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Strongly Conjugated Hydroporphyrin Dyads: Extensive Modification of Hydroporphyrins' Properties by Expanding the Conjugated System

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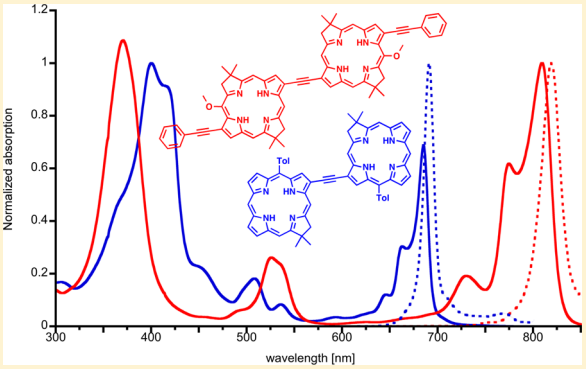
Supporting Information

ABSTRACT: We report the synthesis and basic photophysical characterization of strongly conjugated hydroporphyrin (chlorin and bacteriochlorin) dyads. Hydroporphyrins are connected at their respective 13 (β) or 15 (*meso*) positions by ethynyl or butadiynyl linkers. Synthesis entails a series of palladium-catalyzed reactions, starting from appropriate bromobacteriochlorin or bromochlorin. Strong conjugation in the dyads results in a significant bathochromic shift of longest-wavelength (Q_y-like) band, which in case of the 13−13′ ethynyl-linked bacteriochlorin dyad is positioned past 800 nm. The Q_y-like band is broad and split for the 13−13′ linked chlorin and bacteriochlorin dyads. All dyads exhibit an intense, relatively narrow fluorescence emission band in nonpolar solvents. Bacteriochlorin dyads exhibit a strong dependence of fluorescence intensity on the solvent polarity, which results in more than 10-fold quenching of fluorescence in dimethylformamide. The assembling of hydroporphyrins into strongly conjugated arrays represents an efficient means to tune and expand their optical and photochemical properties, which should greatly broaden the properties attainable for these chromophores.



INTRODUCTION

The expansion of the conjugated π-system in porphyrins is an established way to modify their electronic, spectral, photochemical, and redox properties.[1] An efficient way to expand the π-system in porphyrins is their assembly into strongly conjugated arrays, i.e., arrays where subunits are connected by a linker (most commonly ethynyl or butadiynyl) that assures a strong electronic conjugation between macrocycles. Strong conjugation significantly alters the electronic structure of linked chromophores, so that the properties of the resulting supermolecule are substantially different than a simple sum of properties of its components.

Strongly conjugated porphyrin arrays have been studied extensively;[1−48] in particular, the effects of the position of the linker attachment,[2,3] types of conjugated linker,[2,8,19] the number of porphyrins in the arrays,[12,20] the electronic nature of substituents on the porphyrinic subunits,[6] and conformations of the array[3,18,24,30] on the properties of resulting arrays have been studied in detail. Various physicochemical properties of strongly conjugated porphyrin arrays have been thoroughly investigated, including emission[3,10,12] and electrochemical properties,[6,8,11] ultrafast excited state dynamics,[4,14] excited state singlet[12] and triplet states[5,16] absorption, triplet state energies,[28] triplet-state EPR spectra,[5] third-order electronic polarizability,[21] two-photon absorption properties,[15,22−27,34,39−43,46] and singlet oxygen photosensitization properties.[34,35] A key finding from these studies is that arrangement of porphyrins into strongly conjugated arrays results in strong perturbation of their electronic properties. Such perturbations stem in part from delocalization of porphyrins' frontier molecular orbitals (e.g., HOMO, LUMO, HOMO−1, LUMO+1) over the entire molecule. The strength of electronic interactions between porphyrins and, consequently, the degree of the electronic perturbation depend on both the type of the linker connecting porphyrin subunits[8,19] and the position of linker attachment.[2,3] As a result, the variety of physicochemical properties of the arrays are substantially different than those of their components. In particular, the strongly conjugated porphyrin dyads exhibit much stronger red or even near-infrared (near-IR) absorption and more intense emission than simple porphyrin monomers.[12] The long wavelength absorption bands show significant bathochromic and hyperchromic shift (λ ~700−850 nm, with extinction coefficient ε up to 230,000 M^{-1} cm^{-1}) and fluorescence quantum yield Φ_f up to 0.22.[12] Strongly conjugated porphyrin

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arrays also exhibit strong singlet−singlet[12] and triplet−triplet[5,16] excited state absorption, large hyperpolarizabilities,[21] and increased two-photon absorption cross-section.[15,22−27,34,39−43] The latter property has been utilized in the design of two-photon photosensitizers for photodynamic therapy.[34,42,43,46−48] Strongly conjugated porphyrin arrays also have been proposed for use as molecular wires,[29,31,36,38] near-IR fluorophores for fluorescence imaging,[7,9,13] and fluorescent probes for intracellular viscosity[33] and membrane stress.[17]

Contrary to broadly studied strongly conjugated porphyrin arrays, corresponding hydroporphyrin arrays have been explored much less extensively. Hydroporhyrins (Chart 1) differ from fully unsaturated porphyrins by having one (chlorins) or two (bacteriochlorins) saturated C−C bonds in the core macrocycle. Hydroporphyrins are particularly interesting, since they constitute the chlorophylls and bacteriochlorophylls, the key pigments of the photosynthetic apparatus in plants and bacteria, respectively.[49] Optical and photochemical properties of chlorins and bacteriochlorins differ markedly from those of porphyrins. For example, the reduced symmetry of hydroporphyrins results in stronger and bathochromically shifted long wavelength absorption bands.[50,51]

Optical, photochemical, and redox properties of hydroporphyrins make them particularly attractive for numerous biomedical and energy-related applications.[52−54] The variety of applications of hydroporphyrins require extensive modifications of these properties. The established methods for tuning electronic, absorption, photochemical, and redox properties of hydroporphyrins are (a) substitution on the periphery of the macrocycle,[55−58] (b) chelation of metal cations by the macrocycle,[56,57,59] and (c) installation of an additional five- or six-membered exocyclic ring on the macrocycle periphery.[58,60−63] These approaches allow controlling the absorption and emission maxima, redox potentials, and to some extent, fluorescence and intersystem-crossing quantum yields. However, certain properties are very difficult to achieve for bacteriochlorins utilizing the above-mentioned strategies. For example, for near-IR fluorescence *in vivo* imaging there is an urgent need for brightly fluorescent probes with emission wavelength longer than 800 nm. The currently available long-wavelength absorbing bacteriochlorins (bacteriopurpurini-

Chart 1. Generic Structures of Porphyrin, Chlorin, and Bacteriochlorin Macrocycles

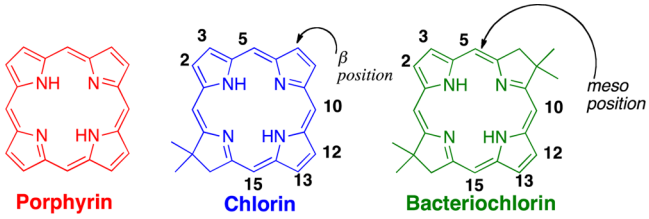

Chart 2. Structures of Target Strongly Conjugated Dyads Studied in This Paper

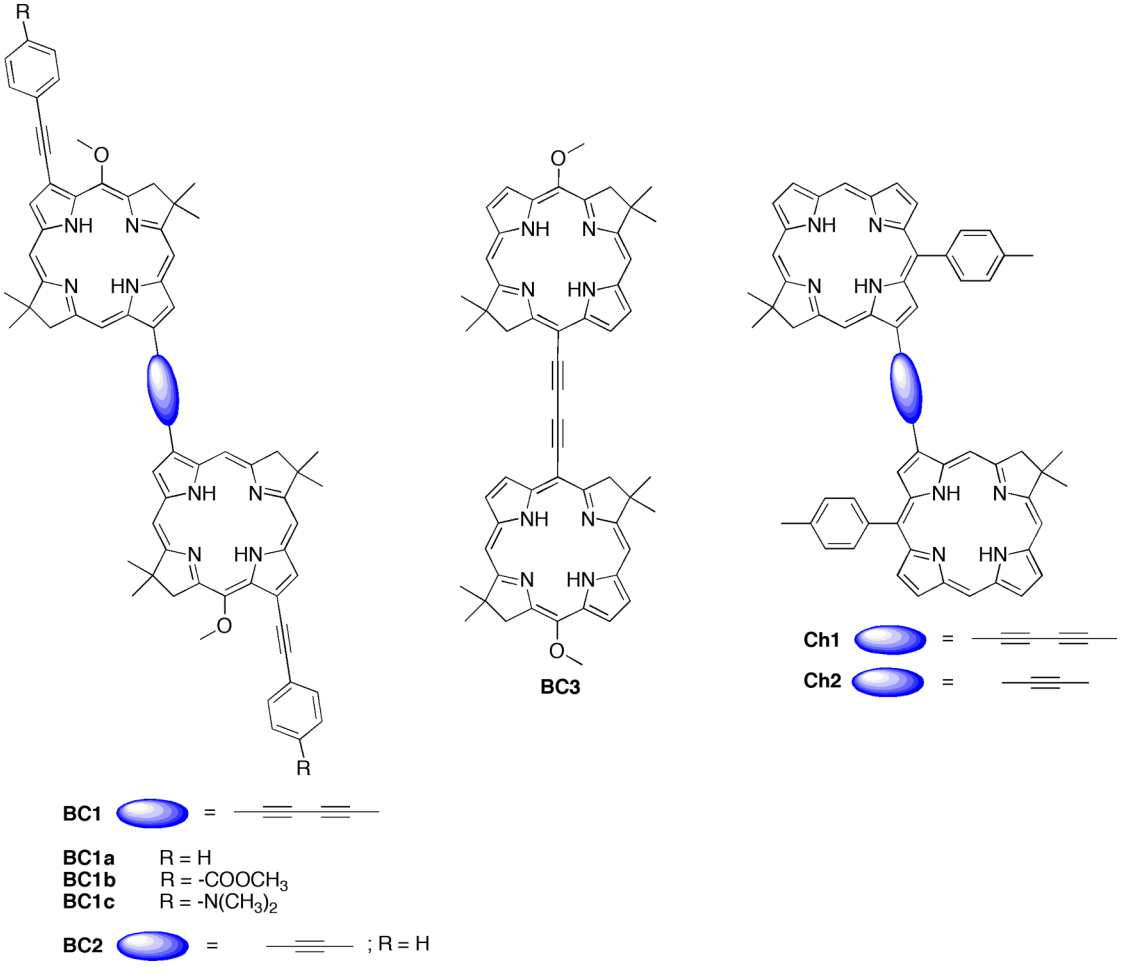

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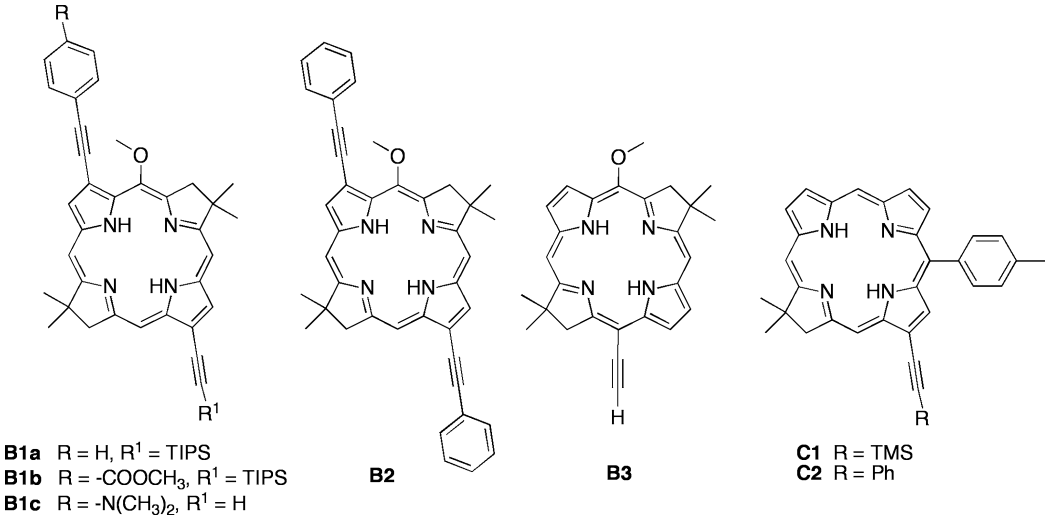
Chart 3. Structures of the Benchmark Monomers Studied in This Paper



mides) exhibit a rather low quantum yield of fluorescence (typically ~0.05 or less).[58,60,63]

To further expand the range of properties attainable for hydroporphyrins and means for fine-tuning these properties, we have embarked on a program of study of highly conjugated hydroporphyrin arrays. Our hypothesis is that, similar to porphyrins, assembly of hydroporphyrins into strongly conjugated arrays will affect their properties much more extensively than simple substitution. Unlike porphyrin arrays, strongly conjugated hydroporphyrin arrays have been far less examined. Wasielewski studied the energy hopping rates in 20−20′ connected chlorins.[64−67] Tamiaki reported the synthesis of a series of 3,3′ connected chlorins with butadiyne linker, together with their absorption and emission characteristic.[68,69] Arnold reported a synthesis of a series of strongly conjugated nickel chlorin and nickel chlorin−nickel porphyrin arrays.[45] Smith,[70,71] Wasielewski,[72,73] and Pandey,[74] studied vinyl-linked chlorin dyads. To the best of our knowledge, there are no reports on analogous types of strongly conjugated bacteriochlorin arrays. This article presents the synthesis and basic photophysical (absorption and fluorescence spectra and fluorescence quantum yields) studies of chlorin−chlorin and bacteriochlorin−bacteriochlorin dyads. Particularly we have focused on bacteriochlorin arrays, as there is no a prior report on such systems. The results provide a foundation for more detailed examination of these properties and exploitation of these systems for a variety of applications.

RESULTS AND DISCUSSIONS

Design. We have designed a series of strongly conjugated hydroporhyrins architectures, which ultimately allow us to examine the influence of several structural factors on the properties of resulting arrays (Chart 2). Each dyad is composed of two identical hydroporphyrin subunits. As bacteriochlorin and chlorin subunits we have chosen fully synthetic macrocycles, which reproduce the essential spectroscopic, photochemical, electronic, and redox properties of the natural photosynthetic pigments[56−58,60,62] and exhibit greater stability toward oxidation and greater synthetic flexibility than naturally occurring hydroporphyrin.

To probe the effect of the position of the linker attachment, we designed sets of bacteriochlorin dyads with a common butadiyne linker attached at the 13−13′ (**BC1**) and 15−15′ (**BC3**) positions of bacteriochlorin monomers (Chart 2). The butadiyne linker has been chosen because of the synthetic simplicity. In order to probe the effect of the electronic nature of substituents on the properties of resulting dyads, butadiyne $\beta-\beta$ linked dyads have been prepared with electron-withdrawing methoxycarbonyl (**BC1b**) and electron-donating dimethylamino (**BC1c**) groups on the phenylacetylene substiutuents. To examine the effect of the type of the conjugated linker between hydroporphyrins, we also prepared the dyad **BC2** in which the hydroporphyrins are connected by an ethynyl linker at their respective 13 positions. For comparison we also prepared strongly conjugated chlorin dyads **Ch1** with a butadiyne linker, analogous to **BC1**, and **Ch2**, with an ethynyl linker, analogous to **BC2**. As benchmark monomers we examined the corresponding bacteriochlorins or chlorins possessing sets of substituents identical to those in the dyads (Chart 3). Thus, bacteriochlorins **B1a−c** serve as benchmarks for dyads **BC1a−c**, **B2** for **BC2**, **B3** for **BC3**, **C1** for **Ch1**, and **C2** for **Ch2**.

Synthesis. *Bacteriochlorin Dyads.* Syntheses of the bacteriochlorin dyads are outlined in Schemes 1−3. Recently we have developed a concise method for preparation of 3,13-nonsymmetrically substituted 5-methoxybacteriochlorins.[75] This method is of key importance for the preparation of $\beta-\beta$ linked dyads. Thus, reaction of 3,13-dibromo-5-methoxybacteriochlorin **1**[73] with TIPS-protected acetylene, in the presence of $Pd(PPh_3)_4$ and K_2CO_3 as a base provides 13-substituted-3-bromobacteriochlorin **2** in 37% yield (Scheme 1). We found that reaction of **1** with TIPS-acetylene is more sluggish than corresponding reactions with aryl-substituted acetylenes reported previously[75] and provides three products: unreacted starting material, 13-desbromobacteriochlorin, and **2**. The yields of reaction also varied significantly from trial to trial (21−44%, the yield 37% reported above represents the most typical yield obtained for numerous trials). The attempts to improve the outcome of the reaction failed. Nevertheless, we were able to isolate the desired compound in sufficient quantity for the next steps.

Initially, we intended to prepare dyads **BC1a−c** by installation of desired substituents on an intermediate dyad with bromine substituents at 3,3′ positions. Thus, *in situ* deprotection of **2** with TBAF and subsequent palladium-

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mediated homocoupling of terminal acetylene-substituted bacteriochlorin provides the butadiyne-linked dibromodyad, with 53% yield (see Scheme S2 of Supporting Information for details). Subsequent attempts for derivatization of the dibromodyad by Sonogashira coupling led to decomposition of the starting material, and desired products could not be isolated. Therefore, we pursued an alternative route, which entails the second Sonogoshira coupling reaction on **2** to yield the corresponding 3,13-disubstituted bacteriochlorins **B1a** and **B1b** in 82% and 77% yield, respectively (Scheme 1). In the case of **B1c** we found difficulties in purification of the TIPS-protected product, due to the coincidentally similar polarities of unreacted 4-ethynyl-*N*,*N*-dimethylaniline and TIPS-protected **B1c**, which precluded separation of the two species via column chromatography. Therefore, we performed deprotection of the crude reaction mixture, using TBAF in THF. The resulting deprotected bacteriochlorin **B1c** could be easily purified and was obtained in 74% overall yield.

The butadiynyl-linked dyads **BC1a–c** have been prepared by employing Cu-free palladium-mediated homocoupling of acetylene-substituted bacteriochlorins.[68,69] The latter were prepared by *in situ* deprotection of TIPS-acetylene-substituted bacteriochlorins with TBAF. Using $Pd(PPh_3)_2Cl_2$ (50 or 100 mol %) in THF/Et_3N (2:1) afforded final dyads in 60–73% yield.

Synthesis of ethyne-linked dyad **BC2** is outlined in Scheme 2. The key step is regioselective Sonogashira coupling of dibromobacteriochlorin **1** with 13-acetylene-substituted bacteriochlorin **3** (obtained by deprotection of **B1a** with TBAF), which afforded 3-phenylacetylene-3′-bromodyad **4** in 63% yield (a small amount of the product of homocoupling of **3** was also detected in the crude reaction mixture). Subsequent Sonogashira coupling of **4** with phenylacetylene provides final dyad **BC2** in 89% yield.

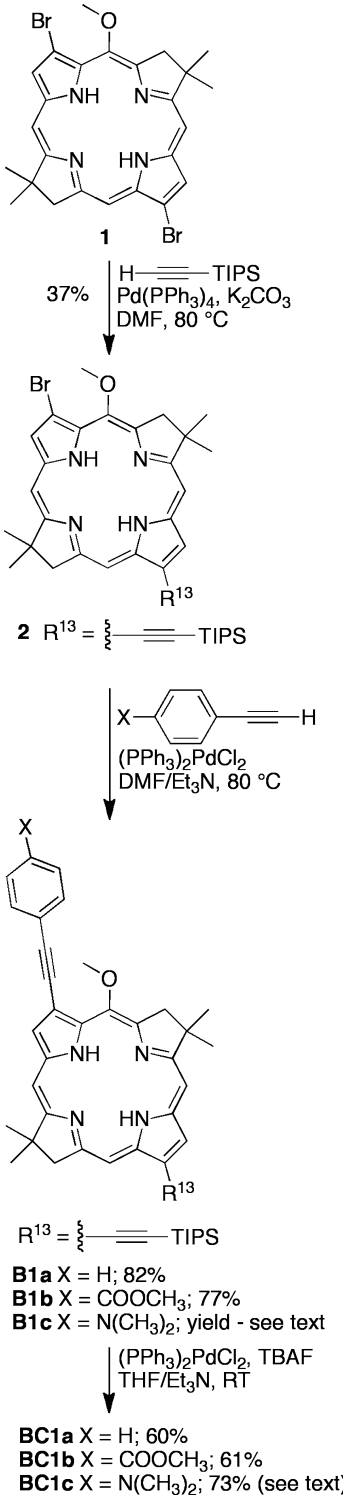
Synthesis of *meso–meso* butadiyne-linked dyad **BC3** (Scheme 3) has been achieved starting from 15-bromo-5-methoxybacteriochlorin **5**, obtained by regioselective bromination of 5-methoxybacteriochlorin[76] (the starting 5-methoxybacteriochlorin was synthesized via debromination of **1**; see Scheme S1 of Supporting Information for details). A subsequent sequence of Sonogashira coupling and deprotection reaction afforded 15-acetylene-substituted bacteriochlorin **B3**. The intermediate TIPS-protected derivative of **B3** could not be purified. Subsequent homocoupling of **B3** under conditions identical as described for **BC1a-c**, afforded the target dyad **BC3** in 65% yield.

Synthesis of Benchmark Monomers. The benchmark monomers **B1a-c** and **B3** are the intermediates in the syntheses of the respective dyads, and their preparation is described above. Benchmark **B2** was prepared by Sonogashira coupling of dibromobacteriochlorin **1** with phenylacetylene in 77% yield (Scheme 4).

Synthesis of Chlorin Dyads. For the synthesis of 13–13′ linked dyads we utilized 13-bromochlorin **6** as the key building block (Schemes 5 and 6). 13-Bromochlorin **6** was synthesized from the tetrahydrodipyrrin and 1,2-dibromo-9-formyldipyrromethene, following the reported procedure for analogous chlorins (see Supporting Information for details).[61,77]

The Sonogashira reaction of **6** with TMS-protected acetylene afforded **C1** in 76% yield, and subsequent removal of TMS group upon treatment with K_2CO_3 in THF/MeOH solution afforded acetylene-substituted chlorin **7** in 83% yield (Scheme 5). The butadiyne-linked dyads **Ch1** was obtained by

Scheme 1



homocoupling of acetylene-substituted chlorin **7** in 66% yield. **Ch2** was subsequently metalated with zinc acetate in $CHCl_3$/MeOH mixture, to provide the corresponding zinc complex **ZnCh2** in 48% yield. The ethynyl-linked dyad **Ch2** was synthesized by Sonogashira reaction of 13-ethynylchlorin **7** with 13-bromochlorin **6** in 35% yield (Scheme 6, the homocoupling product **Ch1** was also isolated in this reaction in 12% yield). The 13-phenylacetylene-substituted benchmark chlorin **C2** was obtained by Sonogoshira reaction of phenyl-

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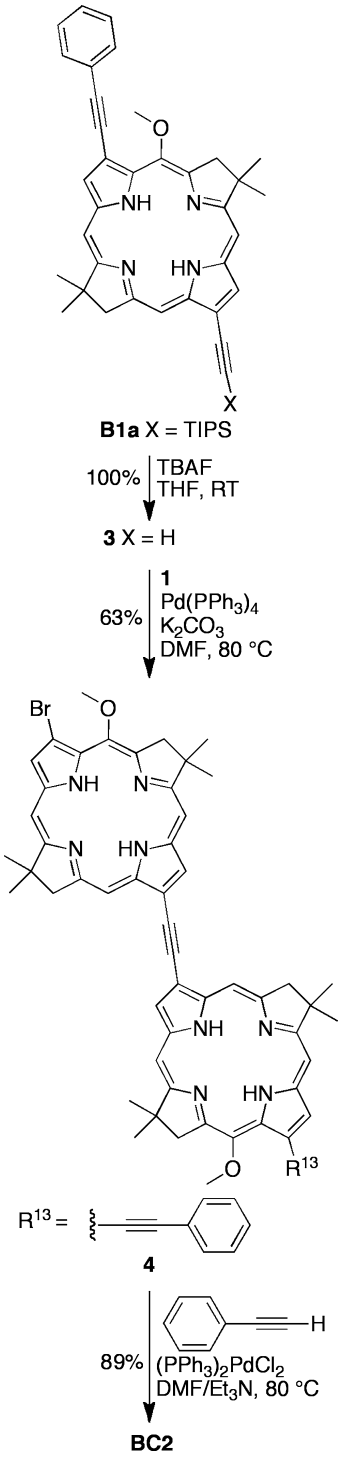
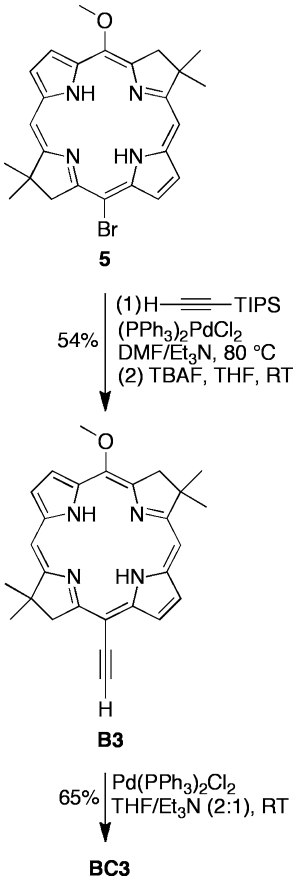
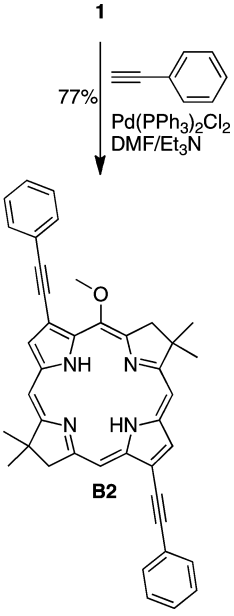
Scheme 2



Scheme 3



Scheme 4



acetylene with **6**, under conditions analogous to those used in preparation of **C1**, in 99% yield (Scheme S3 of Supporting Information).

Characterization. The identities of all new dyads and benchmark monomers were established using ^{1}H and ^{13}C NMR spectroscopy, LD-MS, and HR ESI-MS. The data are consistent with proposed structures.

Absorption Properties. The absorption spectra of bacteriochlorin and chlorin dyads, together with respective monomeric benchmarks are presented in Figures 1 and 2 and Table 1. The benchmark bacteriochlorin and chlorin monomers exhibit absorption typical for analogous synthetic hydroporphyrin derivatives reported previously.[58,75] The $\beta-\beta$ linked bacteriochlorin and chlorin dyads exhibit a significant bathochromic shift of their longest-wavelength Q_y-like absorption bands compared to the position of Q_y bands of respective benchmark monomers. This shift is bigger for ethynyl-linked dyads (864.4 cm^{-1} for **BC2** and 688 cm^{-1} for **Ch2**) than for

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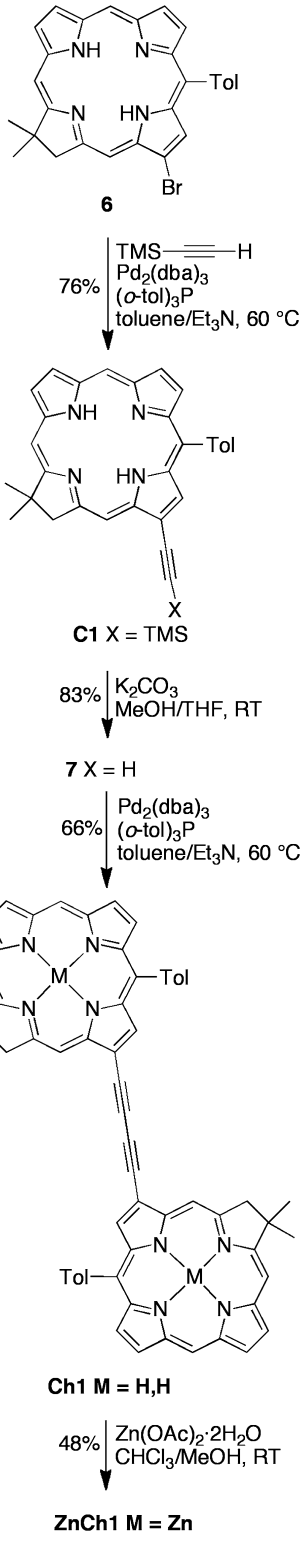
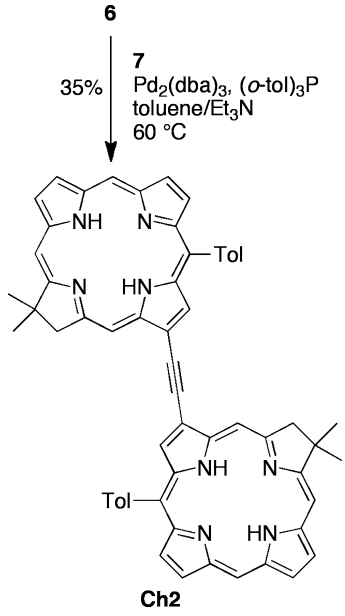
Scheme 5



Scheme 6



butadiynyl-linked dyads (786 cm^{-1} for **BC1a**, 653 cm^{-1} for **Ch1**). For *meso*−*meso* linked **BC3** that shift is less pronounced (350 cm^{-1}). For *β*−*β* linked dyads the position of other absorption features resembles that of respective Q_x and *B* bands in corresponding monomers, while for *meso*−*meso* linked **BC3** the broad absorption feature with the highest maximum centered at 555 nm is present. Note that *B*-like bands for chlorin dyads are markedly broader than for the monomers and show an additional component (shoulder at ∼450 nm) not observed for monomers.

The longest-wavelength Q_y-like bands of *β*−*β* linked bacteriochlorin dyads are significantly broader and in case of both chlorin and bacteriochlorin *β*−*β* linked-dyads split, compared to the narrow and structureless Q_y bands for the corresponding monomers.

The significant broadening of the longest-wavelength Q_y-like features in bacteriochlorin and chlorin dyads can be, at least in part, due to a conformational heterogeneity of strongly conjugated dyads in solution, as was proposed to explain the absorption spectra of highly conjugated porphyrins.[3,18] The DFT calculations indicate that absolute energies for nonplanar conformations (including conformation where both macrocycles are twisted by 90°) are higher in energy by no more than ∼3.0 kJ/mol for **BC1a**, and ∼5.6 kJ/mol for **BC2** compared with the fully planar conformations (see Table S3 in Supporting Information). Consequently, at room temperature there should be a broad distribution of conformations with different torsional angles between mean macrocyclic planes. Twisting out from planarity reduces the electronic conjugation between bacteriochlorin subunits, and thus each conformations would have a slightly different absorption maxima.

The splitting of the longest-wavelength Q_y-like bands in *β*−*β* linked dyads (as well as the presence of broad and split absorption feature in 500−600 nm spectral range for **BC3**) are less clear. One possible reason could be an exciton coupling between both hydroporphyrin macrocycles; however, further detailed spectroscopic and computational examination is required to elucidate their origin.

Molar absorption coefficients *ε* for representative chlorin and bacteriochlorin dyads has been also determined; thus for **Ch2** in toluene $\varepsilon_{401} = 1.3 \times 10^5$ M^{-1} cm^{-1} and $\varepsilon_{687} = 8.4 \times 10^4$ M^{-1} cm^{-1}. For **BC1b** $\varepsilon_{379} = 1.5 \times 10^5$ M^{-1} cm^{-1} and $\varepsilon_{801} = 2.0 \times 10^5$ M^{-1} cm^{-1}.

Emission Properties. The emission properties of bacteriochlorin dyads were initially determined in toluene and are shown in Figures 3 and 4 and Table 2. The emission spectra of dyads show a strong (0,0) band, with the Stokes shift (from the

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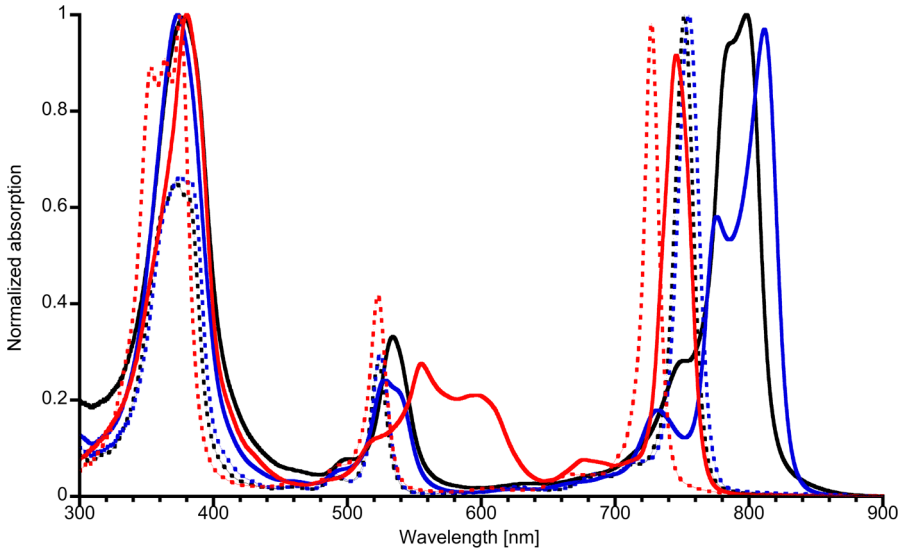

Figure 1. Absorption spectra of bacteriochlorin dyads **BC1a** (black, solid), **BC2** (blue, solid), and **BC3** (red, solid) and corresponding benchmark monomers **B1a** (black, dotted), **B2** (blue, dotted), and **B3** (red, dotted). All spectra were taken in toluene and normalized at the maximum of the highest band.

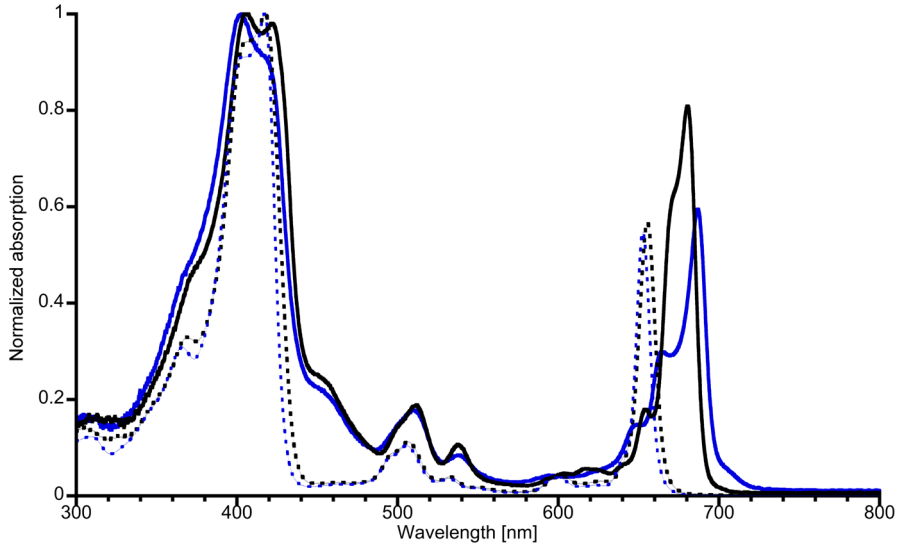

Figure 2. Absorption spectra of chlorin dyads **Ch1** (black, solid) and **Ch2** (blue, solid) and corresponding benchmark monomers **C1** (black, dotted) and **C2** (blue, dotted). All spectra were taken in toluene and normalized at the maximum of the *B* band.

longest-wavelength absorption band maximum) of around 1−7 nm and much weaker vibronic band to the longer wavelength. Each dyad (chlorin and bacteriochlorin) exhibit a structureless (0,0) emission band, which is only slightly broader than for corresponding monomers, which contrasts sharply with the broad and split absorption bands for the same compounds. If the hypothesis that the broadening of the absorption band is due to the conformational heterogeneity (*vide supra*) is correct, this indicates the fast relaxation of the twisted conformations to the planar one in the excited state. Emission apparently occurs only from the planar conformation as was reported for the strongly conjugated porphyrin dyads[4,35] and demonstrated by the fact that fluorescence excitation spectra for dyads closely match their absorption spectra. This assumption is further supported by the rather negligible effect of planarization of **ZnCh1** by DABCO complexation on its emission spectrum (*vide infra*).

The fluorescence quantum yields Φ_f for the bacteriochlorin dyads (in toluene) are similar to the values for corresponding monomers, while Φ_f for chlorin dyads are markedly higher than for the corresponding monomers. Nevertheless, Φ_f for bacteriochlorin dyads is relatively high as for compounds emitting above 800 nm[78] and is substantially higher than for other bacteriochlorin derivatives fluorescent in that spectral window (bacteriopurpurinimides), reported previously.[58,60,63]

Titration of ZnCh1 with DABCO. Insight into potential conformational heterogeneity and its influence on absorption properties of strongly conjugated hydroporphyrin dyads was gained upon titration of the zinc chelate **ZnCh1** with DABCO. (Thus far, we were not able to obtain zinc complexes of bacteriochlorin dyads.) Bidentate DABCO should form 2 + 2 complexes with **ZnCh1**, where DABCO nitrogen will coordinate as axial ligand to zinc located in the center of chlorin macrocycles (Figure S1, Supporting Information). The resulting sandwich complex should restrict the conformational

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Table 1. Absorption Properties of Hydroporphyrin Dyads and Benchmark Monomers, All Spectra Taken in Toluene

compd	λ_B[a]	λ_{Qx}[a]	λ_{Qy}[a]	fwhm,[b] nm (cm^{-1})
BC1a	378	534	799	37 (594)
BC1b	379	536	801	35 (556)
BC1c	375	538	804	36 (568)
BC2	373	538	812	51 (809)
BC3	380	555	746	26 (467)
B1a	379	523	752	16 (284)
B1b	377	525	754	20 (353)
B1c	366	524	753	21 (372)
B2	382	525	755	19 (336)
B3	375	523	727	12 (227)
Ch1	422	538	681	21 (462)
Ch2	417	538	687	16 (343)
C1	417	532	653	10 (236)
C2	418	533	656	13 (304)

[a]The description of absorption bands (*B*, Q_x, and Q_y), which arises from the four-orbital Gouterman model for tetrpyrrolic macrocycles,[47] is valid only for benchmark monomers, not for dyads. In this paper we described the absorption bands of dyads as Q_y-like (*B*-like, etc.) bands. [b]Full-width-at-half-of-maximum of the longest-wavelength absorption band.

mobility within chlorin dyads and enforce a coplanarity of chlorin macrocycles in the dyad, as was observed for strongly conjugated porphyrin dyads.[18] Formation of 2 + 2 complexes of zinc chelates of porphyrin dimers with DABCO was documented for a variety of strongly and weakly conjugated dyads.[18,79]

The complexation of **ZnCh1** with DABCO was monitored by ^{1}H NMR spectroscopy. Thus, treatment of solution of **ZnCh1** in C_6D_6 ($c \approx 2$ mM) with 0.25 and 0.5 equiv of DABCO results in significant broadening of resonances of aromatic protons and near disappearance of resonances of the aliphatic protons of chlorin (see Figure S2, Supporting Information). This suggests formation of a complex with a fast ligands exchange. Addition of 1.0 equiv of DABCO causes sharpening of all chlorin signals (including resonances of aliphatic protons), and the spectrum resembles the one for **ZnCh1** without DABCO. This suggests a formation of a discrete, highly symmetrical complex, and these data are consistent with proposed 2 + 2 complexation.

The results of the spectrophotometric titration of **ZnCh1** with DABCO in toluene are presented in Figure 5. The presence of the several isosbestic points in the spectrophotometric titration suggests that there is an equilibrium between two species, namely, uncoordinated **ZnCh1** and the 2 + 2 **ZnCh1**-DABCO complex. **ZnCh1** exhibits broad and split Q_y-like feature (maxima at 646 and 662 nm) and *B*-like bands at 416 nm. The peak-absorbance ratio of the Q_y-like and *B*-like features is 0.51. Upon titration we observed a significant narrowing and increase in intensity of the Q_y-like absorption feature (relative to *B*). This is accompanied by a disappearance of the maximum at 646 nm and a slight (2 nm) hypsochromic shift of the second band maximum. There is also a slight batchochromic shift (~1 nm) and decrease in the intensity of the *B* band maximum. The peak-absorbance ratio of Q_y-like to *B*-like bands is 1.08.

Contrary to the significant changes in absorption, there are rather small changes in the fluorescence spectrum of **ZnCh1** upon titration (Figure 6). A slight (2 nm) hypsochromic shift of the emission maximum was observed, with slight changes in band shape.

We attribute the above-noted changes to the coplanarization of the chlorin macrocycles in dyads (or at least significant reduction of the distribution of the conformations), enforced by the 2 + 2 coordination with DABCO. This assumption is further supported by results of titration of **ZnCh1** with monodentate pyridine (Figure S3, Supporting Information), and monomer **ZnC2** with DABCO (Figure S4, Supporting Information). In both later cases titration causes slight bathochromic shifts of *B* and Q_y bands (7 and 2 nm, respectively, which is an indication of coordination of zinc cation in tetrapyrrolic macrocycles by nitrogen ligands[18,79]), without marked changes of their shapes and ratio. The observed changes do not appear to be due simply to the

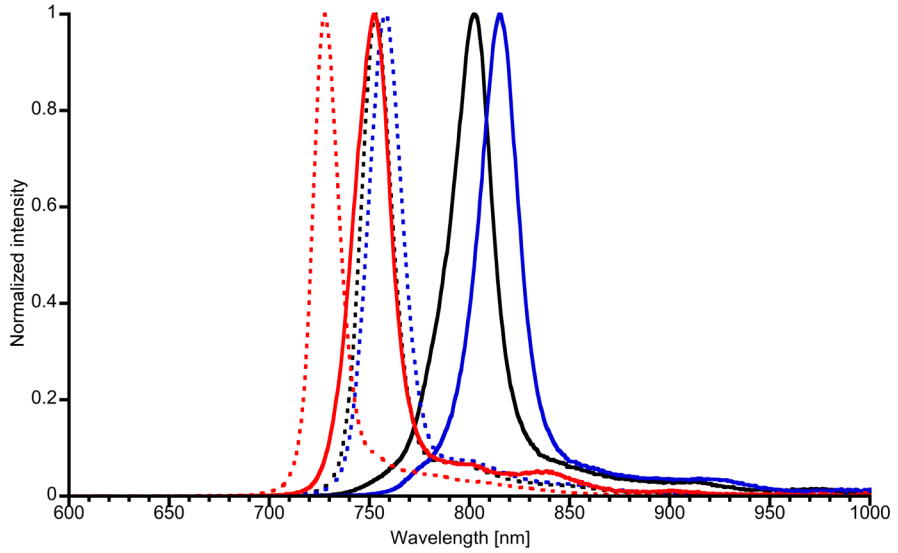

Figure 3. Normalized emission spectra of dyads **BC1a** (black, solid), **BC2** (blue, solid), and **BC3** (red, solid) and corresponding benchmark monomers **B1a** (black, dotted), **B2** (blue, dotted), and **B3** (red, dotted). All spectra were taken in toluene, and each sample was excited at the maximum of the Q_x or Q_x-like bands.

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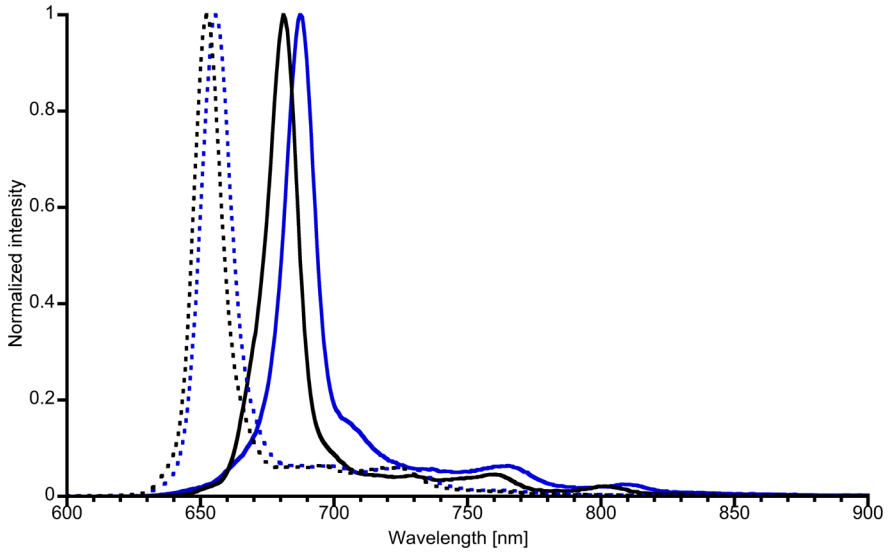

Figure 4. Normalized emission spectra of chlorin dyads **Ch1** (black, solid) and **Ch2** (blue, solid) and corresponding benchmark monomers **C1** (black, dotted) and **C2** (blue, dotted). All spectra were taken in toluene, and each sample was excited at the maximum of the Q_x or Q_x-like feature.

Table 2. Fluorescence Emission Properties of Strongly Conjugated Hydroporphyrin Arrays[a]

compd	λ_{em} (toluene)	Φ_f (toluene)	Φ_f (PhCN)	fwhm, nm (cm^{-1}) (toluene)
BC1a	802	0.17	0.028	23 (355)
BC1b	808	nd[b]	nd[b]	22 (339)
BC1c	811	nd[b]	nd[b]	23 (348)
BC2	815	0.19	0.028	24 (358)
BC3	752	0.18	0.008	22 (385)
B1a	753	0.20	0.21	18 (313)
B1b	758	nd[b]	nd[b]	20 (345)
B1c	757	nd[b]	nd[b]	20 (345)
B2	758	0.21	0.22	19 (327)
B3	728	0.17	0.18	15 (280)
Ch1	681	0.57	0.52	13 (278)
Ch2	687	0.48	0.40	13 (272)
C1	652	0.34	0.31	13 (301)
C2	656	0.39	0.36	13 (299)

[a]All data were obtained in argon-purged solvents at room temperature. Samples were excited at the maximum of their Q_x (or Q_x-like) band. Fluorescence quantum yields Φ_f were determined with respect to free base *meso*-tetraphenyl-porphyrin (FbTPP) in nondegassed toluene. Its quantum yield, 0.070, was established with respect to the zinc chelate ZnTPP in nondegassed toluene (Φ_f = 0.030).[50] [b]Not determined.

breakup of **ZnCh1** aggregates upon coordination, since we did not observe changes in the absorption spectrum upon significant (~20-fold) dilution (not shown).

Solvent Polarity Dependence of the Absorption and Emission Properties. Subsequently, we examined the optical and photochemical properties of dyads and benchmark monomers in solvents of different polarities. Absorption and emission properties of compounds in five solvents were examined. The solvents [and empirical polarity values][80] were toluene [ET(30) = 33.9 kcal/mol], tetrahydrofuran (THF) [ET(30) = 37.4 kcal/mol], dichloromethane (CH_2Cl_2) [ET(30) = 40.7 kcal/mol], benzonitrile (PhCN) [ET(30) = 42.5 kcal/mol], and *N*,*N*-dimethylformamide (DMF) [ET(30) = 43.2 kcal/mol]. The absorption bands maxima of dyads in these solvents are showed in Table S1 of Supporting Information. The absorption and emission maxima for both bacteriochlorin and chlorin dyads are fairly independent of solvent polarity; the absorption maxima shift ±3 nm in solvents examined.

All bacteriochlorin dyads examined showed significant quenching of fluorescence in polar solvents. For example, for **BC1a** Φ_f is reduced nearly 6-fold in PhCN compared to toluene (0.028 vs 0.17). Even more dramatic reduction of Φ_f is observed for **BC3** (0.008 vs 0.18). Further reduction of Φ_f is observed in DMF (Figure 7 and Table S2 in Supporting Information). Solvents with the intermediate polarities (THF, CH_2Cl_2,) caused the reduction of Φ_f commensurate their polarity (Figure 7, Table S2 in Supporting Information). Φ_f values for benchmark monomers vary only slightly with the solvent polarity. The only exception is **B1c**, for which fluorescence is moderately quenched in polar solvents (by 0.7-fold in DMF vs toluene); however, even for the latter case, the quenching of fluorescence is much less than for any of bacteriochlorin dyads.

The fluorescence intensity of analogous chlorin dyads **Ch1** and **Ch2** is almost invariant of solvent polarity in moderately polar solvents (THF, dichloromethane, PhCN). The emission is markedly quenched in highly polar DMF solvent, although the quenching is much less extensive than in case of bacteriochlorin dyads (0.44 and 0.78 intensity in DMF that of in toluene, for **Ch1** and **Ch2**, respectively). The fluorescence intensity of chlorin benchmark monomers is almost independent of the solvent polarity.

The determination of processes responsible for observed fluorescence quenching in polar solvents is beyond the scope of this paper and is a subject of ongoing studies. The close similarity of the absorption spectra of dyads in all examined solvents and lack of any significant broadening of absorption bands in polar solvents exclude the possible aggregation of dyads as a reason for fluorescence quenching. The evident dependence of the degree of fluorescence quenching on solvent polarity suggests a contribution of internal charge-transfer (CT) configurations (stabilized as the polarity of solvent increases) to the nature and deactivation of the lowest singlet excited state. The fluorescence quenching has been previously reported for a strongly conjugated porphyrin dyad by Anderson

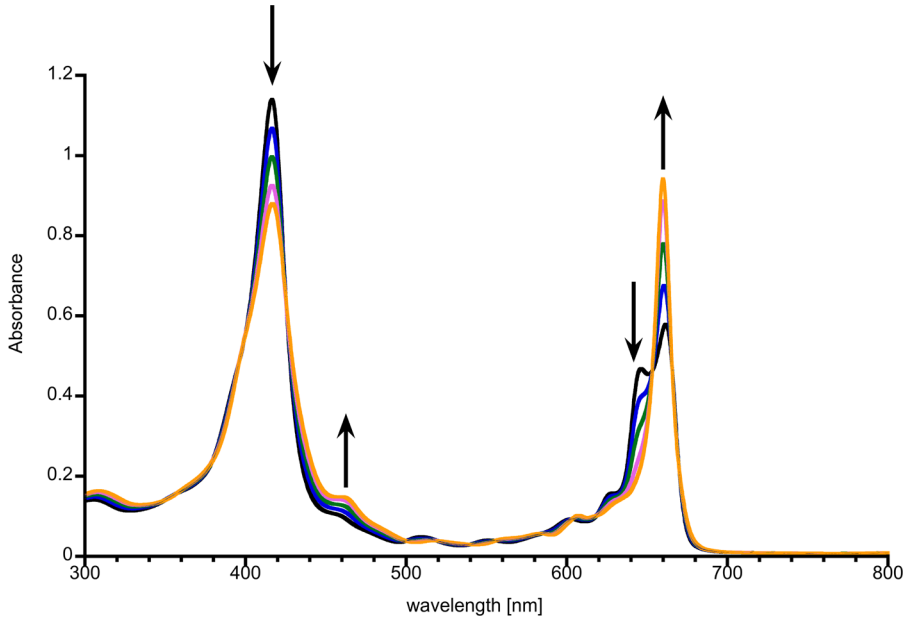

Figure 5. Titration of **ZnCh1** in toluene ($c \approx 5\ \mu$M) with DABCO (c = 1.0 mM, 2 μL increments).

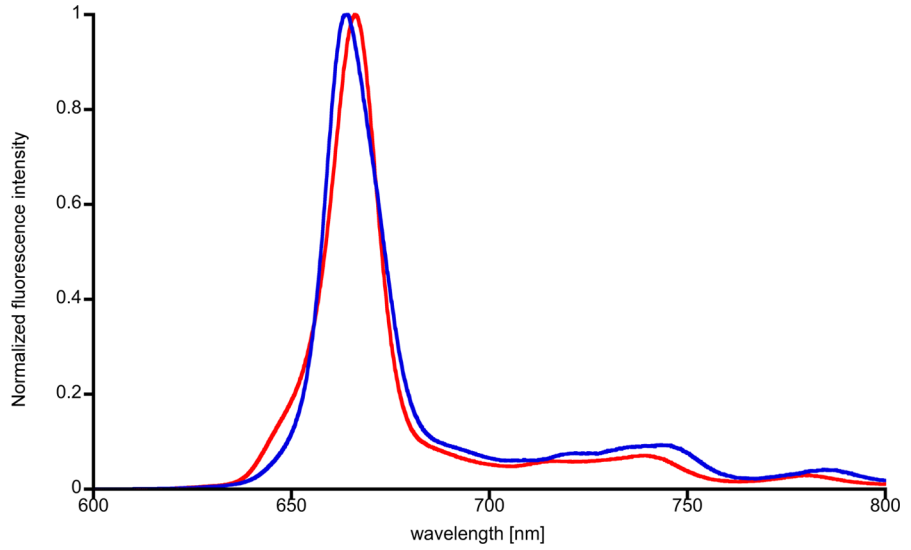

Figure 6. Comparison of fluorescence spectra of **ZnCh1** without (red) and with (blue) DABCO.

(albeit Anderson observed a lack of fluorescence regardless of solvent polarity).[18] Wasielewski reported a significant fluorescence quenching ("2 order of magnitude") for magnesium chelate of a vinyl-linked chlorin dyad in DMF, compared to toluene.[72,73] Contribution of CT configuration to the first singlet excited state as a reason for fluorescence quenching has been proposed for the above-mentioned systems, as well as for directly linked chlorin-porphyrin dyads.[81] However, further thorough spectroscopic, electrochemical, and computational studies are required to understand the observed solvent-polarity dependence of fluorescence quantum yields.

■ CONCLUSION AND OUTLOOK

Assembly of hydroporphyrins into strongly conjugated dyads significantly modifies their optical spectroscopic and photochemical properties. As expected, strongly conjugated chlorins and bacteriochlorin dyads exhibit significant bathochromic shift on their long-wavelength absorption bands compared to the respective monomers. The strongly conjugated bacteriochlorin dyads exhibit relatively strong fluorescence in nonpolar solvents, while their fluorescence is strongly quenched in polar media. Overall, strongly conjugated hydroporphyrin arrays exhibit interesting and complex spectroscopic and photochemical properties, which are interesting from a fundamental point of view and important for consideration of possible applications of such dyads. Further synthetic, spectroscopic, and computational studies are necessary to fully understand and control the excited state properties of the new architectures reported here. That knowledge will help guide engineering the spectral and photochemical properties that are desired for the certain applications. Numerous such applications can be envisaged. For example, the strong absorption and emission above 800 nm, manifested in nonpolar solvents, can be exploited for near-IR *in vivo* bioimaging, though for such applications it would be highly beneficial to achieve the same fluorescence properties in an aqueous

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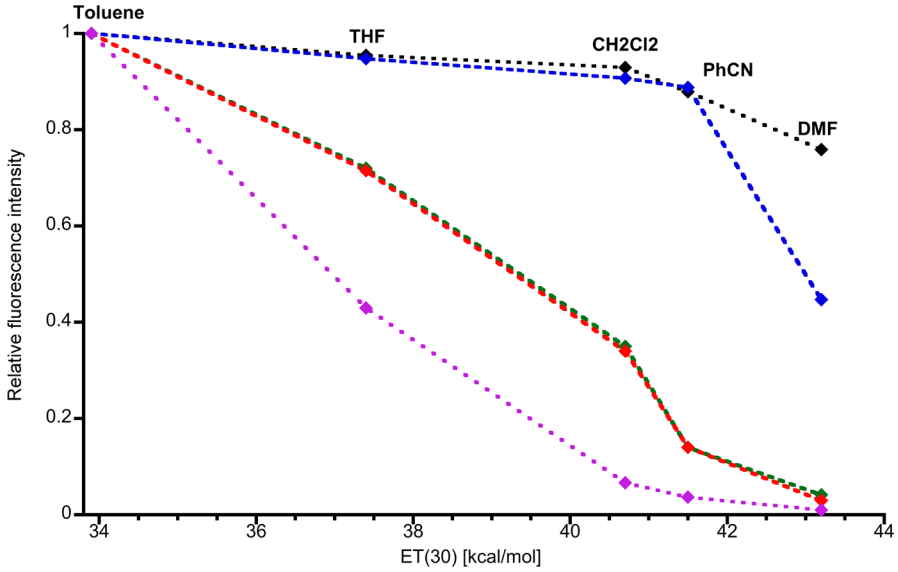

Figure 7. Plot of dependence of relative fluorescence intensity vs empirical polarity ET(30) for **Ch2**, (black), **Ch1** (blue), **BC1a** (red), **BC2** (green), and **BC3** (violet). Fluorescence quantum yield in toluene was takes as 1. All spectra were taken in air-equilibrated solvents, except for PhCN, for which fluorescence quantum yield was determined in argon-purged PhCN and compared with that obtained in argon-purged toluene. Samples were excited at the maxima of their Q_x or Q_x-like bands (for bacteriochlorins) or *B* or *B*-like band (for chlorins). Emission intensities are corrected for different solvent refractive index. Values of the relative intensities for bacteriochlorin dyads in DMF are approximate, due to the very weak fluorescence signal.

environment most suitable for biological applications. Also, the polarity dependence of fluorescence intensity can be utilized for construction of polarity sensitive/activatable probes.[82] These collective properties also can be exploited for use in novel solar energy conversion systems.

EXPERIMENTAL SECTION

General Experimental Section. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were collected at room temperature in $CDCl_3$ unless noted otherwise. Chemical shifts (δ) were callibrated using solvent peaks (^{1}H signals: residual proton signals 7.26 ppm for chloroform; ^{13}C signals: 77.0 for $CDCl_3$). All solvents and commercialy available reagents were used as received. Palladium coupling reactions were performed using commercially available anhydrous solvents (toluene and DMF). A FT-ICR analyzer was used for ESI HRMS.

Known compounds **1**,[76] **S2**,[83] and **S3**[84] were synthesized following published procedures. Known compound **5** was prepared by bromination of 5-methoxybacteriochlorin **S1**.[76] **S1** was previously synthesized via self-condensation of corresponding dihydrodipyrrin.[76] Here **S1** was prepared by debromination of the corresponding 3,13-dibromo-5-methoxybacteriochlorin **1**, analogously to the previously reported synthesis of fully unsubstituted bacteriochlorin.[85]

DFT calculations were performed using Spartan 10 for Windows, on a PC equipped with Pentium Dual Core 2.70 GHz CPU and 2.00 MB RAM.

General Procedure for Palladium-Catalyzed Cross-Coupling Reactions. Unless noted otherwise, all of the palladium-catalyzed cross-coupling reactions were conducted following the following general procedure: All solid reagents, except palladium catalyst, were placed in a Schlenk flask, and solvent was added. The resulting mixture was deoxygenated using a freeze/thaw cycle (twice), and the flask was filled with nitrogen. A sample of palladium catalyst was added, the resulting mixture was further deoxygenated using freeze/thaw cycles (three times), and the reaction flask was then filled with nitrogen. In the case when trimethylsilylacetylene or triisopropylsilylacetylene was used, it was added at this point after freeze/thaw cycles. The reaction mixture was allowed to warm to room temperature and placed in the preheated oil bath.

3-Bromo-5-methoxy-8,8,18,18-tetramethyl-13-[(2-(triisopropylsilyl)ethynyl)]bacteriochlorin (2). Following the General Procedure, a mixture of 3,13-dibromo-5-methoxy-8,8,18,18-tetramethyl-bacteriochlorin **1** (114 mg, 204 μmol), triisopropylsilylacetylene (60 μL, 268 μmol), potassium carbonate (276 mg, 2000 μmol), and tetrakis(triphenylphosphine)palladium (30.5 mg, 26 μmol) in DMF (20 mL) was stirred at 80 °C under nitrogen. After 16 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. A residue was purified with column chromatography (silica, hexanes/CH_2Cl_2 (2:1)) to afford a green solid (49.4 mg, 37%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.89 (s, 1H), −1.71 (s, 1H), 1.34−1.43 (m, 21H), 1.93 (s, 12H), 4.34 (s, 3H), 4.40 (s, 2H), 4.41 (s, 2H), 8.49 (s, 1H), 8.53 (s, 1H), 8.69 (d, J = 2.4 Hz, 1H), 8.77 (d, J = 1.8 Hz, 1H), 8.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.6, 18.9, 30.8, 31.1, 45.6, 47.5, 51.6, 64.4, 96.3, 96.4, 97.5, 98.6, 101.5, 105.3, 117.2, 124.2, 125.7, 126.5, 134.1, 135.4, 138.8, 154.5, 161.3, 169.9, 170.0; MS ($[M + H]^+$, M = $C_{36}H_{47}BrN_4OSi$) calcd 659.2775, obsd (MALDI-MS) 659.3, (HRMS, ESI) 659.2789.

5-Methoxy-8,8,18,18-tetramethyl-3-phenylethynyl-13-[(triisopropylsilyl)ethynyl]bacteriochlorin (B1a). Following the General Procedure, a mixture of **2** (32 mg, 49 μmol), phenylacetylene (10.7 μL, 98 μmol), and bis(triphenylphosphine)palladium dichloride (3.4 mg, 4.9 μmol) in DMF (4 mL) and Et_3N (2 mL) was stirred at 80 °C under nitrogen. After 5 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. A residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (3:1)) to afford a green solid (27 mg, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.72 (s, 1H), −1.56 (s, 1H), 1.33−1.44 (m, 21H), 1.946 (s, 6H), 1.953 (s, 6H), 4.41 (s, 2H), 4.44 (s, 2H), 4.51 (s, 3H), 7.41−7.46 (m, 1H), 7.48−7.53 (m, 2H), 7.86−7.91 (m, 2H), 8.52 (s, 1H), 8.53 (s, 1H), 8.76 (d, J = 1.8 Hz, 1H), 8.80 (d, J = 2.4 Hz, 1H), 8.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.6, 18.9, 30.8, 31.1, 45.4, 45.6, 51.7, 64.4, 87.4, 93.5, 96.3, 97.1, 97.3, 98.6, 101.5, 112.2, 117.3, 124.2, 124.4, 125.6, 128.1, 128.5, 131.2, 131.7, 134.3, 135.6, 135.7, 138.8, 154.6, 161.3, 169.7, 170.4; MS ($[M + H]^+$, M = $C_{44}H_{52}N_4OSi$) calcd 681.3983, obsd (MALDI-MS) 681.3, (HRMS, ESI) 681.3963.

13-Ethynyl-5-methoxy-8,8,18,18-tetramethyl-3-phenylethynylbacteriochlorin (3). A mixture of **B1a** (14 mg, 21 μmol) and TBAF (1 M, 42 μL, 42 μmol) in THF (4 mL) was stirred for 1 h. The reaction mixture was concentrated, and the residue was purified with

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silica column chromatography (hexanes/CH_2Cl_2 (3:2)) to afford a green solid (10.8 mg, 100%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.83 (s, 1H), −1.62 (s, 1H), 1.94 (s, 12H), 3.88 (s, 1H), 4.40 (s, 2H), 4.44 (s, 2H), 4.50 (s, 3H), 7.40−7.46 (m, 1H), 7.47−7.53 (m, 2H), 7.84−7.89 (m, 2H), 8.54 (s, 2H), 8.79 (d, J = 2.4 Hz, 1H), 8.81 (d, J = 1.8 Hz, 1H), 8.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.9, 31.0, 45.5, 45.6, 47.6, 51.5, 64.5, 78.9, 84.0, 87.2, 93.7, 96.3, 97.0, 97.6, 112.8, 115.0, 124.3, 124.8, 125.8, 128.2, 128.5, 131.4, 131.7, 134.7, 135.1, 135.6, 138.2, 155.3, 160.9, 170.1, 170.2; MS ([M + H]$^+$, M = $C_{35}H_{32}N_4O$) calcd 525.2649, obsd (MALDI-MS) 525.0, (HRMS, ESI) 525.2653.

3-[(4-Methoxycarbonylphenyl)ethynyl]-5-methoxy-8,8,18,18-tetramethyl-13-[(triisopropylsilyl)ethynyl]-bacteriochlorin (B1b). Following the General Procedure, a mixture of **2** (6.3 mg, 9.6 μmol), methyl 4-ethynylbenzoate (3.1 mg, 19 μmol), and bis(triphenylphosphine)palladium dichloride (0.7 mg, 1.0 μmol) in DMF (2 mL) and Et_3N (1 mL) was stirred at 80 °C under nitrogen. After 6 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. A residue was purified with column chromatography (silica, hexanes/CH_2Cl_2 (1:2)) to afford a pinkish-green solid (5.4 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.58 (s, 1H), −1.46 (s, 1H), 1.33−1.42 (m, 21H), 1.93 (s, 6H), 1.94 (s, 6H), 3.99 (s, 3H), 4.38 (s, 2H), 4.41 (s, 2H), 4.48 (s, 3H), 7.90 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 7.9 Hz, 2H), 8.47 (s, 1H), 8.50 (s, 1H), 8.74 (d, J = 1.8 Hz, 1H), 8.76 (d, J = 1.8 Hz, 1H), 8.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.6, 18.9, 29.7, 30.8, 31.1, 45.3, 45.8, 47.3, 51.9, 52.3, 64.4, 90.8, 92.6, 96.4, 97.2, 97.3, 99.0, 101.3, 111.0, 117.9, 123.9, 126.1, 129.2, 129.2, 129.7, 131.2, 131.5, 134.0, 135.5, 136.3, 139.1, 154.3, 161.8, 166.8, 169.5, 171.1; MS ([M + H]$^+$, M = $C_{46}H_{54}N_4O_3Si$) calcd 739.4038, obsd (MALDI-MS) 739.1, (HRMS, ESI) 739.4039

13-Ethynyl-3-[(4-*N*,*N*-dimethylaminophenyl)ethynyl]-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (B1c). Following the General Procedure, a mixture of **2** (16 mg, 24 μmol), 4-ethynyl-*N*,*N*-dimethylaniline (7.0 mg, 48 μmol), and bis(triphenylphosphine) palladium dichloride (1.7 mg, 2.4 μmol) in DMF (5 mL) and Et_3N (2.5 mL) was stirred at 80 °C under nitrogen. After 5 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. A residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (1:2)) to afford a mixture of the product and unknown byproducts. The resulting mixture was dissolved in THF (4 mL) and treated with TBAF (40 μL, 1 M in THF) for 0.5 h. After being concentrated, the residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (1:2)) to afford a red solid (10.2 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.95 (s, 1H), −1.67 (s, 1H), 1.94 (s, 12H), 3.08 (s, 6H), 3.87 (s, 1H), 4.40 (s, 2H), 4.45 (s, 2H), 4.51 (s, 3H), 6.82 (d, J = 9.2 Hz, 2H), 7.75 (d, J = 9.2 Hz, 2H), 8.53 (s, 1H), 8.56 (s, 1H), 8.78 (t, J = 1.8 Hz, 2H), 8.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.90, 30.95, 40.3, 45.3, 45.8, 47.9, 51.3, 64.5, 79.1, 83.6, 85.1, 95.5, 96.2, 96.5, 97.7, 111.1, 112.0, 114.0, 114.7, 124.7, 125.0, 131.7, 132.9, 134.3, 135.4, 135.5, 137.8, 150.2, 155.9, 160.2, 169.2, 170.6; MS ([M + H]$^+$, M = $C_{37}H_{37}N_5O$) calcd 568.3071, obsd (MALDI-MS) 568.1, (HRMS, ESI) 568.3089.

BC1a. Following the General Procedure, a mixture of **B1a** (10 mg, 15 μmol), TBAF (1 M in THF, 30 μL, 30 μmol), and bis(triphenylphosphine)palladium dichloride (5.3 mg, 7.5 μmol) in THF (3 mL) and Et_3N (1.5 mL) was stirred at room temperature for 13 h. The mixture was concentrated, and the residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (1:2)) to afford a pinkish-red solid (4.6 mg, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.74 (s, 2H), −1.46 (s, 2H), 1.98 (s, 24H), 4.47 (s, 4H), 4.49 (s, 4H), 4.52 (s, 6H), 7.39−7.46 (m, 6H), 7.88 (d, J = 8.6 Hz, 4H), 8.57 (s, 2H), 8.62 (s, 2H), 8.84 (d, J = 2.4 Hz, 2H), 8.94 (d, J = 1.8 Hz, 2H), 9.08 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 30.9, 31.0, 45.3, 45.8, 47.9, 51.4, 64.6, 79.5, 81.3, 87.1, 94.1, 96.7, 96.9, 98.0, 113.6, 114.1, 124.2, 125.4, 125.5, 128.3, 128.5, 131.7, 131.9, 134.9, 135.4, 135.6, 138.9, 156.3, 161.0, 169.8, 171.0; MS ([M + H]$^+$, M = $C_{70}H_{62}N_8O_2$) calcd 1047.5068, obsd (MALDI-MS) 1047.4, (HRMS, ESI) 1047.5067.

BC1b. Following the General Procedure, a mixture of **B1b** (10 mg, 14 μmol), TBAF (1 M in THF, 28 μL, 28 μmol), and bis(triphenylphosphine)palladium dichloride (4.9 mg, 7.0 μmol) in THF (3 mL) and Et_3N (1.5 mL) was stirred at room temperature for 16 h. The mixture was concentrated, and the residue was purified with silica column chromatography (CH_2Cl_2) to afford a violet-red solid (4.8 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 Hz) δ −1.64 (s, 2H), −1.41 (s, 2H), 1.99 (s, 24H), 4.00 (s, 6H), 4.46 (s, 4H), 4.49 (s, 4H), 4.51 (s, 6H), 7.92 (d, J = 8.0 Hz, 4H), 8.17 (d, J = 8.6 Hz, 4H), 8.57 (s, 2H), 8.61 (s, 2H), 8.84 (d, J = 2.4 Hz, 2H), 8.94 (d, J = 1.8 Hz, 2H), 9.06 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 30.9, 31.0, 45.5, 45.7, 47.7, 51.6, 52.3, 64.6, 79.4, 81.5, 90.4, 93.1, 96.7, 97.2, 98.0, 112.4, 114.7, 125.3, 125.9, 129.0, 129.3, 129.7, 131.5, 131.8, 135.0, 135.4, 135.6, 139.1, 156.0, 161.5, 166.7, 170.4, 170.8; MS ([M + H]$^+$, M = $C_{74}H_{66}N_8O_6$) calcd 1163.5178, obsd (MALDI-MS) 1163.7. HRMS is not available due to the poor ionization under ESI conditions.

BC1c. Following the General Procedure, a mixture of **B1c** (8.4 mg, 15 μmol) and bis(triphenylphosphine)palladium dichloride (5.3 mg, 7.5 μmol) in THF (3 mL) and Et_3N (1.5 mL) was stirred at room temperature. After 12 h, an additional batch of bis-(triphenylphosphine)palladium dichloride (5.3 mg, 7.5 μmol) was added. The mixture was stirred for additional 4 h. The resulting mixture was concentrated, and the residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (1:2)) to afford a pinkish-red solid (6.1 mg, 73%). ^{1}H NMR ($CDCl_3$, 400 Hz) δ −1.80 (s, 2H), −1.46 (s, 2H), 1.98 (s, 24H), 3.09 (s, 12H), 4.47 (s, 4H), 4.48 (s, 4H), 4.52 (s, 6H), 6.82 (d, J = 9.2 Hz, 4H), 7.76 (d, J = 8.6 Hz, 4H), 8.54 (s, 2H), 8.61 (s, 2H), 8.80 (d, J = 1.8 Hz, 2H), 8.91 (d, J = 1.8 Hz, 2H), 9.08 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 30.9, 31.0, 40.3, 45.1, 46.0, 48.1, 51.2, 64.6, 81.1, 85.1, 96.4, 96.6, 98.1, 109.1, 111.0, 112.0, 113.3, 115.4, 124.5, 125.2, 132.1, 132.9, 134.2, 135.5, 136.0, 138.7, 150.2, 156.9, 160.4, 169.1, 171.4; MS ([M + H]$^+$, M = $C_{74}H_{72}N_{10}O_2$) calcd 1133.5912, obsd (MALDI-MS) 1133.5, (HRMS, ESI) 1133.5865.

Compound 4. Following the General Procedure, a mixture of **1** (10 mg, 19 μmol), **3** (10.6 mg, 19 μmol), potassium carbonate (26.2 mg, 190 μmol), and tetrakis(triphenylphosphine)palladium (2.2 mg, 1.9 μmol) in DMF (4 mL) was stirred at 80−85 °C under nitrogen. After 14 h, the reaction mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. The residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (1:1)) to afford a pinkish-red solid (12.1 mg, 63%). ^{1}H NMR ($CDCl_3$, 400 Hz) δ −1.77 (s, 1H), −1.61 (s, 1H), −1.47 (s, 1H), −1.33 (s, 1H), 2.01 (s, 6H), 2.02 (s, 18H), 4.39 (s, 3H), 4.48 (s, 2H), 4.50 (s, 2H), 4.55 (s, 3H), 4.58 (s, 4H), 7.42−7.48 (m, 1H), 7.52 (d, J = 7.0 Hz, 2H), 7.87−7.93 (m, 2H), 8.56 (s, 1H), 8.60 (s, 1H), 8.69 (s, 1H), 8.72 (s, 1H), 8.75 (d, J = 2.4 Hz, 1H), 8.85 (d, J = 1.8 Hz, 1H), 9.11 (d, J = 1.8 Hz, 1H), 9.13 (d, J = 2.4 Hz, 1H), 9.33 (s, 1H), 9.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 30.91, 30.93, 31.0, 45.6, 45.7, 45.8, 47.6, 51.7, 51.9, 64.51, 64.52, 87.3, 91.9, 93.7, 96.5, 96.6, 97.1, 97.6, 97.8, 105.8, 112.7, 116.8, 116.9, 124.6, 124.7, 124.86, 124.94, 126.9, 128.2, 128.5, 131.5, 131.7, 134.4, 134.7, 135.5, 135.6, 135.7, 136.0, 138.5, 155.2, 155.3, 161.3, 170.0, 170.1, 170.3, 170.4; MS ([M + H]$^+$, M = $C_{60}H_{57}BrN_8O_2$) calcd 1001.3861, obsd (MALDI-MS) 1002.0, (HRMS, ESI) 1001.3861.

BC2. Following the General Procedure, a mixture of **4** (9.5 mg, 9.5 μmol), phenylacetylene (2.2 μL, 20 μmol) and bis-(triphenylphosphine)palladium dichloride (0.7 mg, 1.0 μmol) in DMF (4 mL) and Et_3N (2 mL) was stirred at 80−85 °C under nitrogen. After 5 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. The residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (3:2)) to afford a pinkish-red solid (8.6 mg, 89%). ^{1}H NMR ($CDCl_3$, 400 Hz) δ −1.62 (s, 2H), −1.33 (s, 2H), 2.02 (s, 24H), 4.49 (s, 4H), 4.54 (s, 6H), 4.57 (s, 4H), 7.42−7.48 (m, 2H), 7.52 (t, J = 7.3 Hz, 4H), 7.89 (d, J = 6.7 Hz, 4H), 8.59 (s, 2H), 8.69 (s, 2H), 8.84 (d, J = 1.8 Hz, 2H), 9.10 (d, J = 1.8 Hz, 2H), 9.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 30.9, 31.1, 45.6, 45.7, 47.6, 51.9, 64.5, 87.3, 91.9, 93.7, 96.6, 97.1, 97.6, 112.7, 116.9, 124.3, 124.7, 124.9, 128.2, 128.5, 131.5, 131.7, 134.7, 135.6, 136.0, 138.5, 155.2, 161.3, 170.1, 170.4; MS ([M + H]$^+$,

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M = $C_{68}H_{62}N_8O_2$) calcd 1023.5068, obsd (MALDI-MS) 1023.2, (HRMS, ESI) 1023.5097.

15-Ethynyl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (B3). Following the General Procedure, a mixture of 15-bromo-5-methoxy-8,8,18,18-tetramethyl-bacteriochlorin **5**[76] (40 mg, 83 μmol), triisopropylsilylacetylene (38 μL, 170 μmol), and bis-(triphenylphosphine)palladium dichloride (5.6 mg, 8 μmol) in DMF (10 mL) and Et_3N (5 mL) was stirred at 80−90 °C under nitrogen. After 5 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. The residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (2:1)) to afford a mixture of the product and unknown byproducts. This mixture in THF (2 mL) was treated with TBAF (1 M, 100 μL, 100 μmol) for 0.5 h. After being concentrated, the residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (1:1)) to afford a pinkish-green solid (19 mg, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.95 (s, 1H), −1.69 (s, 1H), 1.97 (s, 12H), 3.94 (s, 1H), 4.38 (s, 2H), 4.49 (s, 3H), 4.57 (s, 2H), 8.63−8.67 (m, 2H), 8.68 (s, 1H), 8.74 (dd, J = 1.8, 4.3 Hz, 1H), 8.92 (dd, J = 1.8, 4.3 Hz, 1H), 9.09 (dd, J = 1.8, 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.0, 31.4, 45.1, 45.7, 47.4, 52.1, 65.2, 82.4, 85.7, 92.1, 97.2, 98.7, 118.1, 120.8, 121.5, 123.7, 131.7, 131.5, 136.0, 136.1, 138.8, 153.5, 163.1, 168.6, 169.8; MS ([M + H]$^+$, M = $C_{27}H_{28}N_4O$) calcd 425.2336, obsd (MALDI-MS) 425.0, (HRMS, ESI) 425.2326

BC3. Following the General Procedure, a mixture of **B3** (10.8 mg, 25 μmol) and bis(triphenylphosphine)palladium dichloride (18.2 mg, 26 μmol) in THF (4 mL) and Et_3N (2 mL) was stirred at room temperature for 11 h. The mixture was concentrated, and the residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (1:2)) to afford a pinkish-red solid (7.0 mg, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.70 (s, 2H), −1.38 (s, 2H), 1.98 (s, 12H), 2.04 (s, 12H), 4.38 (s, 4H), 4.50 (s, 6H), 4.79 (s, 4H), 8.63−8.68 (s, 4H), 8.70 (s, 2H), 8.81 (d, J = 4.3 Hz, 2H), 8.91 (d, J = 4.3 Hz, 2H), 9.30 (d, J = 4.9 Hz, 2H); ^{13}C NMR spectrum is not available due to the low solubility of **BC3**; MS ([M + H]$^+$, M = $C_{54}H_{54}N_8O_2$) calcd 847.4443, obsd (MALDI-MS) 847.6, (HRMS, ESI) 847.4424.

3,13-Bis(phenylethynyl)-5-methoxy-8,8,18,18-tetramethyl-bacteriochlorin (B2). Following the General Procedure, a mixture of **1** (12 mg, 22 μmol), phenylacetylene (8.8 μL, 81 μmol), and bis(triphenylphosphine)palladium dichloride (1.4 mg, 2.0 μmol) in DMF (4 mL) and Et_3N (2 mL) was stirred at 80 °C under nitrogen. After 5 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. The residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (2:1)) to afford a pinkish-green solid (10 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.72 (s, 1H), −1.52 (s, 1H), 1.95 (s, 12H), 4.42 (s, 2H), 4.44 (s, 2H), 4.51 (s, 3H), 7.40−7.55 (m, 6H), 7.88 (t, J = 8.2 Hz, 4H), 8.53 (s, 1H), 8.55 (s, 1H), 8.79 (s, 1H), 8.80 (s, 1H), 8.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.8, 31.0, 45.5, 45.6, 47.5, 51.8, 64.4, 84.5, 87.3, 93.6, 96.3, 96.5, 97.1, 97.4, 112.4, 116.8, 123.6, 124.4, 125.0, 128.1, 128.5, 128.6, 131.3, 131.7, 131.8, 134.4, 135.6, 135.9, 138.2, 154.8, 161.2, 169.8, 170.4; MS ([M + H]$^+$, M = $C_{41}H_{36}N_4O$) calcd 601.2962, obsd (MALDI-MS) 601.0, (HRMS, ESI) 601.2957.

BC1-Br$_2$. Following the General Procedure, a mixture of **B1a** (11 mg, 17 μmol), TBAF (1 M in THF, 34 μL, 34 μmol), and bis(triphenylphosphine)palladium dichloride (6.0 mg, 8.5 μmol) in THF (4 mL) and Et_3N (2 mL) was stirred at room temperature for 15 h. The mixture was concentrated, and residue was purified with silica column chromatography (hexanes/CH_2Cl_2 (2:3)) to afford a red solid (4.4 mg, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −1.88 (s, 2H), −1.58 (s, 2H), 1.97 (s, 12H), 1.98 (s, 12H), 4.36 (s, 6H), 4.45 (s, 4H), 4.49 (s, 4H), 8.53 (s, 2H), 8.65 (s, 2H), 8.76 (d, J = 2.4 Hz, 2H), 8.95 (d, J = 1.8 Hz, 2H), 9.10 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.9, 45.3, 46.0, 47.9, 51.2, 64.7, 79.4, 81.3, 96.3, 96.7, 98.3, 106.8, 114.0, 125.5, 127.4, 134.6, 135.1, 135.5, 138.9, 156.3, 161.0, 169.5, 171.3; MS ([M + H]$^+$, M = $C_{54}H_{52}Br_2N_8O_2$) calcd 1003.2652, obsd (MALDI-MS) 1004.7, (HRMS, ESI) 1003.2651.

5-Methoxy-8,8,18,18-tetramethyl-bacteriochlorin (S1).[76]

Following a reported procedure with modification,[85] a mixture of 3,13-dibromo-5-methoxy-8,8,18,18-tetramethylbacteriochlorin **1** (85 mg, 0.15 mmol), tri-*o*-tolylphosphine (91 mg, 0.30 mmol), ammonium formate (184 mg, 3.0 mmol), and $Pd_2(dba)_3$ (130 mg, 0.15 mmol) in toluene (5 mL) was stirred at 100 °C for 2 h. After solvent was removed, the residue was purified by silica column chromatography (hexane/CH_2Cl_2 (2:1)) to afford green solid (41 mg, 66%). Characterization data (^{1}H NMR, LD-MS, HRMS, absorption, emission) are consistent with those reported in literature.[76]

13-Bromo-18,18-dimethyl-10-tolylchlorin (6). A solution of 1-formyl-5-tolyldipyrromethane **S2**[83] (0.552 g, 2.09 mmol) in THF (20 mL) was treated with solid NBS (744 mg, 4.18 mmol) at −78 °C. The resulting mixture was stirred at −78 °C for 45 min. The cooling bath was removed, a mixture of hexanes (15 mL) and water (15 mL) was added, and the resulting mixture was allowed to warm to room temperature. The organic layer was separated, washed (water and brine), dried (K_2CO_3), and concentrated. The resulting yellow solid was treated with a small amount of dichloromethane, and the resulting solid was filtered, washed with a small amount of dichloromethane, and dried to afford a yellow solid, which was used for the next step without further purification: 530 mg, 60%. Following a reported procedure,[61] a mixture of 2,3,4,5-tetrahydro-1,3,3-trimethyldipyrrin **S3**[84] (0.228 g, 1.20 mmol) and 8,9-dibromo-1-formyl-5-(4-methylphenyl)dipyrromethane (0.471 g, 1.12 mmol) in dichloromethane (36 mL) was treated with a solution of *p*-toluenesulfonic acid monohydrate (1.1 g, 6.0 mmol) in methanol (15 mL), and the resulting solution was stirred at room temperature for 30 min. A sample of 2,2,6,6-tetramethylpiperidine (6.0 mL, 35 mmol) was added, and the reaction mixture was concentrated. The resulting yellowish-brown solid was suspended in acetonitrile (120 mL), and 2,2,6,6-tetramethylpiperidine (6.1 mL, 36 mmol), anhydrous zinc acetate (3.3 g, 18 mmol), and silver triflate (0.93 g, 3.6 mmol) were added. The resulting mixture was refluxed for 18 h exposed to air, then concentrated, dissolved in dichloromethane, and filtered through a short column of silica using dichloromethane. The bluish green fractions containing chlorins were collected and concentrated. The resulting dark green solid was dissolved in dichloromethane (160 mL) and treated with trifluoroacetic acid (1.01 mL, 13.7 mmol). The reaction mixture was stirred for 4 h at room temperature. Saturated aqueous sodium bicarbonate (50 mL) was added, and resulting mixture was stirred vigorously for 5 min. The organic layer was separated, washed with water and brine, dried (Na_2SO_4), filtered, and concentrated. The crude was purified by silica gel column chromatography (hexanes/dichloromethane (2:1)) to afford a dark green solid (0.14 g, 23%). ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.21 (bs, 1H), −1.86 (bs, 1H), 2.07 (s, 6H), 2.69 (s, 3H), 4.67 (s, 2H), 7.54 (d, J = 7.8 Hz, 2H), 8.01 (d, J = 7.8 Hz, 2H), 8.64 (d, J = 4.4 Hz, 1H), 8.85 (s, 1H), 8.90 (s, 1H), 8.95−8.93 (m, 2H), 9.15 (s, 1H), 9.23 (d, J = 4.4 Hz, 1H), 9.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.3, 46.6, 52.2, 94.9, 95.0, 107.5, 112.5, 121.6, 123.9, 127.8, 128.7, 128.8, 132.6, 132.7, 133.7, 134.1, 134.9, 136.3, 137.9, 138.3, 141.5, 151.6, 153.0, 163.2, 176.0; ESI-MS ([M + H]$^+$, M = $C_{29}H_{25}N_4Br$), calcd 509.1342, obsd 509.2 (MALDI), 509.1341 (HRMS, ESI).

18,18-Dimethyl-13-trimethylsilylethynyl-10-tolylchlorin (C1). Following the General Procedure, a mixture of **6** (70 mg, 0.14 mmol), trimethylsilyl acetylene (0.02 mL, 0.2 mmol), $Pd_2(dba)_3$ (37.6 mg, 0.0410 mmol), and P(o-tol)$_3$ (50 mg, 0.16 mmol) in anhydrous toluene/triethylamine (5:1, 60 mL) was stirred at 60 °C. After 2 h, trimethylsilyl acetylene (0.02 mL, 0.2 mmol), $Pd_2(dba)_3$ (37.6 mg, 0.0410 mmol), and P(o-tol)$_3$ (50 mg, 0.16 mmol) were added, and the reaction mixture was stirred at 60 °C overnight. The reaction mixture was concentrated, and product was purified by silica column chromatography (hexanes/dichloromethane (2:1)) to afford a dark green solid (50 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): −2.06 (bs, 1H), −1.69 (bs, 1H), 0.50 (s, 9H), 2.05 (s, 6H), 2.67 (s, 3H), 4.67 (s, 2H), 7.52 (d, J = 7.8 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 8.63 (d, J = 4.4 Hz, 1H), 8.84 (s, 1H), 8.91−8.89 (m, 3H), 9.17 (d, J = 4.4 Hz, 1H), 9.23 (s, 1H), 9.75 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.42, 21.6, 31.2, 46.7, 52.0, 94.5, 95.2, 100.1, 101.9, 107.1, 116.7, 122.7, 124.0, 127.8, 128.9, 130.6, 132.5, 132.8, 133.6, 134.1, 135.1, 137.6, 138.4, 140.0, 141.8, 151.9, 152.9, 163.3, 176.3; MS ([M + H]$^+$, M =

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$C_{34}H_{34}N_4Si$, calcd 527.2626, obsd 527.4 (MALDI), 527.2634 (HRMS, ESI).

13-Ethynyl-18,18-dimethyl-10-tolylchlorin (7). A solution of **C1** (49 mg, 0.093 mmol) in a mixture of THF and methanol (20 mL, 1:1) was treated with K_2CO_3 (16 mg, 0.12 mmol) and stirred at room temperature for 30 min. The reaction mixture was diluted with 10 mL dichloromethane and treated with 10 mL water. The organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography (silica, hexanes/dichloromethane (2:1)) afforded a dark green solid (35 mg, 83%). ^{1}H NMR −2.05 (bs, 1H), −1.66 (bs, 1H), 2.06 (s, 6H), 2.68 (s, 3H), 3.87 (s, 1H), 4.65 (s, 2H), 7.53 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 8.64 (d, J = 4.1 Hz, 1H), 8.85 (s, 1H), 8.90 (d, J = 4.1 Hz, 1H), 8.92 (m, 2H), 9.20 (d, J = 4.6 Hz, 1H), 9.26 (s, 1H), 9.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 31.2, 46.7, 51.9, 79.1, 84.1, 94.6, 95.1, 107.1, 115.5, 122.9, 124.1, 127.8, 129.0, 130.9, 132.5, 132.9, 133.4, 134.1, 135.2, 137.7, 138.4, 139.9, 141.9, 152.1, 152.9, 163.2, 176.5; MS ([M + H]$^+$, M = $C_{31}H_{26}N_4$), calcd 455.2230, obsd 455.4 (MALDI), 455.2224 (HRMS, ESI).

Ch1. Following the General Procedure, a mixture of **7** (20 mg, 0.044 mmol), $Pd_2(dba)_3$ (6.0 mg, 0.0066 mmol), and P(o-tol)$_3$ (8.0 mg, 0.026 mmol) in anhydrous toluene/triethylamine (5:1, 12 mL) was stirred at 60 °C. After 2 h, TLC analysis showed the presence of starting material, additional batches of $Pd_2(dba)_3$ (6.0 mg, 0.0066 mmol) and P(o-tol)$_3$ (8.0 mg, 0.026 mmol) were added, and stirring was continued for a further 2 h. TLC showed the complete consumption of the starting material, and the reaction mixture was concentrated and purified by silica gel column chromatography using hexanes/dichloromethane (2:1). A trace amount of unidentified side products was eluted first, and then the green band corresponding to the product was eluted. A lot of product still left on the column, which was finally eluted with dichloromethane. Fractions containing products were combined, concentrated, dissolved in a minimal amount of dichloromethane, and treated with methanol to afford the pure product as a greenish-brown solid (14 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ −1.87 (bs, 1H), −1.41 (bs, 1H), 2.10 (s, 6H), 2.72 (s, 3H), 4.73 (s, 2H), 7.59 (d, J = 7.3 Hz, 2H), 8.07 (d, J = 7.8 Hz, 2H), 8.68 (d, J = 4.6 Hz, 1H), 8.86 (s, 1H), 8.91 (d, J = 4.1 Hz, 1H), 8.94 (d, J = 4.1 Hz, 1H), 9.07 (s, 1H), 9.21 (d, J = 5.0 Hz, 1H), 9.42 (s, 1H), 9.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.2, 46.9, 51.9, 94.7, 95.5, 107.0, 108.9, 114.9, 123.2, 124.4, 127.9, 129.3, 131.2, 132.5, 133.2, 133.7, 134.2, 135.5, 137.8, 138.3, 140.7, 142.2, 152.4, 152.9, 163.5, 176.9 (Due to the low solubility of **Ch1** its ^{13}C NMR spectra shows very low signal-to-noise ratio); MS ([M + H]$^+$, M = $C_{62}H_{50}N_8$, calcd 907.4237, obsd 907.8 (MALDI) 907.4218 (HRMS, ESI).

Ch2. Following the General Procedure, a mixture of **7** (20 mg, 0.044 mmol), **6** (24 mg, 0.048 mmol), $Pd_2(dba)_3$ (12.1 mg, 0.0132 mmol), and P(o-tol)$_3$ (16.1 mg, 0.0529 mmol) in anhydrous toluene/triethylamine (5:1, 24 mL) was stirred at 60 °C. After 2 h, the TLC analysis showed a complete consumption of the starting material. The reaction mixture was concentrated, and product was purified by silica gel column chromatography (hexanes/dichloromethane (2:1 to 1:1)). The first band (green) was the self-coupled chlorin dimer **Ch1**. The second band (green) was the cross-coupled product. The product streaked on the column. The final purification of both fractions was done using preparative TLC (silica, dichloromethane/hexanes (1:1)) to afford the homocoupled dyad **Ch1** (5 mg, 12%) and the cross-coupled dyad **Ch2** (14 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ −1.91 (bs, 1H), −1.45 (bs, 1H), 2.13 (s, 6H), 2.74 (s, 3H), 4.82 (s, 2H), 7.62 (d, J = 7.8 Hz, 2H), 8.14 (d, J = 7.8 Hz, 2H), 8.71 (d, J = 4.1 Hz, 1H), 8.91 (s, 1H), 8.96 (d, J = 4.1 Hz, 2H), 9.23 (apparent bs, 2H), 9.71 (s, 1H), 9.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.3, 46.8, 52.2, 91.7, 94.6, 95.6, 107.2, 117.2, 122.7, 124.0, 127.9, 129.0, 130.1, 132.6, 132.9, 134.3, 135.2, 137.7, 138.6, 140.0, 141.9, 152.0, 153.1, 163.5, 176.4; MS ([M + H]$^+$, M = $C_{60}H_{50}N_8$, calcd 883.4231, obsd 884.2 (MALDI), 883.4257 (HRMS, ESI).

18,18-Dimethyl-13-phenylethynyl-10-tolylchlorin (C2). Following the General Procedure, a mixture of **6** (40 mg, 0.079 mmol), phenylacetylene (0.01 mL, 0.09 mmol), $Pd_2(dba)_3$ (21.7 mg, 0.0237 mmol), and P(o-tol)$_3$ (29 mg, 0.095 mmol) in anhydrous toluene/triethylamine (5:1, 36 mL) was stirred at 60 °C. After 2 h additional batches of phenylacetylene (0.01 mL, 0.09 mmol), $Pd_2(dba)_3$ (21.7 mg, 0.0237 mmol), and P(o-tol)$_3$ (29 mg, 0.095 mmol) were added, and stirring was continued at 60 °C overnight. The reaction mixture was concentrated and purified by silica gel column chromatography (hexanes/dichloromethane (2:1)) to afford the product as a dark green solid (42 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.02 (bs, 1H), −1.62 (bs, 1H), 2.07 (s, 6H), 2.70 (s, 3H), 4.69 (s, 2H), 7.56−7.45 (m, 5H), 7.88 (d, J = 7.4 Hz, 2H), 8.05 (d, J = 8.2 Hz, 2H), 8.67 (d, J = 4.1 Hz, 1H), 8.87 (s, 1H), 8.92 (d, J = 4.1 Hz, 2H), 8.96 (s, 1H), 9.20 (d, J = 5.0 Hz, 1H), 9.34 (s, 1H), 9.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.2, 46.7, 52.1, 84.8, 94.5, 95.2, 96.5, 107.2, 117.0, 122.5, 123.8, 123.9, 127.8, 128.7, 128.9, 130.0, 131.9, 132.5, 132.8, 134.0, 134.2, 135.0, 137.6, 138.5, 129.8, 141.7, 151.9, 153.0, 163.3, 176.3; MS ([M + H]$^+$, M = $C_{37}H_{30}N_4$), calcd 531.2543, obsd 531.3 (MALDI) 531.2542 (HRMS, ESI).

ZnC2. A solution of **C2** (6 mg, 0.01 mmol) in $CHCl_3$/MeOH (5:1, 5 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (125 mg, 0.569 mmol). The resulting mixture was stirred at room temperature. After 3 h TLC analysis (hexanes/dichloromethane 1:1) showed complete consumption of starting material and essentially quantitative formation of zinc complex. Mixture was diluted with CH_2Cl_2, washed (saturated aqueous sodium bicarbonate and brine), dried (Na_2SO_4), and concentrated. Column chromatography (silica, hexanes/dichloromethane 1:1) provided a green solid (5 mg, 80%). ^{1}H NMR δ 2.04 (s, 6H), 2.68 (s, 3H), 4.56 (s, 2H), 7.41−7.52 (m, 5H), 7.82−7.84 (m, 2H), 7.97 (d, J = 7.8 Hz, 2H), 8.64 (d, J = 4.2 Hz, 1H), 8.57 (s, 1H), 8.74 (d, J = 4.4 Hz, 1H), 8.82 (d, J = 4.2 Hz, 1H), 8.84 (s, 1H), 9.03 (s, 1H), 9.04 (d, J = 4.4 Hz, 1H), 9.54 (s, 1H); MS ([M + H]$^+$, M = $C_{37}H_{28}N_4Zn$) calcd 593.1678, obsd 593.1 (MALDI), 593.1699 (HRMS, ESI).

ZnCh1. A solution of dimer **Ch1** (2 mg, 2 μmol) in a mixture of chloroform and methanol (6 mL, 5:1) was treated with zinc acetate dihydrate (24 mg, 0.11 mmol), and the reaction mixture was stirred at room temperature for 3 h. Saturated aqueous sodium bicarbonate was added, the organic layer was washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography (silica, dichloromethane) afforded a green solid (1 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 12H), 2.71 (s, 6H), 4.56 (s, 4H), 7.55 (d, J = 7.8 Hz, 4H), 7.99 (d, J = 7.8 Hz, 4H), 8.56 (m, 4H), 8.73 (d, J = 4.1 Hz, 2H), 8.76 (d, J = 4.6 Hz, 2H), 8.95 (s, 2H), 8.99 (d, J = 4.1 Hz, 2H), 9.04 (s, 2H), 9.45 (s, 2H); MS ([M + H]$^+$, M = $C_{62}H_{46}N_8Zn_2$, calcd 1031.2, obsd 1031.5 (MALDI); HRMS ESI spectrum is not available due to the poor ionization of sample under ESI conditions.

■ ASSOCIATED CONTENT

Supporting Information

Additional synthetic schemes, complete results of DFT calculations, additional spectra for titration of zinc complexes with nitrogen ligands, properties of bacteriochlorin and chlorin dyads and monomers in solvents of different polarity, and copies of ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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