substituted Chlorins. The known chlorins **FbC** and **FbC-M^{10}** (and their corresponding Zn(II) complexes) were prepared according to reported procedures.[10] The known chlorin **ZnC-T^5** was prepared by a streamlined procedure[10] wherein all steps (bromination of the 1-acyldipyrromethane, carbonyl reduction, acid-catalyzed condensation, and metal-mediated oxidative cyclization) were carried out in one flask over a 1 day period in 20% overall yield (see the Supporting Information). Demetalation of **ZnC-T^5** with TFA afforded **FbC-T^5**.

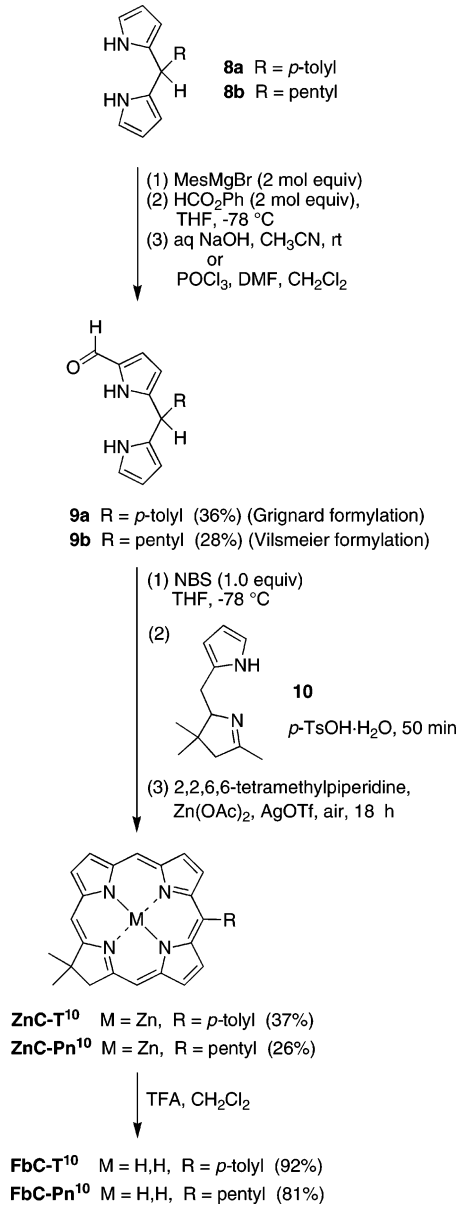
The 10-substituted chlorins **ZnC-T^{10}** and **ZnC-Pn^{10}** were prepared by standard procedures[10] as shown in Scheme 6. The synthesis of chlorin **ZnC-T^{10}** began with known 5-*p*-tolyldipyrromethane **8a**.[61] Treatment[16] of a solution of **8a** in THF at room temperature with 2 molar equiv of MesMgBr and then at −78 °C with 2 molar equiv of phenyl formate afforded 1-formyl-5-*p*-tolyldipyrromethane (**9a**) in 36% yield. Following the streamlined chlorin synthesis,[10] **9a** was treated with 1.0 molar equiv of NBS at −78 °C to give the crude 9-bromo-1-formyl-5-*p*-tolyldipyrromethane (Eastern half). Condensation of the latter with tetrahydrodipyrrin **10**[15] (Western half) in CH_2Cl_2 containing methanolic *p*-TsOH·H_2O afforded a clear reddish-brown solution over 40−50 min. Neutralization with 2,2,6,6-tetramethylpiperidine afforded the crude tetrahydrobiladiene-*ab* as a yellow solid, which was subjected to metal-mediated oxidative cyclization [2,2,6,6-tetramethylpiperidine, $Zn(OAc)_2$, and AgOTf in refluxing acetonitrile in the presence of air] for 18 h. The resulting zinc chelate of the 10-*p*-tolylchlorin (**ZnC-T^{10}**) was obtained in 37% yield. Treatment of **ZnC-T^{10}** with TFA gave the free base chlorin **FbC-T^{10}** in 92% yield.

Formylation of 5-pentyldipyrromethane **8b**[14] under Vilsmeier conditions afforded 1-formyldipyrromethane **9b** in 28% yield. Bromination of **9b** provided 9-bromo-1-formyl-5-pentyldipyrromethane, which was treated in the same manner as described for **9a** to provide **ZnC-Pn^{10}** in 26% yield. Demetalation of **ZnC-Pn^{10}** with dilute TFA provided **FbC-Pn^{10}** in 81% yield.

B. Masking the 15-Position of 5- or 10-Substituted Chlorins. The bromination of chlorins that bear a substituent at the 5- or 10-position was performed in THF (2 mM) at room temperature.[11] The reaction of **FbC-T^5**, **FbC-T^{10}**, and **FbC-Pn^{10}** was typically complete within 30 min and provided the corresponding 15-bromochlorin (**FbC-T^{5}Br^{15}**, **FbC-T^{10}Br^{15}**, **FbC-Pn^{10}Br^{15}**) in a yield of 54−62% (Scheme 7). A small amount of an unidentified dibromochlorin and the starting material typically also were isolated from each reaction mixture. The 15-bromo-10-mesitylchlorin **FbC-M^{10}Br^{15}** was previously prepared in like manner from **FbC-M^{10}**.[11]

(61) Zaidi, S. H. H.; Fico, R. M., Jr.; Lindsey, J. S. *Org. Process Res. Dev.* **2006**, *10*, 118−134.

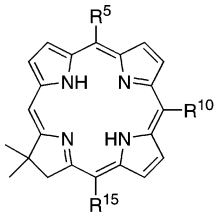
SCHEME 6



An aryl group at the 15-position of a chlorin was introduced by Suzuki coupling of the 15-bromochlorin under conditions employed previously with chlorins.[8,11,23] Thus, reaction of a 15-bromochlorin with 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane in the presence of $Pd(PPh_3)_4$ (30 mol %) and K_2CO_3 afforded the corresponding 15-phenylchlorin in 50−80% yield. Each reaction also provided a small amount (∼10%) of the debrominated chlorin (detected by NMR spectroscopy and LD-MS). Such byproducts typically exhibited polarity similar to that of the desired 15-phenylchlorin and required repetitive column chromatography using a quite nonpolar eluent [e.g., hexanes/toluene (1:2)] to obtain the target 15-phenylchlorin (**FbC-T^{5}P^{15}**, **FbC-T^{10}P^{15}**, **FbC-M^{10}P^{15}**, and **FbC-Pn^{10}P^{15}**) in acceptable purity.

C. Bromination of 15-Substituted Chlorins. Bromination of the 10-arylchlorin **FbC-M^{10}P^{15}** or **FbC-T^{10}P^{15}** provided the corresponding 7-bromochlorin **FbC-Br^{7}M^{10}P^{15}** or **FbC-Br^{7}T^{10}P^{15}** in 66 or 63% yield, respectively (Scheme 8). TLC analysis of the crude reaction mixture in each case showed three spots: a trace of unidentified, easily separable dibromochlorin of unknown structure; the expected **FbC-Br^{7}P^{15}** as the dominant species; and a small amount of unreacted starting material. TLC analysis of each purified 7-substituted chlorin also showed one spot; however, given that **FbC-Br^{7}P^{15}** and **FbC-Br^{8}P^{15}** have comparable polarity, this was insufficient proof of homogeneity. LD-MS obviously cannot distinguish the two isomers. Proof of

SCHEME 7



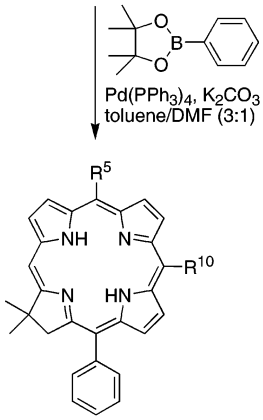
	R^5	R^{10}
FbC-T^{10}	H	*p*-tolyl
FbC-M^{10}	H	mesityl
FbC-Pn^{10}	H	pentyl
FbC-T^5	*p*-tolyl	H

R^{15} = H

NBS, THF, rt

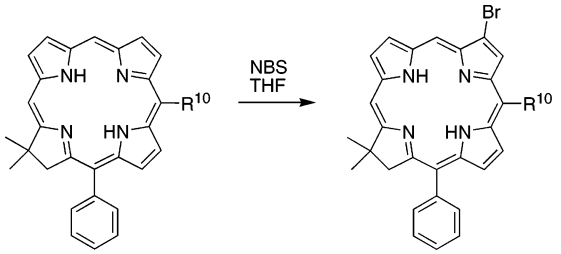
R^{15} = Br

	R^5	R^{10}	Yield
FbC-T^{10}Br^{15}	H	*p*-tolyl	61%
FbC-M^{10}Br^{15}	H	mesityl	55%
FbC-Pn^{10}Br^{15}	H	pentyl	54%
FbC-T^{5}Br^{15}	*p*-tolyl	H	62%



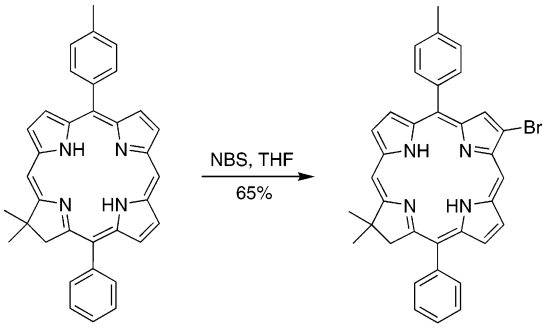
	R^5	R^{10}	Yield
FbC-T^{10}P^{15}	H	*p*-tolyl	79%
FbC-M^{10}P^{15}	H	mesityl	62%
FbC-Pn^{10}P^{15}	H	pentyl	82%
FbC-T^{5}P^{15}	*p*-tolyl	H	64%

SCHEME 8



FbC-T^{10}P^{15}	R^{10} = *p*-tolyl	**FbC-Br^{7}T^{10}P^{15}**	62%
FbC-M^{10}P^{15}	R^{10} = mesityl	**FbC-Br^{7}M^{10}P^{15}**	66%
FbC-Pn^{10}P^{15}	R^{10} = pentyl	**FbC-Br^{7}Pn^{10}P^{15}**	see text

SCHEME 9



homogeneity came from ^{1}H NMR spectroscopy, which showed only one chlorin. Taking into consideration the sensitivity of ^{1}H NMR spectroscopy, the purity of the sample was estimated to be >95%. Thus, any 8-bromochlorin formed was at the <5% level.

On the other hand, bromination of 10-pentylchlorin **FbC-Pn^{10}P^{15}** provided a rather complex mixture of products. The main fraction consisted of an inseparable mixture of two components in ~3:1 ratio. The major component proved to be the 7-substituted chlorin **FbC-Br^{7}Pn^{10}P^{15}**, whereas the minor component is tentatively assigned as the 20-substituted chlorin **FbC-Pn^{10}P^{15}Br^{20}**. Thus, the presence of an aryl, but not pentyl, group at the 10-position enables facile access via bromination to the 7-bromochlorin.

Bromination of **FbC-T^{5}P^{15}** (which lacks a 10-substituent) provided the corresponding 8-bromochlorin **FbC-T^{5}Br^{8}P^{15}** in 65% yield (Scheme 9). A small amount of another bromochlorin, tentatively assigned as 20-bromochlorin **FbC-T^{5}P^{15}Br^{20}**, was readily separated and isolated in ~6% yield. The small quantity obtained of the latter product precluded 2D NMR analysis, and the assignment of the structure remains provisional. This route constitutes a simple method for preparing 8-bromochlorins.

The regiochemistry of bromination of the chlorins was determined on the basis of 2D NMR spectroscopy (gCOSY and NOESY). The characteristic features of the ^{1}H NMR spectra of **FbC-Br^{7}M^{10}P^{15}**, **FbC-Br^{7}T^{10}P^{15}**, and **FbC-T^{5}Br^{8}P^{15}** include the following: (1) disappearance of two resonances (doublets) attributed to H^7 and H^8; and (2) appearance of a new singlet, attributed to H^8 (H^7 in the case of **FbC-T^{5}Br^{8}P^{15}**) at ~8.40−8.65 ppm. The full assignment of the ^{1}H NMR spectra for 7- and 8-substituted chlorins is provided in the Supporting Information. The identity of **FbC-Br^{7,8}P^{15}** was established by comparison of the ^{1}H NMR spectrum of the isolated product with that of **FbC-P^{15}**. The disappearance of resonances attributed to H^7 and H^8 was observed, whereas the chemical shifts of the other resonances remained unchanged.

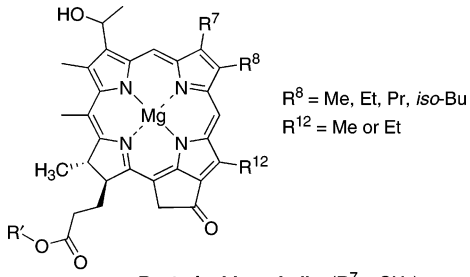
III. Spectroscopic Studies of Chlorins. The chlorins were characterized by absorption spectroscopy, LD-MS, FAB-MS, ^{1}H NMR spectroscopy, and, where permitted by solubility and sample size, ^{13}C NMR spectroscopy. The absorption spectra of the 7-substituted chlorins (in toluene at room temperature) are summarized in Table 1. For comparison, the spectral parameters also are listed for chlorophylls *a* and *b* (see Figure 1), the related chlorins bacteriochlorophylls *c* and *e*,[1,62] and the free base

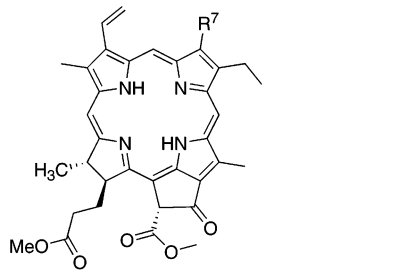
TABLE 1. Spectral Properties of Chlorins[a]

compound	λ_B (fwhm) in nm	λ_{Q_y} (fwhm) in nm	I_B/I_{Q_y}[b]	$\Delta\nu$ (cm^{-1})[c]
chlorophyll *a*[d]	429 (39)	661 (17)	1.29	0
chlorophyll *b*[d]	453 (22)	642 (16)	2.84	448
Bchl *c*[e]	433	663	1.54	0
Bchl *e*[e]	462	649	3.78	325
ZnC-T^{10}	405 (13)	605 (12)	4.1	0
ZnC-Br^{7}T^{10}	410 (14)	603 (12)	3.2	55
ZnC-E^{7}T^{10}	421 (14)	605 (12)	5.6	0
ZnC-A^{7}T^{10}	426 (18)	598 (13)	6.2	194
ZnC-F^{7}T^{10}	428 (19)	598 (13)	6.6	194
Me Pheo *a*[f]	411	668	2.08	0
Me Pheo *b*[f]	436	655	4.92	297
FbC-T^{10}	405 (34)	635 (9)	2.8	0
FbC-Br^{7}T^{10}	407 (34)	635 (9)	3.8	0
FbC-E^{7}T^{10}	415 (35)	639 (10)	4.5	−99
FbC-A^{7}T^{10}	420 (17)	634 (11)	9.1	25

[a] In toluene at room temperature unless noted otherwise. [b] Ratio of the intensities of the B and Q_y bands. [c] The spectral shift of the Q_y band relative to that of the corresponding benchmark compound (chlorophyll *a*, bacteriochlorophyll *c*, **ZnC-T^{10}**, methyl pheophorbide *a*, or **FbC-T^{10}**). A negative value indicates a bathochromic shift; a positive value indicates a hypsochromic shift. [d] In diethyl ether.[2] [e] Bacteriochlorophyll in acetone.[62] [f] Methyl pheophorbide in THF.[63,64]

CHART 2





chlorins methyl pheophorbides[63] *a* and *b* (Chart 2). The latter are free base analogues of chlorophylls *a* and *b* wherein the phytyl ester has been converted to a methyl ester.

The presence of the 7-substituents examined herein causes a change of the position of the absorption bands in the blue region (B band) and in the red region (Q_y band). In general, the 7-substituents cause a bathochromic shift of the B band and a hypsochromic shift of the Q_y band. This is the same trend observed for chlorophyll *b* versus chlorophyll *a*, and bacteriochlorophyll *c* versus bacteriochlorophyll *e*, though the magnitude of the effect is less pronounced for the synthetic chlorins

(62) Porra, R. J. In *Chlorophylls and Bacteriochlorophylls. Biochemistry, Biophysics, Functions and Applications*; Grimm, B., Porra, R. J., Rüdiger, W., Scheer, H., Eds.; Springer: Dordrecht, The Netherlands; pp 95−107.

(63) Hynninen, P. H.; Lötjönen, S. *Synthesis* **1980**, 539−541.

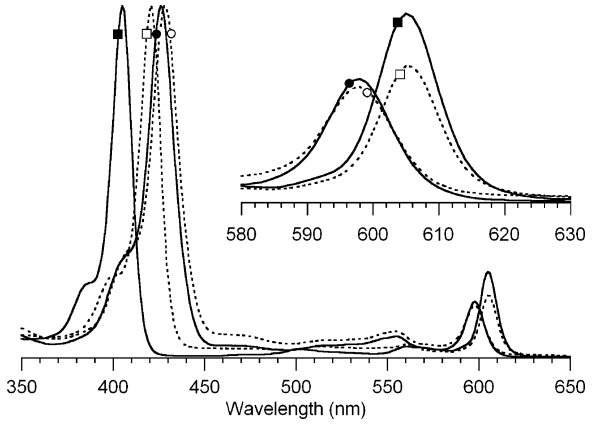


FIGURE 2. Absorption spectra (normalized) in toluene at room temperature of **ZnC-T^{10}** (solid square), **ZnC-E^{7}T^{10}**(open square), **ZnC-A^{7}T^{10}** (solid circle), and **ZnC-F^{7}T^{10}** (open circle).

examined here. By contrast, the presence of the same types of substituents at the 3- or 13-position causes a bathochromic shift of both the B band and the Q_y band.[9] Relatively few other chlorins bearing 7-substituents are available for systematic comparison, given that the known 7-conjugating substituents other than formyl include carboxylic acid,[37] carbomethoxy,[41] vinyl,[49] imine,[50,51] and cyano.[65] The presence of an ammonium point charge at the 7-position also has been examined.[52] The absorption spectra of the **ZnC-T^{10}** series of compounds are shown in Figure 2 (see the Supporting Information for additional spectra).

The major observations concerning the synthetic chlorins prepared herein are as follows:

(1) A 7-TIPS-ethynyl group causes a bathochromic shift of 16 nm in the B band region [**ZnC-E^{7}T^{10}** (421 nm) versus **ZnC-T^{10}** (405 nm)], whereas the position of the Q_y band is unchanged [**ZnC-E^{7}T^{10}** (605 nm) versus **ZnC-T^{10}** (605 nm)]. This behavior is different from that of the 13-substituted chlorin **ZnC-M^{10}E^{13}** (M = mesityl) where the presence of the ethynyl groups causes a bathochromic shift of both the B and Q_y bands (413, 627 nm).

(2) The presence of the acetyl group at the 7-position causes a bathochromic shift of 21 nm of the B band [**ZnC-A^{7}T^{10}** (426 nm) versus **ZnC-T^{10}** (405 nm)], whereas the Q_y band was shifted hypsochromically [**ZnC-A^{7}T^{10}** (598 nm) versus **ZnC-T^{10}** (605 nm)]. The I_B/I_{Q_y} ratio increased from 4.1 to 6.2.

(3) In the case of 7-formylchlorin **ZnC-F^{7}T^{10}**, the B and Q_y bands appear at 428 and 598 nm, respectively. Similar to that of the 7-acetyl group, here also there occurred a bathochromic shift of the B band, a hypsochromic shift of the Q_y band, and an increase in the I_B/I_{Q_y} ratio (from 4.1 to 6.6).

Finally, the spectrum of the 7-formylchlorin **ZnC-F^{7}T^{10}** (or 7-acetylchlorin **ZnC-A^{7}T^{10}**) can be compared with that of analogous 13-substituted chlorins bearing a 10-aryl group. The 13-formylchlorin **ZnC-M^{10}F^{13}** (or 13-acetylchlorin **ZnC-M^{10}A^{13}**) exhibits principal absorption bands at 418 and 634 nm (or 418 and 632 nm) and I_B/I_{Q_y} ratio of 2.2 (or 2.2).[12,23] Thus, moving the formyl (or acetyl) group from the 13-position to the 7-position results in a 36 nm (or 34 nm) hypsochromic shift of the Q_y band, a 10 (or 8) nm bathochromic shift of the B band, and much greater relative absorption of the B versus Q_y band [I_B/I_{Q_y} ratio = 6.6 (or 6.2)]. These results indicate the strong dependence of the substitution site at the perimeter of the chlorin macrocycle for a given auxochrome to elicit a given spectral change.

Outlook

Two complementary routes have been developed to gain access to 7-substituted chlorins. The first route employs reaction of a bromo-substituted Eastern half with a Western half to give the 7-bromochlorin. The second route employs 7-bromination of a 10,15-diarylchlorin. The former route is synthetically more demanding than the latter but has broader scope owing to the lack of requirements for substituents at the 10- and 15-positions. The presence of carbonyl substituents (acetyl, formyl) at the 7-position causes a bathochromic shift of the B band and a hypsochromic shift of the Q_y band. However, the magnitude of both shifts was substantially less than that observed in the naturally occurring chlorophylls. The latter possess a keto group (in the isocyclic ring) and a vinyl group that are positioned in conjugation with the chromophore along the *y*-axis (which bisects rings A and C). The magnitude of the shift also was less than that observed in the naturally occurring bacteriochlorophylls *c* and *e*, which contain the isocyclic ring but not the vinyl group. Realizing the full magnitude of the spectral difference observed due to 7-methyl versus 7-formyl substituents in the natural compounds likely may also require the presence of the keto-bearing isocyclic ring.

We note that, in a simple chlorin lacking any substituents, the 7- and 8-positions are identical owing to their positions on opposite sides of the mirror plane that includes the *x*-axis of the molecule and that bisects rings B and D; however, in chlorophylls or other chlorins that bear an unsymmetrical pattern of substituents, a substituent at the 7- versus 8-position is not necessarily expected to cause identical effects. Further study with synthetic analogues is required to delineate this issue. Regardless, the zinc chelate of the 7-formylchlorin (**ZnC-F^{7}T^{10}**) or 7-acetylchlorin (**ZnC-A^{7}T^{10}**) already results in a Q_y band positioned at 598 nm, which is shorter than that for any synthetic zinc chlorin prepared to date. The zinc chlorin (**ZnC**) lacking any substituents other than the 18,18-dimethyl group in the reduced ring absorbs at 603 nm,[22] and the corresponding chlorin with a single aryl group (e.g., **ZnC-T^{10}**) absorbs at 605 nm. In conjunction with other synthetic chlorins that we have prepared, the long-wavelength absorption band can now be tuned with fine precision from 598 to 667 nm (zinc chlorins) or 633 to 687 nm (free base chlorins).[12,22,24]

Experimental Section

2-(4-Methylbenzoyl)pyrrole (2). Following a general procedure,[58] a solution of pyrrole (2.20 g, 33.0 mmol) in THF (35 mL) under argon was treated with MesMgBr (33 mL, 1.0 M THF solution) for 15 min. The solution was cooled to −78 °C. Then a solution of Mukaiyama reagent **1** (8.00 g, 16.6 mmol) in THF (17 mL) was added. The reaction mixture was stirred at −78 °C for 20 min followed by room temperature for 20 min. Then the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl. The resulting mixture was extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated. The resulting solid was chromatographed [silica, hexanes/CH_2Cl_2/ethyl acetate (8:1:1)] to give a yellow solid (2.19 g, 71%): mp 120−121 °C (dec) [lit.[59] mp 118−119 °C]; ^{1}H NMR δ 2.43 (s, 3H), 6.33−6.40 (m, 1H), 6.84−6.90 (m, 1H), 7.10−7.20 (m, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz,

(64) Dixon, J. M.; Taniguchi, M.; Lindsey, J. S. *Photochem. Photobiol.* **2005**, *81*, 212−213.
(65) Nichol, A. W. *J. Chem. Soc. (C)* **1970**, 903−910.

2H), 9.66 (br s, 1H); ^{13}C NMR δ 21.6, 98.5, 120.4, 124.9, 129.3, 129.4, 131.2, 135.0, 143.3, 184.1. Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.83; H, 6.02; N, 7.32.

4-Bromo-2-(4-methylbenzoyl)pyrrole (3). Following a procedure for bromination of acyldipyrromethanes,[8] a solution of **2** (1.5 g, 8.1 mmol) in dry THF (32 mL) at −78 °C under argon was treated portionwise with NBS (1.4 g, 8.1 mmol). The reaction mixture was stirred for 1 h at −78 °C. Hexanes was added to the reaction mixture at −20 °C. The reaction mixture was then allowed to warm to 0 °C. Ethyl acetate was added. The organic layer was washed with water, dried (Na_2SO_4), and concentrated. The resulting brown solid was purified by column chromatography [silica, hexanes/CH_2Cl_2/ethyl acetate (9:0.5:0.5 then 7:2:1)] to afford a yellow solid (1.32 g, 62%): mp 172−174 °C (dec); ^{1}H NMR δ 2.34 (s, 3H), 6.85−6.91 (m, 1H), 7.09−7.19 (m, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 9.62 (br s, 1H); ^{13}C NMR δ 21.8, 98.4, 120.4, 124.9, 129.3, 129.4, 131.2, 135.0, 143.3, 184.2. Anal. Calcd for $C_{12}H_{10}BrNO$: C, 54.57; H, 3.82; N, 5.30. Found: C, 54.53; H, 3.77; N, 5.24.

2-Bromo-9-decylthio-5-*p*-tolyldipyrromethane (5). A solution of **3** (305 mg, 1.15 mmol) in dry THF/methanol (22 mL, 10:1) at 0 °C was treated with $NaBH_4$ (655 mg, 17.2 mmol). The mixture was stirred for 2 h. Water was added, and the resulting mixture was extracted with ethyl acetate. The organic layer was separated, dried (Na_2SO_4), and concentrated to dryness. The resulting residue was dissolved in toluene (11.6 mL), whereupon decylthiopyrrole **4** (246 mg, 1.15 mmol) was added. The solution was treated with $InCl_3$ (25.4 mg, 0.115 mmol) at room temperature. The reaction was monitored by TLC [silica, hexanes/ethyl acetate (3:1)]. After 30 min, the reaction mixture was quenched by addition of 1 M NaOH. The resulting mixture extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated. The resulting residue was purified by column chromatography [silica, hexanes/CH_2Cl_2/ethyl acetate (9.5:0.25:0.25 then 9.0:0.5:0.5)] to afford a yellow oil (469 mg, 83%): ^{1}H NMR δ 0.88 (t, J = 7.2 Hz, 3H), 1.25−1.32 (m, 14H), 1.46−1.52 (m, 2H), 2.34 (s, 2H), 2.58 (t, J = 7.2 Hz, 2H), 5.33 (s, 1H), 5.88−5.88 (m, 1H), 5.89−5.93 (m, 1H), 6.25−6.28 (m, 1H), 6.67−6.68 (m, 1H), 7.06 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.85 (br s, 2H); ^{13}C NMR δ 14.3, 21.2, 22.8, 28.6, 29.4, 29.5, 29.7, 29.8, 30.1, 32.1, 38.2, 43.9, 96.4, 109.3, 110.1, 116.9, 117.2, 119.4, 128.2, 128.4, 129.6, 129.7, 133.3, 134.4, 137.3, 137.8. Anal. Calcd for $C_{26}H_{35}BrN_2S$: C, 64.05; H, 7.24; N, 5.75. Found: C, 64.14; H, 7.44; N, 5.62.

2-Bromo-5-*p*-tolyldipyrromethane (7). A solution of **3** (178 mg, 0.674 mmol) in dry THF/methanol (11 mL, 10:1) at 0 °C was treated with $NaBH_4$ (383 mg, 10.1 mmol). The mixture was stirred for 2 h. Water was added, and the resulting mixture was extracted with ethyl acetate. The organic layer was separated, dried (Na_2SO_4), and concentrated. The resulting crude solid was dissolved in 1,4-dioxane (8.5 mL), whereupon pyrrole (748 μL, 10.7 mmol) was added. The solution was treated with 10% aqueous HCl (850 μL), and the mixture was stirred for 15−20 min at room temperature. The formation of dipyrromethane was monitored by TLC [silica, hexanes/ethyl acetate (3:1)]. After 20 min, the reaction mixture was diluted with ethyl acetate. Saturated aqueous $NaHCO_3$ was added. The mixture was washed with water. The organic layer was separated, dried (K_2CO_3), and concentrated. The resulting residue was purified by column chromatography [silica, hexanes/CH_2Cl_2/ethyl acetate (9:0.5:0.5 then 8:1:1)] to afford a brown oil (112 mg, 52%): ^{1}H NMR (THF-d_8) δ 2.28 (s, 3H), 5.28 (s, 1H), 5.64−5.66 (m, 2H), 5.92−5.94 (m, 1H), 6.58−6.62 (m, 2H), 7.05 (s, 4H), 9.74 (br s, 1H), 10.00 (br s, 1H); ^{13}C NMR (THF-d_8) δ 21.2, 44.9, 95.7, 107.8, 108.1, 110.3, 117.9, 118.0, 129.3, 129.6, 133.4, 135.8, 136.7, 141.0; FAB-MS obsd 314.0432, calcd 314.0419 ($C_{16}H_{15}BrN_2$). Note: Careful handling of the solution of compound **7** is required. All of the workup operations including solvent removal should be done without heating, and preferably under chilled conditions.

Zn(II)-7-Bromo-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (ZnC-Br^{7}T^{10}) from 5 + 6. Following a streamlined procedure,[10] a solution of **5** (201 mg, 0.412 mmol) and **6** (90.0 mg, 0.412 mmol) in anhydrous CH_2Cl_2 (12 mL) was treated with a solution of *p*-TsOH·H_2O (392 mg, 2.06 mmol) in anhydrous methanol (3 mL) under argon. The resulting red reaction mixture was stirred at room temperature for 50 min. A sample of 2,2,6,6-tetramethylpiperidine (0.700 mL, 4.12 mmol) was added. The reaction mixture was concentrated. The resulting solid was dissolved in CH_3CN (41 mL) and subsequently treated with 2,2,6,6-tetramethylpiperidine (1.75 mL, 10.3 mmol), $Zn(OAc)_2$ (1.13 g, 6.18 mmol), and AgOTf (318 mg, 1.24 mmol). The resulting suspension was refluxed for 20 h exposed to air. The crude mixture was filtered through a pad of silica (CH_2Cl_2). The filtrate was chromatographed [silica, hexanes then hexanes/CH_2Cl_2 (1:2)] to afford a green solid (17.8 mg, 7.6%): ^{1}H NMR δ 1.99 (s, 6H), 2.67 (s, 3H), 4.46 (s, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 8.49 (s, 1H), 8.53 (s, 1H), 8.56 (d, J = 4.4 Hz, 1H), 8.61 (s, 1H), 8.65 (d, J = 4.4 Hz, 1H), 8.67 (d, J = 4.4 Hz, 1H), 9.00 (d, J = 4.4 Hz, 1H), 9.61 (s, 1H); LD-MS obsd 570.2; FAB-MS obsd 570.0416, calcd 570.0398 ($C_{29}H_{23}BrN_4Zn$); λ_{abs} 410, 603 nm.

Zn(II)-7-Bromo-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (ZnC-Br^{7}T^{10}) from 7 + 6. Following a streamlined procedure,[10] a solution of **7** (90.0 mg, 0.285 mmol) in dry THF (3.0 mL) at −78 °C under argon was treated portionwise with NBS (51.0 mg, 0.285 mmol). The reaction mixture was stirred for 1 h at −78 °C. The cooling bath was removed, and the reaction mixture was then allowed to warm to 0 °C. Hexanes was added, and the minimum amount of ethyl acetate was used to transfer the reaction mixture to a separatory funnel. The mixture was washed with ice-cold water. The organic layer was separated, dried (K_2CO_3), and concentrated. (Note: All of the workup operations including solvent removal should be done without heating, and preferably under chilled conditions.) The resulting crude dibromodipyrromethane (**7-α-Br**) was dissolved in anhydrous CH_2Cl_2 (4.0 mL), whereupon compound **6** (62.2 mg, 0.285 mmol) was added. The solution was treated with a solution of *p*-TsOH·H_2O (271 g, 1.42 mmol) in anhydrous methanol (1.0 mL) under argon. The resulting red reaction mixture was stirred at room temperature for 40 min. A sample of 2,2,6,6-tetramethylpiperidine (0.607 mL, 3.55 mmol) was added. The reaction mixture was concentrated. The resulting yellow solid was dissolved in CH_3CN (28.5 mL) and subsequently treated with 2,2,6,6-tetramethylpiperidine (1.22 mL, 7.12 mmol), $Zn(OAc)_2$ (784 mg, 4.27 mmol), and AgOTf (220 mg, 0.855 mmol). The resulting suspension was refluxed for 14 h exposed to air. The crude mixture was filtered through a pad of silica (CH_2Cl_2). The filtrate was chromatographed [silica, hexanes/CH_2Cl_2 (2:1→1:1→1:2)] to afford a green solid (68.2 mg, 41%): ^{1}H NMR δ 1.99 (s, 6H), 2.67 (s, 3H), 4.46 (s, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 8.49 (s, 1H), 8.53 (s, 1H), 8.56 (d, J = 4.4 Hz, 1H), 8.61 (s, 1H), 8.65 (d, J = 4.4 Hz, 1H), 8.67 (d, J = 4.4 Hz, 1H), 9.00 (d, J = 4.4 Hz, 1H), 9.61 (s, 1H); ^{13}C NMR δ 21.7, 31.1, 45.5, 50.4, 94.7, 97.4, 106.9, 116.5, 123.6, 127.2, 127.7, 127.9, 129.6, 133.7, 133.8, 133.9, 137.4, 139.0, 142.8, 145.9, 146.3, 146.4, 153.8, 154.7, 160.0, 171.8; LD-MS obsd 570.2; FAB-MS obsd 570.0416, calcd 570.0398 ($C_{29}H_{23}BrN_4Zn$); λ_{abs} 410, 603 nm.

7-Bromo-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (FbC-Br^{7}T^{10}). A solution of **ZnC-Br^{7}T^{10}** (9.60 mg, 0.0167 mmol) in CH_2Cl_2 (1.0 mL) was treated dropwise with TFA (40.0 μL, 0.485 mmol) over a 2 min period. The solution was stirred at room temperature for 3 h. CH_2Cl_2 was added. The mixture was washed with saturated aqueous $NaHCO_3$, water, and brine. The organic layer was separated, dried (Na_2SO_4), and concentrated. The resulting residue was chromatographed [silica, hexanes then hexanes/CH_2Cl_2 (1:1)] to afford a greenish-purple solid (7.3 mg, 87%): ^{1}H NMR δ −2.25 (br s, 1H), −1.94 (br s, 1H), 2.05 (s, 6H), 2.69 (s, 3H), 4.61 (s, 2H), 7.54 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 8.66 (s, 1H), 8.78−8.82 (m, 2H), 8.89 (s, 1H), 8.94 (dd, J = 4.4, 2.0 Hz, 1H), 9.00 (s, 1H), 9.27 (dd, J = 4.4, 2.0 Hz, 1H), 10.02 (s,

1H); ^{13}C NMR (75 MHz) δ 21.7, 31.3, 46.7, 52.1, 94.6, 97.3, 104.8, 120.6, 121.7, 123.8, 123.9, 127.9, 129.1, 129.3, 132.4, 134.1, 134.5, 135.4, 137.7, 138.4, 140.1, 141.6, 146.8, 150.5, 163.6, 176.1; LD-MS obsd 508.9; FAB-MS obsd 508.1257, calcd 508.1263 ($C_{29}H_{25}BrN_4$); λ_{abs} 408, 634 nm.

7-Acetyl-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (FbC-A^{7}T^{10}). Following a procedure for Stille coupling with chlorins,[9] a mixture of **FbC-Br^{7}T^{10}** (8.20 mg, 0.0161 mmol), tributyl(1-ethoxyvinyl)tin (22 μL, 0.064 mmol), and $(PPh_3)_2PdCl_2$ (2.26 mg, 0.00322 mmol) was refluxed in THF (1.5 mL) for 18 h in a Schlenk line. The reaction mixture was treated with 10% aqueous HCl (0.5 mL) at room temperature for 2 h. CH_2Cl_2 was added, and the organic layer was separated. The organic layer was washed with saturated aqueous $NaHCO_3$, water, and brine. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed [silica, hexanes/CH_2Cl_2 (1:1)] to afford a purple solid (5.3 mg, 69%): ^{1}H NMR (THF-d_8) δ $-$1.77 (br s, 1H), $-$1.41 (br s, 1H), 2.03 (s, 6H), 2.68 (s, 3H), 2.92 (s, 3H), 4.58 (s, 2H), 7.58 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 7.6 Hz, 2H), 8.72 (d, J = 4.4 Hz, 1H), 8.80 (d, J = 4.4 Hz, 1H), 8.92 (s, 1H), 8.42$-$8.43 (s, 1H + d, 1H, overlapped), 9.04 (s, 1H), 9.33 (d, J = 4.4 Hz, 1H), 10.96 (s, 1H); ^{13}C NMR δ 21.7, 30.0, 31.1, 46.7, 51.8, 94.2, 96.9, 109.3, 109.4, 123.81, 123.85, 124.3, 127.9, 129.6, 131.3, 134.1, 135.4, 135.9, 137.8, 138.3, 138.4, 141.2, 143.1, 147.9, 148.0, 164.4, 177.5, 197.6; LD-MS obsd 472.1; FAB-MS obsd 472.2275, calcd 472.2263 ($C_{31}H_{28}N_4O$); λ_{abs} 420, 634 nm.

13-Acetyl-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (FbC-A^{7}T^{10}). A solution of **ZnC-Br^{7}T^{10}** (17.5 mg, 0.0305 mmol) in CH_2Cl_2 (2.0 mL) was treated dropwise with TFA (71 μL, 0.92 mmol). The solution was stirred at room temperature for 3 h. CH_2Cl_2 was added, and the organic layer was washed with saturated aqueous $NaHCO_3$, water, and brine. The organic layer was separated, dried (Na_2SO_4), and concentrated. The resulting crude solid was used in the next step. Following a procedure for Stille coupling,[9] a mixture composed of the crude sample of **FbC-Br^{7}T^{10}**, tributyl(1-ethoxyvinyl)tin (41.2 μL, 0.122 mmol), and $(PPh_3)_2PdCl_2$ (4.30 mg, 0.00610 mmol) was refluxed in THF (2.0 mL) for 18 h in a Schlenk line. The reaction mixture was treated with 10% aqueous HCl (1.1 mL) at room temperature for 2 h. CH_2Cl_2 was added, and the organic layer was separated. The organic layer was washed (saturated aqueous $NaHCO_3$, water, and brine), dried (Na_2SO_4), and concentrated. The residue was chromatographed [silica, hexanes/CH_2Cl_2 (1:1)] to afford a purple solid (9.6 mg, 66%). The characterization data (^{1}H NMR, LD-MS, FAB-MS, UV$-$vis) were consistent with those for the product obtained as described in the stepwise procedure.

Zn(II)-7-Acetyl-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (ZnC-A^{7}T^{10}). A solution of **FbC-A^{7}T^{10}** (3.2 mg, 0.0068 mmol) in $CHCl_3$ (2.0 mL) was treated with a solution of $Zn(OAc)_2\cdot 2H_2O$ (22.3 mg, 0.101 mmol) in methanol (0.5 mL). The reaction mixture was stirred at room temperature for 16 h. The crude mixture was concentrated and chromatographed (silica, CH_2Cl_2) to afford a green solid (3.2 mg, 88%): ^{1}H NMR δ 2.02 (s, 6H), 2.65 (s, 3H), 3.05 (s, 3H), 4.52 (s, 2H), 7.55 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 8.69 (d, J = 4.4 Hz, 1H), 8.72$-$8.74 (s, 1H + d, 1H, overlapped), 8.84$-$8.85 (s, 1H + d, 1H, overlapped), 9.04 (s, 1H), 9.26 (d, J = 4.4 Hz, 1H), 10.92 (s, 1H); LD-MS obsd 534.2; FAB-MS obsd 534.1392, calcd 534.1398 ($C_{31}H_{26}N_4OZn$); λ_{abs} 426, 598 nm.

Zn(II)-17,18-Dihydro-18,18-dimethyl-10-*p*-tolyl-7-[2-(triisopropylsilyl)ethynyl]porphyrin (ZnC-E^{7}T^{10}). Following a general procedure,[9] samples of **ZnC-Br^{7}T^{10}** (20.1 mg, 0.0351 mmol) and triisopropylsilylacetylene (23.4 μL, 0.105 mmol) were coupled using $Pd_2(dba)_3$ (6.43 mg, 0.00702 mmol) and P(*o*-tol)$_3$ (13.8 mg, 0.0456 mmol) in toluene/TEA (5:1, 15 mL) at 60 °C under argon. After 22 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was chromatographed [silica, hexanes then hexanes/CH_2Cl_2 (1:1)] to afford a green solid (18.1 mg, 76%): ^{1}H NMR δ 1.35$-$1.38 (m, 21H), 1.99 (s, 6H), 2.68 (s, 3H), 4.45 (s, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.93 (d, J = 7.6 Hz, 2H), 8.46 (s, 1H), 8.53 (d, J = 4.4 Hz, 1H), 8.56 (s, 1H), 8.58 (s, 1H), 8.63 (d, J = 4.4 Hz, 1H), 8.65 (d, J = 4.4 Hz, 1H), 8.96 (d, J = 4.4 Hz, 1H), 9.76 (s, 1H); ^{13}C NMR δ 11.9, 18.8, 19.2, 21.7, 31.0, 45.5, 50.3, 94.4, 97.2, 97.6, 103.1, 107.1, 122.0, 124.4, 127.0, 127.7, 127.8, 131.4, 133.7, 133.8, 137.3, 139.2, 145.8, 146.46, 146.49, 147.6, 153.9, 155.0, 159.8, 171.9; LD-MS obsd 672.7; FAB-MS obsd 672.2626, calcd 672.2627 ($C_{40}H_{44}N_4SiZn$); λ_{abs} 421, 605 nm.

17,18-Dihydro-18,18-dimethyl-10-*p*-tolyl-7-[2-(triisopropylsilyl)ethynyl]porphyrin (FbC-E^{7}T^{10}). A solution of **ZnC-E^{7}T^{10}** (8.20 mg, 0.0122 mmol) in CH_2Cl_2 (1.0 mL) was treated dropwise with TFA (28.0 μL, 0.366 mmol) over a 2 min period. The solution was stirred at room temperature for 3 h. CH_2Cl_2 was added, and the organic layer was washed (saturated aqueous $NaHCO_3$ and water), dried (Na_2SO_4), and concentrated. The resulting solid was chromatographed [silica, hexanes then hexanes/CH_2Cl_2 (4:1)] to afford a green solid (6.1 mg, 82%): ^{1}H NMR δ $-$2.11 (br s, 1H), $-$1.71 (br s, 1H), 1.25$-$1.38 (m, 21H), 2.06 (s, 6H), 2.68 (s, 3H), 4.61 (s, 2H), 7.53 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 8.71 (s, 1H), 8.76$-$8.78 (m, 2H), 8.84 (s, 1H), 8.92 (d, J = 4.4 Hz, 1H), 8.97 (s, 1H), 9.21 (d, J = 4.4 Hz, 1H), 10.1 (s, 1H); LD-MS obsd 610.1; FAB-MS obsd 610.3496, calcd 610.3492 ($C_{40}H_{46}N_4Si$); λ_{abs} 415, 639 nm.

Zn(II)-7-Formyl-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (ZnC-F^{7}T^{10}). Following a procedure for CO-mediated formylation,[12] a mixture of **ZnC-Br^{7}T^{10}** (12.1 mg, 0.0211 mmol), $(PPh_3)_2PdCl_2$ (3.00 mg, 0.00422 mmol, 20 mol %), PPh_3 (1.10 mg, 0.00422 mmol, 20 mol %), and sodium formate (3.60 mg, 0.0527 mmol) was dried in a Schlenk flask for 1 h. DMF (1.6 mL) was added, and CO gas was bubbled through the reaction mixture for 2 h. Then, the reaction mixture was heated at 108 °C under a balloon containing CO for 24 h. The reaction mixture was allowed to cool to room temperature. The reaction mixture was treated with CH_2Cl_2 and water. The organic layer was separated, washed (water, brine), dried (Na_2SO_4), and concentrated. The resulting solid was chromatographed [silica, hexanes $\rightarrow$ hexanes/CH_2Cl_2 (1:2) $\rightarrow$ CH_2Cl_2] to afford the starting chlorin (32%) followed by the title compound as a green solid (4.1 mg, 37%): ^{1}H NMR δ 1.99 (s, 6H), 2.65 (s, 3H), 4.41 (s, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 8.40$-$8.46 (m, 3H), 8.46 (d, J = 4.4 Hz, 1H), 8.61 (d, J = 4.4 Hz, 1H), 8.75 (s, 1H), 8.98 (d, J = 4.4 Hz, 1H), 10.23 (s, 1H), 10.95 (s, 1H); ^{13}C NMR δ 21.6, 30.8, 31.1, 46.3, 50.9, 94.2, 97.3, 109.4, 128.1, 128.2, 129.6, 134.4, 134.5, 135.3, 135.5, 135.9, 138.0, 140.8, 144.5, 144.9, 147.5, 148.6, 149.4, 156.1, 157.6, 161.2, 174.0, 188.1; LD-MS obsd 520.1; FAB-MS obsd 520.1251, calcd 520.1242 ($C_{30}H_{24}N_4OZn$); λ_{abs} 428, 598 nm.

1-Formyl-5-*p*-tolyldipyrromethane (9a). Following a procedure for the formylation of dipyrromethanes,[16] a sample of **8a** (2.36 g, 10.0 mmol) in THF (20 mL) was treated with MesMgBr (20 mL, 1.0 M in THF). After 15 min, the reaction mixture was cooled to $-$78 °C. Phenyl formate was added (2.18 mL) in one portion. The reaction mixture was stirred at $-$78 °C for 1 h. The cooling bath was removed, and stirring was continued for 1 h. The reaction mixture was quenched by the addition of saturated aqueous NH_4Cl. The resulting mixture was extracted with CH_2Cl_2. The organic layer was washed (water, brine) and concentrated. The resulting dark oil was dissolved in CH_3CN (40 mL) and treated with 2 M aqueous NaOH (40 mL). The resulting mixture was stirred vigorously at room temperature for 1 h. Water was added, and the mixture was extracted with CH_2Cl_2. The organic phase was washed (saturated aqueous NH_4Cl, water, brine), dried (Na_2SO_4), and concentrated. The resulting residue was chromatographed [silica, hexanes then CH_2Cl_2/ethyl acetate (9:1)] to afford a yellow solid (0.958 g, 36%): mp 181$-$183 °C (dec); ^{1}H NMR δ 2.33 (s, 3H), 5.48 (s, 1H), 5.94$-$5.96 (m, 1H), 6.85$-$6.12 (m, 1H), 6.14$-$6.17 (m, 1H), 6.68$-$6.71 (m, 1H), 6.88$-$6.90 (m, 1H), 7.05 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 8.12 (br s, 1H), 9.30 (s, 1H), 9.44 (br s, 1H); ^{13}C NMR δ 21.2, 43.9, 107.9, 108.8, 110.9, 118.0,

122.4, 128.4, 129.8, 130.8, 132.4, 137.4, 137.5, 143.0, 178.8; FAB-MS obsd 264.1265, calcd 264.1263 ($C_{17}H_{16}N_2O$).

1-Formyl-5-pentyldipyrromethane (9b). A sample of DMF (10 mL) was treated with $POCl_3$ (1.50 mL, 16.4 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 10 min (Vilsmeier reagent). A solution of **8b** (2.00 g, 9.25 mmol) in anhydrous DMF (30 mL) was treated with the freshly prepared Vilsmeier reagent (6.97 mL, 11.4 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 1.5 h. The reaction mixture was poured slowly into an ice-cooled mixture of CH_2Cl_2 (50 mL) and 2 M aqueous NaOH (50 mL). The resulting mixture was stirred for 20 min, the organic layer was separated, and the water phase was extracted with CH_2Cl_2. The combined organic extract was washed (aqueous NH_4Cl, water, and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2 → CH_2Cl_2/ethyl acetate (5:1)] afforded a light-pink solid (0.632 g, 28%): mp 82−84 °C; ^{1}H NMR δ 0.83−0.87 (m, 3H), 1.24−1.31 (m, 6H), 2.03−2.05 (m, 2H), 4.07−4.10 (m, 1H), 6.04−6.05 (m, 1H), 6.12−6.14 (m, 1H), 6.18−6.20 (m, 1H), 6.68−6.70 (m, 1H), 6.95−6.96 (m, 1H), 8.78 (br s, 1H), 9.35 (s, 1H), 10.28 (br s, 1H); ^{13}C NMR δ 14.2, 22.6, 27.6, 31.8, 33.9, 38.4, 105.4, 108.2, 109.6, 117.5, 124.8, 132.0, 132.3, 146.9, 178.8. Anal. Calcd for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.47. Found: C, 73.58; H, 8.26; N, 11.38.

Zn(II)-17,18-Dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (ZnC-T^{10}). Following a streamlined procedure,[10] a solution of **9a** (310 mg, 1.17 mmol) in dry THF (12 mL) at −78 °C under argon was treated portionwise with NBS (209 mg, 1.17 mmol). The reaction mixture was stirred for 1 h at −78 °C. The cooling bath was removed, and the reaction mixture was allowed to warm to 0 °C. Ethyl acetate was added. The organic layer was washed with water, dried (Na_2SO_4), and concentrated. The resulting crude bromoformyldipyrromethane was used in the next reaction. The crude product was dissolved in anhydrous CH_2Cl_2 (32 mL), whereupon **10** (223 mg, 1.17 mmol) was added. The solution was treated with a solution of *p*-TsOH·H_2O (1.11 g, 5.87 mmol) in anhydrous methanol (8 mL) under argon. The resulting red reaction mixture was stirred at room temperature for 50 min. A sample of 2,2,6,6-tetramethylpiperidine (1.98 mL, 11.7 mmol) was added. The reaction mixture was concentrated. The resulting solid was dissolved in CH_3CN (117 mL) and subsequently treated with 2,2,6,6-tetramethylpiperidine (4.96 mL, 29.2 mmol), $Zn(OAc)_2$ (3.22 g, 17.5 mmol), and AgOTf (902 mg, 3.51 mmol). The resulting suspension was refluxed for 18 h exposed to air. The crude mixture was filtered through a pad of silica (CH_2Cl_2). The filtrate was chromatographed [silica, hexanes/CH_2Cl_2 (1:2)] to afford a green solid (212 mg, 37%): ^{1}H NMR (THF-d_8) δ 2.04 (s, 6H), 2.67 (s, 3H), 4.54 (s, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 7.6 Hz, 2H), 8.43 (d, J = 4.4 Hz, 1H), 8.57−8.63 (m, 4H), 8.73 (d, J = 4.4 Hz, 1H), 8.79 (d, J = 4.4 Hz, 1H), 9.04 (d, J = 4.4 Hz, 1H), 9.60 (s, 1H); ^{13}C NMR δ 21.7, 31.0, 45.4, 50.3, 94.2, 97.0, 109.4, 124.0, 126.7, 127.2, 127.6, 128.1, 129.2, 132.9, 133.3, 133.8, 137.1, 139.6, 145.8, 146.1, 146.4, 147.6, 153.1, 154.0, 159.1, 171.0; LD-MS obsd 492.3; FAB-MS obsd 492.1302, calcd 492.1292 ($C_{29}H_{24}N_4Zn$); λ_{abs} 405, 605 nm.

17,18-Dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (FbC-T^{10}). A solution of **ZnC-T^{10}** (65.3 mg, 0.133 mmol) in CH_2Cl_2 (3.5 mL) was treated dropwise with TFA (307 μL, 3.99 mmol) over a 3 min period. The solution was stirred at room temperature for 3 h. CH_2Cl_2 was added, and the organic layer was washed (saturated aqueous $NaHCO_3$ and water) and then dried (Na_2SO_4). The organic layer was concentrated and chromatographed [silica, hexanes then hexanes/CH_2Cl_2 (1:1)] to afford a purple solid (52.3 mg, 92%): ^{1}H NMR (300 MHz) δ −2.30 (br s, 1H), −1.92 (br s, 1H), 2.07 (s, 6H), 2.69 (s, 3H), 4.65 (s, 2H), 7.54 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 7.6 Hz, 2H), 8.67 (d, J = 4.4 Hz, 1H), 8.83 (br s, 2H), 8.90 (s, 1H), 8.96 (d, J = 4.4 Hz, 1H), 8.98 (d, J = 4.4 Hz, 1H), 9.03 (s, 1H), 9.24 (d, J = 4.4 Hz, 1H), 9.86 (s, 1H); LD-MS obsd 430.6; FAB-MS obsd 431.2222, calcd 431.2236 [$(M + H)^+$, M = $C_{29}H_{26}N_4$]; λ_{abs} 405, 635 nm.

15-Bromo-17,18-dihydro-18,18-dimethyl-10-*p*-tolylporphyrin (FbC-T^{10}Br^{15}). A solution of **FbC-T^{10}** (57.1 mg, 0.132 mmol) in THF (65 mL) was treated with NBS (23.6 mg, 0.132 mmol). The resulting mixture was stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2 (∼50 mL) and quenched by addition of saturated aqueous $NaHCO_3$. The organic layer was separated, dried (Na_2SO_4), and concentrated. Column chromatography of the resulting solid [silica, hexanes → hexanes/CH_2Cl_2 (1:1)] provided a trace amount of unidentified dibromochlorin (first fraction) followed by the title compound as a purple solid (41.2 mg, 61%): ^{1}H NMR δ −2.10 (br s, 1H), −1.94 (br s, 1H), 2.06 (s, 6H), 2.69 (s, 3H), 4.69 (s, 2H), 7.53 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.6 Hz, 2H), 8.61 (d, J = 4.4 Hz, 1H), 8.76 (d, J = 4.4 Hz, 1H), 8.83 (s, 1H), 8.88 (d, J = 4.4 Hz, 1H), 8.92 (d, J = 4.4 Hz, 1H), 9.19 (d, J = 4.4 Hz, 1H), 9.20 (d, J = 4.4 Hz, 1H), 9.73 (s, 1H); LD-MS obsd 508.9; FAB-MS obsd 508.1257, calcd 508.1263 ($C_{29}H_{25}BrN_4$); λ_{abs} 404, 642 nm.

Zn(II)-17,18-Dihydro-18,18-dimethyl-10-pentylporphyrin (ZnC-Pn^{10}). A solution of **9b** (0.244 g, 1.00 mmol) in THF (10 mL) was treated with NBS (0.178 g, 1.00 mmol) at −78 °C. The resulting mixture was stirred at −78 °C for 1 h, brought to ∼ −20 °C, and quenched by addition of hexanes/water (40 mL, 1:1). The resulting mixture was extracted with ethyl acetate. The organic extract was washed with water and brine, dried (Na_2SO_4), and concentrated to afford the crude 1-bromo-9-formyl-5-pentyldipyrromethane (0.302 g, 93%), which was used in the next step without further purification. A solution of crude 1-bromo-9-formyl-5-pentyldipyrromethane (0.162 g, 0.500 mmol) and Western half **10** (0.095 g, 0.50 mmol) in CH_2Cl_2 (10.8 mL) was treated with a solution of *p*-TsOH·H_2O (0.475 g, 2.50 mmol) in MeOH (8.25 mL) at room temperature. The resulting mixture was stirred at room temperature for 30 min, quenched by addition of 2,2,6,6-tetramethylpiperidine (0.630 mL, 3.71 mmol), and concentrated. The resulting yellow-brown solid was dissolved in CH_3CN (50 mL) and treated with 2,2,6,6-tetramethylpiperidine (2.10 mL, 12.4 mmol), $Zn(OAc)_2$ (1.37 g, 7.50 mmol), and AgOTf (0.385 g, 1.50 mmol). The resulting mixture was refluxed for 24 h and concentrated. The resulting black residue was chromatographed [silica, hexanes/CH_2Cl_2 (1:1)]. The green-violet fraction was collected and rechromatographed with protection from light [silica, hexanes/CH_2Cl_2/Et_3N (50:50:1)] to afford a green solid (61 mg, 26%). **ZnC-Pn^{10}** is rather unstable in solution and during routine handling. It is recommended to carry out the demetalation reaction immediately after purification of the Zn(II) complex. By contrast, **FbC-Pn^{10}** is much more stable. Data for the title compound: ^{1}H NMR (300 MHz) δ 0.97 (t, J = 7.4 Hz, 3H), 1.44−1.57 (m, 2H), 1.67−1.77 (m, 2H), 1.99 (s, 6H), 2.32−2.42 (m, 2H), 4.43 (s, 2H), 4.51−4.56 (m, 2H), 8.47 (s, 1H), 8.51 (s, 1H), 8.56 (d, J = 4.2 Hz, 1H), 8.66 (d, J = 4.2 Hz, 1H), 8.75 (d, J = 4.2 Hz, 1H), 8.96 (d, J = 4.2 Hz, 1H), 8.98 (d, J = 4.2 Hz, 1H), 9.19 (d, J = 4.2 Hz, 1H), 9.39 (s, 1H); ^{13}C NMR δ 14.14, 23.0, 31.1, 33.1, 35.3, 37.7, 45.5, 50.3, 93.9, 96.6, 109.3, 124.6, 126.0, 126.8, 127.3, 128.3, 130.1, 133.1, 145.8, 145.9, 146.1, 147.4, 152.8, 154.4, 158.7, 171.2; LD-MS obsd 472.4; FAB-MS obsd 472.1600, calcd 472.1605 ($C_{27}H_{28}N_4Zn$); λ_{abs} 405, 604 nm.

17,18-Dihydro-18,18-dimethyl-10-pentylporphyrin (FbC-Pn^{10}). Following a reported procedure,[11] a sample of **ZnC-Pn^{10}** (80 mg, 0.17 mmol) in CH_2Cl_2 (70 mL) was treated with TFA (1.30 mL). The resulting mixture was stirred at room temperature for 1 h and then neutralized by addition of excess Et_3N (5 mL). The resulting mixture was concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (1:1)] to afford a green solid (57 mg, 81%): ^{1}H NMR δ −2.19 (br s, 1H), −1.76 (br s, 1H), 0.95 (t, J = 7.2 Hz, 3H), 1.47−1.56 (m, 2H), 1.70−1.77 (m, 2H), 2.01 (s, 6H), 2.42−2.50 (m, 2H), 4.56 (s, 2H), 4.76−4.78 (m, 2H), 8.81 (s, 1H), 8.82−8.83 (m, 1H), 8.86−8.87 (m, 1H), 8.91 (s, 1H), 9.01 (d, J = 4.4 Hz, 1H), 9.15−9.16 (m, 1H), 9.24 (d, J = 4.4 Hz, 1H), 9.34−9.35 (m, 1H), 9.75 (s, 1H); ^{13}C NMR δ 14.4, 23.0, 31.3, 33.0, 34.9, 37.9, 46.5, 52.0, 93.8, 96.5, 107.1, 122.5, 123.1, 123.6, 125.4, 128.5, 129.1, 132.9, 133.9, 135.4, 139.3, 141.4, 150.2, 153.0, 162.4, 175.6;

LD-MS obsd 410.1; FAB-MS obsd 411.2547, calcd 411.2543 [(M + H)$^+$, M = $C_{27}H_{30}N_4$]; λ_{abs} 394, 636 nm.

15-Bromo-17,18-dihydro-18,18-dimethyl-10-pentylporphyrin (FbC-Pn^{10}Br^{15}). A solution of **FbC-Pn^{10}** (69.4 mg, 0.169 mmol) in THF (85 mL) was treated with NBS (1.69 mL, 0.100 M in THF). The resulting reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and quenched by addition of saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The organic extract was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography (silica, hexanes/CH_2Cl_2 (5:2)] provided an unidentified dibromochlorin (first fraction, purple-brown) and **FbC-Pn^{10}Br^{15}** (second fraction, purple-brown). Data for the title compound: purple-brown solid; 44 mg (54%); ^{1}H NMR (300 MHz) δ −2.19 (br s, 1H), −1.76 (br s, 1H), 0.94−0.99 (m 3H), 1.49−1.56 (m, 2H), 1.70−1.80 (m, 2H), 2.02 (s, 6H), 2.40−2.48 (m, 2H), 4.64 (s, 2H), 4.75−4.80 (m, 2H), 8.72 (s, 1H), 8.84−8.86 (m, 1H), 8.93 (d, J = 4.4 Hz, 1H), 9.12−9.13 (m, 1H), 9.23 (d, J = 4.4 Hz, 1H), 9.25−9.27 (m, 1H), 9.33−9.34 (m, 1H), 9.64 (s, 1H); LD-MS 488.4; FAB-MS obsd 489.1652, calcd 489.1648 ($C_{27}H_{29}N_4Br$); λ_{abs} 401, 642 nm.

17,18-Dihydro-18,18-dimethyl-10-pentyl-15-phenylporphyrin (FbC-Pn^{10}P^{15}). Samples of **FbC-Pn^{10}Br^{15}** (41.9 mg, 0.0856 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (176 mg, 0.862 mmol), $Pd(PPh_3)_4$ (30.0 mg, 0.026 mmol), and K_2CO_3 (94 mg, 0.68 mmol) were placed in a Schlenk flask. The flask was pumped-purged with argon three times. A degassed mixture of toluene/DMF (3:1, 8.5 mL) was added. The resulting mixture was stirred at 90−95 °C for 20 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated. The crude product was dissolved in CH_2Cl_2 and chromatographed [silica, hexanes/CH_2Cl_2 (1:1)] to afford a trace amount of putative **PdC-Pn^{10}P^{15}** (first fraction, blue-violet) and a second fraction (brown). The latter was concentrated and rechromatographed [silica, hexanes/CH_2Cl_2 (2:1)] to afford a brown-violet solid (34 mg, 82%): ^{1}H NMR δ −2.12 (br s, 1H), −1.96 (br s, 1H), 0.93−0.96 (m, 3H), 1.48−1.53 (m, 2H), 1.71−1.75 (m, 2H), 1.94 (s, 6H), 2.40−2.47 (m, 2H), 4.14 (s, 2H), 4.78−4.82 (m, 2H), 7.70−7.71 (m, 3H), 7.88−7.90 (m, 2H), 8.28 (d, J = 4.4 Hz, 1H), 8.80 (s, 1H), 8.88 (d, J = 4.4 Hz, 1H), 9.00 (d, J = 4.4 Hz, 1H), 9.16 (d, J = 4.4 Hz, 1H), 9.24 (d, J = 4.4 Hz, 1H), 9.26 (d, J = 4.4 Hz, 1H), 9.71 (s, 1H); ^{13}C NMR (75 MHz) δ 14.4, 23.0, 31.4, 33.0, 35.4, 38.0, 46.2, 52.4, 94.1, 106.4, 112.0, 123.5, 123.6, 123.7, 124.7, 127.6, 128.1, 128.3, 129.5, 132.68, 132.73, 134.7, 134.9, 140.1, 141.2, 143.8, 151.1, 152.8, 161.8, 175.6; LD-MS obsd 486.7; FAB-MS obsd 487.2866, calcd 487.2856 [(M + H)$^+$, M = $C_{33}H_{34}N_4$); λ_{abs} 399, 641 nm.

17,18-Dihydro-18,18-dimethyl-15-phenyl-10-*p*-tolylporphyrin (FbC-T^{10}P^{15}). Following a reported procedure,[11] samples of **FbC-T^{10}Br^{15}** (32 mg, 0.063 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (130 mg, 0.637 mmol), $Pd(PPh_3)_4$ (22.2 mg, 0.0192 mmol), and K_2CO_3 (70 mg, 0.51 mmol) were placed in a Schlenk flask. The flask was pumped-purged with argon three times. A degassed mixture of toluene/DMF (3:1, 6.3 mL) was added. The resulting mixture was stirred at 90−95 °C for 19 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated. The crude product was chromatographed [silica, CH_2Cl_2/hexanes (1:1)]. The first fraction (blue, trace) was discarded, and the second (green-brown) was concentrated and rechromatographed [silica, hexanes/CH_2Cl_2 (3:2)] to afford a green-purple solid (25 mg, 79%): ^{1}H NMR (300 MHz) δ −2.14 (br s, 1H), −1.96 (br s, 1H), 1.96 (s, 6H), 2.66 (s, 3H), 4.17 (s, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.67−7.72 (m, 3H), 7.86−7.88 (m, 2H), 7.99 (d, J = 7.8 Hz, 2H), 8.24 (d, J = 4.6 Hz, 1H), 8.63 (d, J = 4.6 Hz, 1H), 8.67 (d, J = 4.4 Hz, 1H), 8.89 (s, 1H), 8.91−8.92 (m, 2H), 9.17 (d, J = 4.2 Hz, 1H), 9.77 (s, 1H); ^{13}C NMR δ 21.8, 31.5, 46.3, 52.4, 95.1, 104.2, 112.9, 122.7, 123.8, 124.5, 127.8, 128.3, 128.6, 129.1, 132.6, 132.9, 134.1, 135.1, 135.3, 137.7, 138.8, 140.9, 141.4, 143.3, 147.8, 150.4, 160.2, 176.1; LD-MS obsd 506.3; FAB-MS obsd 506.2462, calcd 506.2470 ($C_{35}H_{30}N_4$); λ_{abs} 410, 641 nm.

17,18-Dihydro-18,18-dimethyl-10-mesityl-15-phenylporphyrin (FbC-M^{10}P^{15}). Samples of **FbC-M^{10}Br^{15}** (38.7 mg, 0.0720 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (150 mg, 0.735 mmol), $Pd(PPh_3)_4$ (25.5 mg, 0.0221 mmol), and K_2CO_3 (80 mg, 0.58 mmol) were placed in a Schlenk flask. The flask was pump-purged with argon three times. A degassed mixture of toluene/DMF (3:1, 7.3 mL) was added. The resulting mixture was stirred at 90−95 °C for 19 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated. Column chromatography [silica, hexanes/CH_2Cl_2 (2:1)] afforded a trace of putative **PdC-M^{10}P^{15}** [first fraction (blue) and a second fraction (green)]. The latter was rechromatographed twice [first column: silica, hexanes/CH_2Cl_2 (3:1); second column: silica, hexanes/toluene (1:2)] to afford a green solid (23.8 mg, 62%): ^{1}H NMR δ −2.10 to −1.90 (br, 2H), 1.84 (s, 6H), 1.98 (s, 6H), 2.60 (s, 3H), 4.20 (s, 2H), 7.23 (s, 2H), 7.65−7.72 (m, 3H), 7.90−7.92 (m, 2H), 8.21 (d, J = 4.4 Hz, 1H), 8.44 (d, J = 4.4 Hz, 1H), 8.50 (d, J = 4.4 Hz, 1H), 8.88 (d, J = 4.4 Hz, 1H), 8.90 (s, 1H), 8.94 (d, J = 4.4 Hz, 1H), 9.20 (d, J = 4.4 Hz, 1H), 9.76 (s, 1H); ^{13}C NMR (75 MHz) δ 21.5, 21.7, 31.5, 46.2, 52.4, 94.7, 106.5, 112.2, 120.9, 123.7, 123.9, 126.8, 127.6, 127.8, 128.0, 128.1, 129.0, 131.6, 132.6, 132.7, 134.4, 135.1, 137.6, 138.5, 139.3, 140.4, 140.7, 143.4, 152.0, 152.4, 162.4, 175.2; LD-MS obsd 534.6; FAB-MS obsd 535.2857, calcd 535.2856 ($C_{37}H_{34}N_4$); λ_{abs} 411, 640 nm.

7-Bromo-17,18-dihydro-18,18-dimethyl-10-mesityl-15-phenylporphyrin (FbC-Br^{7}M^{10}P^{15}). A solution of **FbC-M^{10}P^{15}** (14.5 mg, 0.0271 mmol) in THF (13.5 mL) was treated with NBS (0.270 mL, 0.100 M in THF). The resulting reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (~50 mL) and quenched by addition of saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The organic extract was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography [silica, hexanes/CH_2Cl_2 (2:3)] provided an unidentified dibromochlorin (first fraction, red-brown) and a second fraction (green-brown). The latter was rechromatographed [silica, hexanes/CH_2Cl_2 (2:1)] to afford a brown solid (11 mg, 66%): ^{1}H NMR δ −2.02 (br s, 1H), −1.92 (br s, 1H), 1.83 (s, 6H), 1.97 (s, 6H), 2.59 (s, 3H), 4.18 (s, 2H), 7.22 (s, 2H), 7.68−7.70 (m, 3H), 7.88−7.89 (m, 2H), 8.19 (d, J = 4.6 Hz, 1H), 8.43 (s, 1H), 8.48 (d, J = 4.6 Hz, 1H), 8.88 (s, 1H), 8.93 (d, J = 4.6 Hz, 1H), 9.23 (d, J = 4.6 Hz, 1H), 9.92 (s, 1H); ^{13}C NMR δ 21.4, 21.5, 31.4, 46.3, 52.4, 95.0. 104.0, 112.7, 120.9, 121.0, 124.0, 124.3, 127.4, 127.7, 127.9, 128.2, 128.8, 131.6, 132.6, 134.4, 135.5, 137.9, 138.0, 139.3, 141.0, 141.4, 143.2, 148.0, 150.2, 163.0, 175.9; LD-MS obsd 612.8; FAB-MS obsd 613.1958, calcd 613.1961 [(M + H)$^+$, M = $C_{37}H_{33}N_4Br$]; λ_{abs} 411, 640 nm.

7-Bromo-17,18-dihydro-18,18-dimethyl-15-phenyl-10-*p*-tolylporphyrin (FbC-Br^{7}T^{10}P^{15}). A solution of **FbC-T^{10}P^{15}** (19 mg, 0.038 mmol) in THF (19 mL) was treated with NBS (0.375 mL, 0.100 M in THF). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (~30 mL) and quenched by the addition of saturated aqueous $NaHCO_3$. The organic phase was separated, washed with water and brine, dried (Na_2SO_4), and concentrated. The resulting brown solid was chromatographed [silica, hexanes/CH_2Cl_2 (1:1)]. The first fraction (purple-brown) was collected and rechromatographed [silica, hexanes/CH_2Cl_2 (3:2)]. The first fraction (pink-brown) was discarded, and the second (pink-purple-brown) was concentrated to provide a purple-brown solid (14 mg, 63%): ^{1}H NMR δ −2.12 (br s, 1H), −1.96 (br s, 1H), 1.96 (s, 6H), 2.66 (s, 3H), 4.17 (s, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.68−7.70 (m, 3H), 7.86−7.92 (m, 2H), 7.96 (d, J = 7.8 Hz, 2H), 8.22 (d, J = 4.4 Hz, 1H), 8.61 (s, 1H), 8.64 (d, J = 4.4 Hz, 1H), 8.89 (s, 1H), 8.93 (d, J = 4.4 Hz, 1H), 9.24 (d, J = 4.4 Hz, 1H), 9.96 (s, 1H); ^{13}C NMR δ 21.7, 31.4, 46.3, 52.4, 95.0, 104.2, 112.8, 120.4, 122.7, 123.7, 124.4, 127.7, 128.2, 128.6, 129.0, 132.6, 132.8, 134.1, 135.0, 135.3, 137.7, 138.8, 140.9, 141.4,

143.2, 147.7, 150.3, 163.1, 176.1 (the resonance of one carbon is apparently overlapped with another); LD-MS obsd 584.2; FAB-MS obsd 585.1648, calcd 585.1648 [$(M + H)^+$, M = $C_{35}H_{29}N_4Br$]; λ_{abs} 412, 639 nm.

15-Bromo-17,18-dihydro-18,18-dimethyl-5-*p*-tolylporphyrin (FbC-T^{5}Br^{15}). A solution of **FbC-T^5** (72.0 mg, 0.167 mmol) in THF (67 mL) was treated with NBS (1.67 mL, 0.100 M in THF). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (~50 mL) and quenched by the addition of aqueous $NaHCO_3$. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The organic extract was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography [silica, hexanes/CH_2Cl_2 (1:1)] afforded a trace amount of an unidentified dibromochlorin (first fraction, pink-brown) and the title compound (second fraction, brown). Data for the title compound: purple-violet crystals (52.8 mg, 62%); ^{1}H NMR δ −2.23 (br s, 1H), −1.68 (br s, 1H), 2.02 (s, 6H), 2.66 (s, 3H), 4.63 (s, 2H), 7.51 (d, J = 7.8 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 8.62 (d, J = 4.2 Hz, 1H), 8.82 −8.83 (m, 3H), 8.91 (d, J = 4.2 Hz, 1H), 9.11−9.12 (m, 1H), 9.17−9.18 (m, 1H), 9.77 (s, 1H); ^{13}C NMR δ 21.8, 31.8, 46.6, 54.7, 95.4, 95.7, 109.2, 121.9, 123.9, 125.1, 128.0, 128.6, 129.0, 132.4, 133.4, 134.2, 134.3, 136.8, 137.6, 138.5, 139.1, 140.7, 150.8, 154.4, 163.0, 175.7; LD-MS obsd 508.5; FAB-MS obsd 509.1336, calcd 509.1335 [$(M + H)^+$, M = $C_{29}H_{25}N_4Br$]; λ_{abs} 403, 642 nm.

17,18-Dihydro-18,18-dimethyl-15-phenyl-5-*p*-tolylporphyrin (FbC-T^{5}P^{15}). Samples of **FbC-T^{5}Br^{15}** (48.6 mg, 0.095 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (198 mg, 0.971 mmol), $Pd(PPh_3)_4$ (30.6 mg, 0.0264 mmol), and K_2CO_3 (106 mg, 0.769 mmol) were placed in a Schlenk flask. The flask was pump-purged with argon three times. A degassed mixture of toluene/DMF (3:1, 9.6 mL) was added. The resulting mixture was stirred at 90−95 °C for 19 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated. The crude product was chromatographed [silica, CH_2Cl_2/hexanes (2:3)], which afforded three fractions. The first fraction (blue, trace) was discarded, the second contained the title compound (violet), and third contained debrominated byproduct (green, ~4 mg, **FbC-T^5**). Data for the title compound: violet-purple crystals (30.8 mg, 64%); ^{1}H NMR δ −2.12 (s, 1H), −1.62 (s, 1H), 1.97 (s, 6H), 2.67 (s, 3H), 4.23 (s, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.68−7.73 (m, 3H), 7.91−7.94 (m, 2H), 8.05 (d, J = 7.6 Hz, 2H), 8.38−8.40 (m, 1H), 8.68 (d, J = 4.2 Hz, 1H), 8.85−8.89 (m, 2H), 8.92 (s, 1H), 8.95 (d, J = 4.2 Hz, 1H), 9.07−9.09 (m, 1H), 9.83 (s, 1H); ^{13}C NMR δ 21.7, 31.6, 46.4, 52.1, 95.3, 107.9, 111.9, 121.7, 123.3, 124.1, 127.7, 127.9, 128.1, 128.21, 128.25, 132.2, 132.6, 132.8, 134.2, 134.4, 136.0, 137.4, 138.7, 140.2, 141.0, 142.6, 150.9, 153.3, 163.1, 174.2; LD-MS 506.5, FAB-MS obsd 507.2543, calcd 507.2543 [$(M + H)^+$, M = $C_{35}H_{30}N_4$]; λ_{abs} 411, 641 nm.

8-Bromo-17,18-dihydro-18,18-dimethyl-15-phenyl-5-*p*-tolylporphyrin (FbC-T^{5}Br^{8}P^{15}). A solution of **FbC-T^{5}P^{15}** (28.7 mg, 0.0566 mmol) in THF (23 mL) was treated with NBS (0.566 mL, 0.100 M in THF). The resulting mixture was stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2 (~50 mL) and quenched by the addition of saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The organic extract was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography [silica, hexanes/CH_2Cl_2 (3:2)] provided a trace amount of an unidentified dibromochlorin (first fraction, purple), a mixture of two products (second fraction, brown), and unreacted starting material (third fraction, violet). The second fraction was concentrated and rechromatographed [silica, 4.5 diameter × 40 cm, hexanes/CH_2Cl_2 (2:1)] to afford a trace of discarded material (first fraction, pink), the title compound (second fraction, pink-brown), and a second product tentatively assigned as **FbC-T^{5}P^{15}Br^{20}** (third fraction, pink, ~2 mg). Data for the title compound: violet crystals, 21.6 mg (65%); ^{1}H NMR δ −2.02 (br s, 1H), −1.64 (br s, 1H), 1.97 (s, 6H), 2.68 (s, 3H), 4.22 (s, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.69−7.75 (m, 3H), 7.91−7.93 (m, 2H), 8.02 (d, J = 7.8 Hz, 2H), 8.40−8.41 (m, 1H), 8.66 (s, 1H), 8.82−8.87 (m, 2H), 8.91 (s, 1H), 9.14−9.16 (m, 1H), 10.01 (s, 1H); ^{13}C NMR δ 21.7, 31.5, 46.4, 52.1, 95.6, 105.3, 112.3, 120.9, 121.6, 123.9, 124.4, 127.8, 128.0, 128.3, 128.8, 129.0, 132.3, 132.7, 134.3, 134.5, 135.8, 137.7, 138.2, 140.6, 141.6, 142.3, 146.7, 150.9, 164.0, 174.9; LD-MS obsd 585.0, FAB-MS obsd 585.1651, calcd 585.1648 [$(M + H)^+$, M = $C_{35}H_{29}N_4Br$]; λ_{abs} 414, 639 nm.

7,8-Dibromo-17,18-dihydro-18,18-dimethyl-15-phenylporphyrin (FbC-Br^{7,8}P^{15}). A solution of **FbC-P^{15}** (9.1 mg, 0.022 mmol) in THF (11 mL) was treated with NBS (0.440 mL, 0.100 M in THF). The resulting mixture was stirred for 30 min at room temperature. The reaction mixture was diluted with CH_2Cl_2 (~20 mL) and quenched by the addition of saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The organic extract was washed with water and brine, dried (Na_2SO_4), and concentrated. The resulting solid was dissolved in a minimal amount of CH_2Cl_2 and chromatographed [silica, hexanes/CH_2Cl_2 (1:1)]. The first fraction (brown) was collected and rechromatographed [silica, hexanes/CH_2Cl_2 (3:1)] to afford a brown solid (3.9 mg, 31%): ^{1}H NMR −2.41 (br s, 1H), −2.33 (br s, 1H), 1.99 (s, 6H), 4.22 (s, 2H), 7.72−7.78 (m, 3H), 7.90−7.92 (m, 2H), 8.41−8.42 (m, 1H), 8.97 (s, 1H), 8.98−9.01 (m, 1H), 9.17−9.18 (m, 1H), 9.27−9.28 (m, 1H), 9.95 (s, 1H), 10.01 (s, 1H); LD-MS obsd 572.2, FAB-MS obsd 573.0277, calcd 573.0284 [$(M + H)^+$, M = $C_{28}H_{22}N_4Br_2$]; λ_{abs} 406, 635 nm. Note that the small amount and low solubility of **FbC-Br^{7,8}P^{15}** prevented the recording of a ^{13}C NMR spectrum.

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Supporting Information Available: Synthesis of three dipyrromethanes as part of exploratory studies; streamlined synthesis of **ZnC-T^5**; crystallographic data for **ZnC-Br^{7}T^{10}**; complete ^{1}H NMR assignments for selected 7-substituted chlorins; and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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