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Amphiphilic BODIPY-Hydroporphyrin Energy Transfer Arrays with Broadly Tunable Absorption and Deep Red/Near-Infrared Emission in Aqueous Micelles

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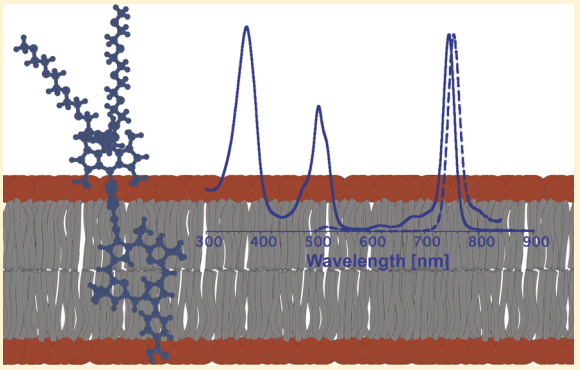
Supporting Information

ABSTRACT: BODIPY-hydroporphyrin energy transfer arrays allow for development of a family of fluorophores featuring a common excitation band at 500 nm, tunable excitation band in the deep red/near-infrared window, and tunable emission. Their biomedical applications are contingent upon retaining their optical properties in an aqueous environment. Amphiphilic arrays containing PEG-substituted BODIPY and chlorins or bacteriochlorins were prepared and their optical and fluorescence properties were determined in organic solvents and aqueous surfactants. The first series of arrays contains BODIPYs with PEG substituents attached to the boron, whereas in the second series, PEG substituents are attached to the aryl at the *meso* positions of BODIPY. For both series of arrays, excitation of BODIPY at 500 nm results in efficient energy transfer to and bright emission of hydroporphyrin in the deep-red (640−660 nm) or near-infrared (740−760 nm) spectral windows. In aqueous solution of nonionic surfactants (Triton X-100 and Tween 20) arrays from the second series exhibit significant quenching of fluorescence, whereas properties of arrays from the first series are comparable to those observed in polar organic solvents. Reported arrays possess large effective Stokes shift (115−260 nm), multiple excitation wavelengths, and narrow, tunable deep-red/near-IR fluorescence in aqueous surfactants, and are promising candidates for a variety of biomedical-related applications.



INTRODUCTION

Multichromophoric energy transfer (ET) arrays enable construction of fluorophores with optical properties that are not available for single chromophores, and thereby can greatly expand the capabilities of fluorescence imaging and biosensing.[1−7] In ET arrays, excitation energy flows from chromophores with higher excited state energies to that with the lowest energy (terminal acceptor) allowing, for example, construction of fluorophores with a large (pseudo)Stokes' shift,[2] development of a family of fluorophores with a common excitation wavelength and variable emission bands,[3,4] and fluorophores with multiple excitation wavelengths.[5] Of particular interest are ET arrays with acceptors emitting in the deep-red or near-infrared spectral window, as they can be potentially used for deep-tissue *in vivo* imaging.[3,6] We employed hydroporphyrins (chlorins and bacteriochlorins) as fluorescent entities in energy transfer arrays, due to their favorable properties for certain bioimaging applications.[3,7] Hydroporphyrins possess narrow (fwhm <25 nm) deep-red or near-IR emission bands, of which the maximum can be precisely tuned across a broad range (650−820 nm), by a variety of structural modifications.[8−11] Collectively, these properties make hydroporphyrins excellent candidates for construction of probes for *in vivo* imaging,[12] and multicolor fluorescence-guided surgery.[13] The latter application would greatly benefit from a family of deep-red or near-IR fluorophores with (a) a large (pseudo)Stokes shift (>100 nm), which allows for higher tumor-to-background ratio, due to elimination of both tissue autofluorescence and detection of the scattered light from excitation, and (b) two excitation wavelengths; a common one in the green spectral window (500 nm), and a unique one in the deep-red/near-IR region (650−900 nm), which enables the selective detection of tumors localized on the surface of the tissue and in deep-tissue.[13] In order to achieve these properties in hydroporphyrins, we recently synthesized a series of BODIPY-chlorin arrays.[7] BODIPYs possess a strong absorption (with extinction coefficient up to 100 000 $M^{-1}\cdot cm^{-1}$), which is tunable across the visible region (500−700 nm).[14] Thus, we prepared a series of arrays, with a common BODIPY absorbing at 500 nm (where hydroporphyrins exhibit rather low absorbance), and different chlorins, absorbing and emitting in 630−680 nm range, and found that excitation of arrays at the maximum of BODIPY absorbance results in strong emission of chlorin, with

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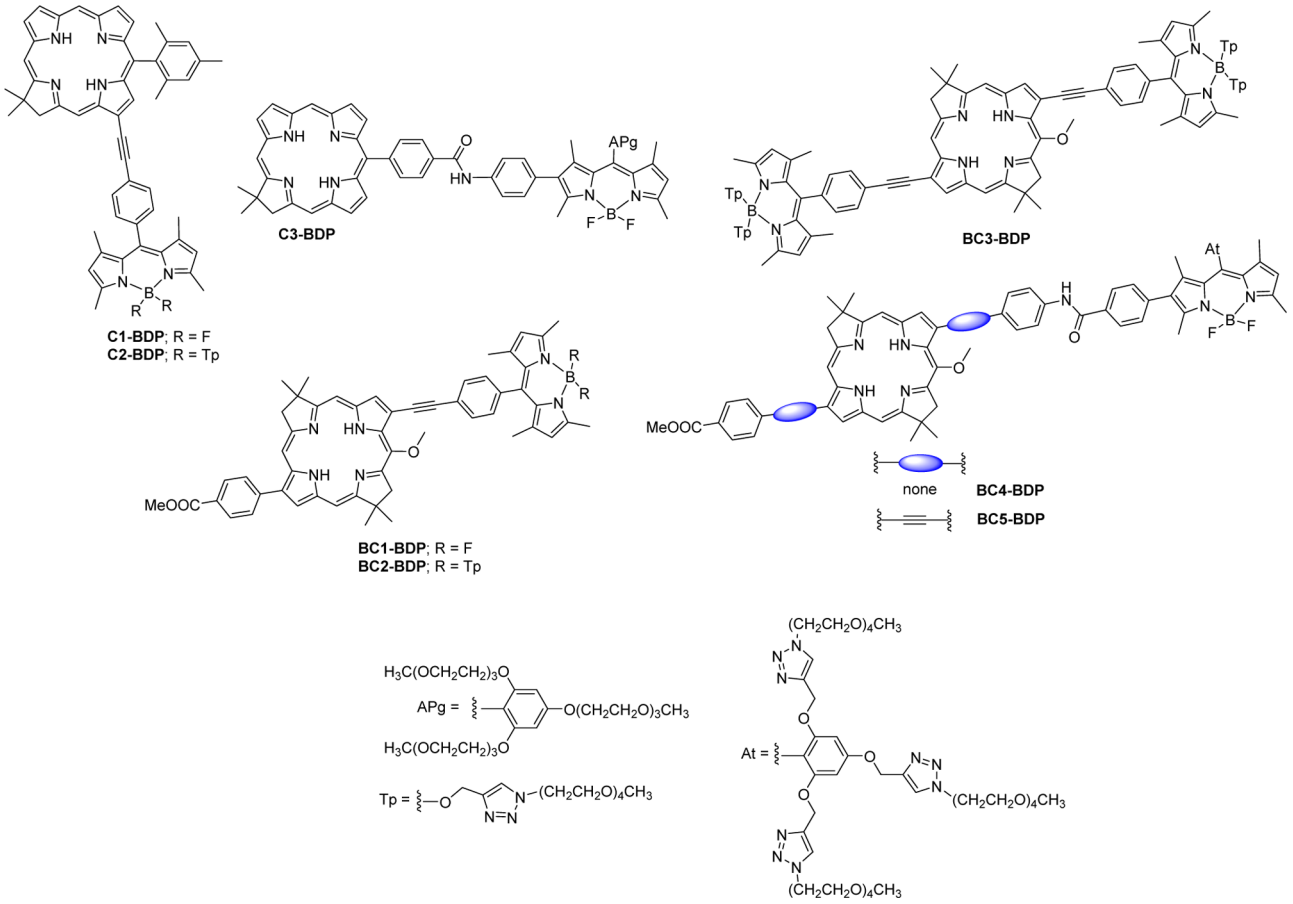
Chart 1. Structures of Chlorin-BODIPY and Bacteriochlorin-BODIPY Dyads



the fluorescence quantum yield (Φ_f) comparable to that obtained from direct chlorin excitation.[7] These favorable properties of BODIPY-chlorin arrays prompted us to further explore this strategy, with two principal aims in mind. First we intend to shift the emission wavelength maxima of BODIPY-hydroporphyrin arrays further into the near-IR spectral window (>700 nm). Our second goal is to develop BODIPY-hydroporphyrin arrays which will be suitable for a broad range of biomedical applications, particularly for *in vivo* imaging.

In order to achieve our first goal, we decided to synthesize a family of bacteriochlorin-BODIPY arrays. Bacteriochlorins possess a strong, long-wavelength absorption Q_y band and emission band in the range of 710−800 nm, as well as a much weaker absorption Q_x band at around 490−550 nm.[11] Therefore, they should be an excellent energy acceptor from BODIPY. BODIPY can function as a either an energy donor or acceptor, as has been demonstrated by the synthesis of a plethora of ET arrays, including BODIPY-porphyrin,[15] BODIPY-corrole,[16] and BODIPY-phthalocyanine[17] arrays. To the best of our knowledge, the only reported BODIPY-bacteriochlorin arrays includes noncovalent assemblies in lipid vesicles[18] or micelles,[19] where energy transfer from BODIPY to bacteriochlorins occurs.

Achieving the second goal requires the ability to prepare arrays that retain their optical and photochemical properties in aqueous media. While reported BODIPY-chlorin arrays exhibit favorable optical properties, i.e., efficient energy transfer from BODIPY to chlorin, and minimal quenching of chlorin fluorescence in both polar and nonpolar organic solvent, they are notoriously hydrophobic, and show no solubility in aqueous media.[7] The preparation of water-soluble arrays containing hydroporphyrins presents several challenges. First, it would require installation of water-solubilizing groups on both hydroporphyrin and BODIPY. There are a large number of water-soluble BODIPY derivatives containing diverse water-solubilizing groups, including sulfonic acids,[20] zwitterionic ammonium-sulfonic acid substituents,[21] phosphonates,[22] polyethylene glycol (PEG),[23] and sugars.[24] Water-soluble synthetic chlorins and bacteriochlorins, containing phosphonate,[25,26] PEG,[26,27] carboxylates,[26,28] or ammonium salts,[26,29] were also reported. However, we presume, that synthesis of arrays containing water-solubilizing groups on both BODIPY and hydroporphyrins would be prohibitively labor- and cost-intensive, since it will add several synthetic and purification steps to already lengthy synthesis of hydrophobic arrays.

Moreover, in highly polar water, an additional concern is the potential for photoinduced electron transfer (PET), between arrays' components, which can significantly quench fluorescence of hydroporphyrin. Significant quenching of fluorescence in polar solvents, attributed to the PET, for particular chlorin-BODIPY arrays,[7] and for other arrays containing hydroporphyrins[30] has been reported.

To circumvent both of the problems, associated with the use of BODIPY-hydroporphyrin arrays in biomedicinal imaging, i.e., lack of water solubility and possible quenching of hydroporphyrin fluorescence by PET, we propose to encapsulate arrays into water-soluble nanostructures: micelles and vesicles. We hypothesize that insertion of the arrays into the hydrophobic part of a micelle/vesicle of low dielectric constant, will preserve arrays' favorable optical properties (high fluorescence quantum yield of hydroporphyrin emission upon

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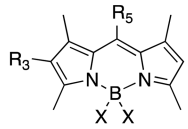
Chart 2. Structures of Novel Hydrophilic BODIPY Monomers Reported Here[a]



Compound	R_3	R_5	X
BDP1	-H	4-HC≡C-C_6H_4-	-Tp
BDP2	-H	-APg	-F
BDP2-NH_2	4-H_2N-C_6H_4-	-APg	-F
BDP3	-H	-At	-F
BDP3-I	-I	-At	-F
BDP3-COOMe	4-MeOOC-C_6H_4-	-At	-F

[a]For −Tp, −APg, and −At, see Chart 1.

excitation at the maximum of BODIPY absorption) in aqueous media. Encapsulation into self-assembled micelles and vesicles is an established way to deliver hydrophobic photonic agents (e.g., fluorophores, or singlet oxygen photosensitizers) to the target cells.[31−33] Thus, for example, tetrapyrrolic macrocycles and phthalocyanines were encapsulated in vesicles made from amphiphilic diblock polymers,[31] Pluronic F127 micelles,[32] and phospholipid bilayers.[33] Photophysical properties of hydroporphyrins were also examined for energy-related applications in phospholipid membranes, SDS, or Triton X-100 micelles.[18,19,34−37] To the best of our knowledge, no synthetic, multichromophoric arrays, containing hydroporphyrins were studied in self-assembled micelles or bilayers.

Previous results suggested that the amphiphilic character of the chlorins and bacteriochlorins greatly facilitates their insertion into micelles or bilayers.[34] Therefore, here we prepared a series of amphiphilic arrays containing novel hydrophilic BODIPY derivatives and hydrophobic chlorins and bacteriochlorins (Chart 1). Preparation of arrays required synthesis of a set of novel, hydrophilic BODIPY derivatives (Chart 2) containing neutral oligoethylene glycol (PEG) water-solubilizing moieties. We then evaluated basic photochemical properties of arrays in organic solvents, as well as in aqueous surfactant solutions.

RESULTS AND DISCUSSION

Design. Amphiphilic hydroporphyrin-BODIPY dyads (Chart 1) include two BODIPY-chlorin dyads (**C2-BDP** and **C3-BDP**) and four bacteriochlorin-BODIPY arrays (dyads **BC2-BDP**, **BC4-BDP**, and **BC5-BDP**, and triad **BC3-BDP**). We also included two hydrophobic dyads **C1-BDP** and **BC1-BDP**, for comparative spectroscopic studies. In arrays **C1-BDP**, **C2-BDP**, **BC1-BDP**, **BC2-BDP**, and **BC3-BDP** the BODIPY is attached via acetylene linker at the hydroporphyrin 13- (or 3,13-) positions. For other dyads, BODIPY subunits are attached to the hydroporphyrin through diaryl-amide linkers, either at the 10-position of chlorin (**C3-BDP**) or 13-position of bacteriochlorin (**BC3-BDP**, **BC4-BDP**, and **BC5-BDP**). In arrays **C1/2-BDP** and **BC1/3-BDP** BODIPY subunits are attached through a linker connected to the *meso* position, while in other dyads the linker is attached to the 3-position of BODIPY. Note that **BC3-BDP** possesses a bolaamphiphilic character, i.e., hydrophilic substituents are situated on both sides of the hydrophobic core.[38]

First, we synthesized hydrophilic BODIPY derivatives, equipped with functional groups suitable for their subsequent attachment to hydroporphyrins (Chart 2). As a water-solubilizing group we have chosen polyethylene-glycol (PEG) chains, due to their lack of charge (charged groups may cause undesirable interactions with biomolecules) and biocompatibility.[39] Two principal architectures of hydrophilic BODIPY derivatives were examined (Chart 2). In **BDP1** two PEG chains are attached to the boron atom, through a triazole moiety. **BDP2−3** possess PEG substituents at the 2,4- and 6-positions of a *meso* aryl group, either directly (**BDP2**) or through triazole (**BDP3**). **BDP1** possesses a terminal acetylene which was further used for attachment to hydroporphyrins. In **BDP2−3**, additional functional groups were installed at the 3-position of BODIPY: iodo, *para*-aminophenyl, and *para*-methoxycarbonylphenyl for compounds **BDP3-I**, **BDP2-NH_2**, and **BDP3-COOMe**, respectively.

Synthesis. *BODIPY Derivatives.* **BDP1** was synthesized following the reported procedures for boron-alkoxylation in BODIPY (Scheme 1).[40,41] Thus, treatment of known **BDP4**[7] with $AlCl_3$ in THF at 40 °C and subsequently with an excess of propargyl alcohol, afforded **BDP5** in 86% yield. Note that the significant excess of alcohol is required for an efficient transformation of BODIPY into *B*-propargyloxy derivative. The PEG moiety was subsequently installed through a "click" reaction with azide **1**,[42] under microwave irradiation,[43] which afforded **BDP6** in 58% yield. Click reaction under microwave irradiation was completed in 30 min. Subsequent removal of the protecting TMS group under standard conditions (K_2CO_3 in MeOH/THF) afforded target **BDP1** in 81% yield.

Synthesis of **BDP2** and subsequently **BDP2-NH_2** (Scheme 2) started from alkylation of 2,4,6-trihydroxybenzaldehyde **2** by tosyl-functionalized triethylene glycol monomethyl ether **3**, which afforded trialkoxyproduct **4** in 47% yield.[44] BODIPY was prepared by standard three-step, one-pot synthesis: reaction of aldehyde **4** with 2,4-dimethylpyrrole, catalyzed by TFA, oxidation of resulting dipyrromethane by DDQ, and reaction with $BF_3{\cdot}OEt_3$ afforded **BDP2** in 9% yield. The low isolated yield is due to extensive chromatographic purification, which was necessary to separate target **BDP2** from impurities. Monoiodination at the 3 position of BODIPY was performed following a published procedure,[45,46] using I_2/HIO_3 system, and monoiodo product **BDP2-I** was isolated in 56% yield. This sample contained a small amount of unidentified impurity, separation of which using column chromatography proved to be very difficult. Subsequent Suzuki reaction of **BDP2-I** with

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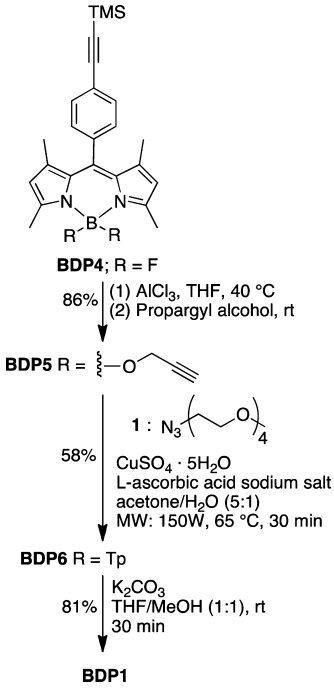
Scheme 1. Synthesis of BDP1

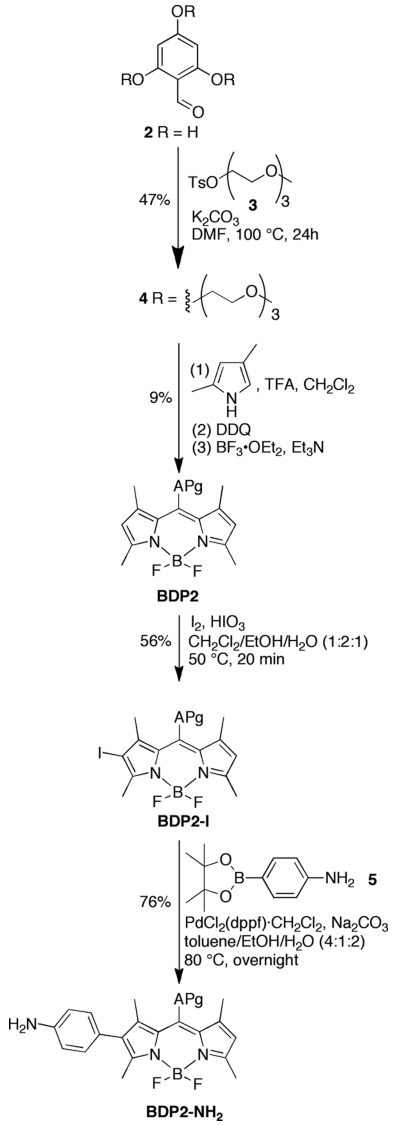


boronic ester **5**, under previously reported conditions,[46] afforded **BDP2-NH$_2$** in 76% yield.

BDP3 and **BDP3-COOMe** were prepared following essentially the same protocol (Scheme 3). Condensation of aldehyde **6**[47] with 2,4-dimethylpyrrole, followed by oxidation with DDQ and complexation with $BF_3{\cdot}OEt_3$ afforded **BDP3′** in 23% yield. Tetraethylene glycol methyl ether chains were installed by microwave-assisted click reaction, which afforded **BDP3** in 62% yield. Since **BDP3** is a hydrophilic and highly polar compound, we decided to perform further derivatization, necessary to obtain **BDP3-I** and **BDP3-COOMe**, on **BDP3′** anticipating that the less polar and hydrophobic BODIPY derivatives would be easier to purify relative to their more polar and hydrophilic PEG-containing congeners (Scheme 4). Thus, iodination of **BDP3′** with I_2/HIO_3 afforded **BDP3′-I** in 46−61% yield. Both **BDP3′** and **BDP3′-I** were indeed much easier to purify through column chromatography than **BDP2** and **BDP2-I**, which is a chief advantage of the **BDP3** series of compounds compared to **BDP2**. At this point, tetraethylene glycol chains needed to be installed, since the presence of terminal acetylene moieties prevents a controlled Suzuki reaction (and any palladium-catalyzed reaction) on **BDP3′-I**. Microwave-assisted click reaction of **BDP3′-I** with azide-terminated triethylene glycol **1** afforded **BDP3-I** in 87% yield. Subsequent Suzuki reaction with boronic ester **7** allowed installation of the *p*-methoxycarbonylphenyl moiety in 70% yield (**BDP3-COOMe**).

Hydroporphyrin-BODIPY Dyads. Syntheses of arrays **C1/2-BDP**, and **BC1/3-BDP** were achieved following the reported procedure for analogous dyads,[7] through Sonogashira reaction of acetylene-terminated BODIPY (**BDP-1** or **BDP-F**) and suitable bromochlorin (**C−Br**[48]) or bromobacteriochlorins (**BC-P**[3] and **BC-Br$_2$**[49]) with moderate yields (26−35%, Schemes 5, 6, and 7). The low yield in the cases of **C2-BDP** and **BC2/3-BDP** is probably, at least in part, due to the lability of B−O bond under reaction conditions. This issue became evident during attempted optimization of Sonogashira reaction

Scheme 2. Synthesis of BDP2 and BDP2-NH$_2$[a]



[a]For APg− see Chart 1.

conditions, when K_2CO_3 was used as a base, and reactions delivered exceptionally low yield of expected product.

Dyad **C3-BDP** was synthesized in reaction of **C−COOH** (obtained quantitatively by hydrolysis of the corresponding methyl ester)[7] and **BDP2-NH$_2$**, in the presence of EDC/DMAP system, in 30% yield (Scheme 8).

For the synthesis of **BC4-BDP** and **BC5-BDP** we first attempted EDC-mediated coupling of acid derived from hydrolysis of **BDP3-COOMe** with amine-functionalized bacteriochlorins **BC-P-NH$_2$** and **BC-E-NH$_2$** (Scheme 10). Required **BC-P-NH$_2$** and **BC-E-NH$_2$** were prepared in palladium coupling reactions of **BC-P**[3] and **BC-E**,[50] respectively (Scheme 9). Hydrolysis of **BDP3-COOMe** resulted in low yield (22%) of corresponding carboxylic acid, due to extensive decomposition of BODIPY, and subsequent EDC-mediated amide formation with **BC-P-NH$_2$** also provided the desired product with moderate yield (22% yield, Scheme 10). Therefore, we pursued a different approach, in which we first installed a boronic pinacolate moiety on the bacteriochlorin and subsequently performed Suzuki reaction with **BDP3-I**. Thus, EDC-mediated reaction of **BC-P-NH$_2$** and **BC-E-NH$_2$**

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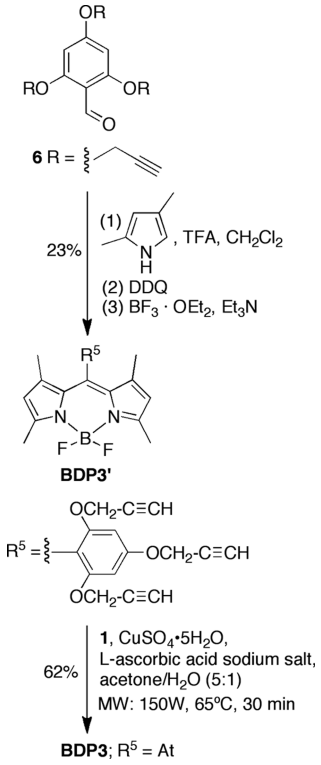
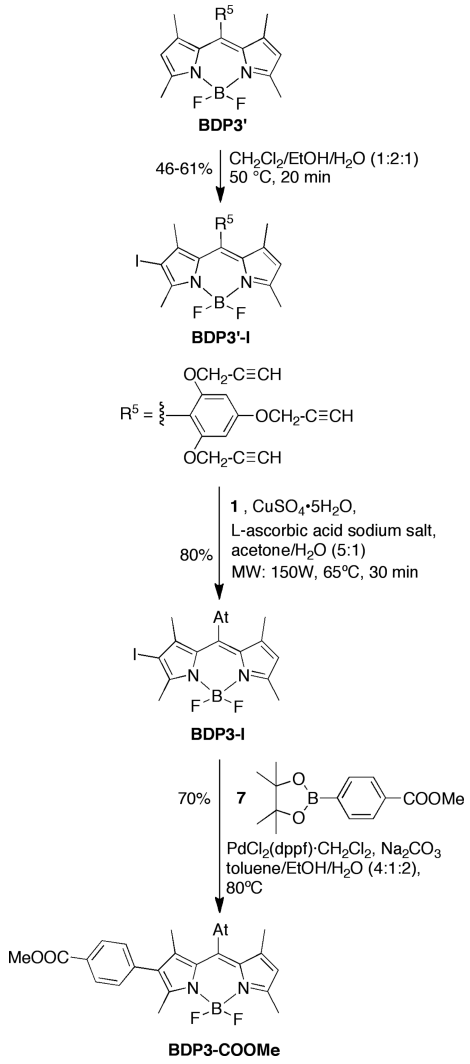
Scheme 3. Synthesis of BDP3[a]



[a]For At− see Chart 1.

Scheme 4. Synthesis of BDP3-COOMe[a]



[a]For At− see Chart 1.

with benzoic acid derivative **8** provides corresponding boronic esters **BC-P-B** and **BC-E-B** in excellent yields (as judged from TLC analysis), however silica column purification provided the target compounds with moderate yields (29% and 33%, respectively, Scheme 11). This is probably due to the reported ability of silica to hydrolyze boronic esters.[51] Therefore, **BC-P-B** and **BC-E-B** were purified by aqueous workup (to remove any excess of **8**) and used directly in the next step. This procedure provides **BC-P-B** and **BC-E-B** in >70% yield, with approximately 90% or greater purity. Subsequent Suzuki reaction of **BC-P-B** and **BC-E-B** with **BDP3-I** provides the corresponding dyads in 22% and 30% yields, respectively (Scheme 12).

Characterization. The new BODIPY monomers and arrays were characterized by ^{1}H and ^{13}C NMR and MS. ^{1}H NMR spectra of BODIPY-hydroporphyrin arrays indicated resonances of both hydroporphyrins and BODIPY units. High-resolution ESI-MS shows peaks of m/z consistent with proposed structures. Note that some BODIPY derivatives (dyads and monomers) consistently show excessive number of protons from the PEG substituents. However, excessive chromatographic purification does not change the proton ratio, and other analytical methods do not show the presence of the PEG impurities. High-resolution MS show m/z consistent with proposed structures.

One of our main concerns here was the stability of **BDP1** in regards to B−O bonds, which are prone to reactions with acids, bases, and nucleophiles.[40,41] This rises the questions whether such derivatives are stable under typical conditions used for bioimaging studies, and whether presence of B−O bonds permits synthetic manipulations on monomers and arrays containing a **BDP1**-type structure, necessary for their further elaboration. Thus, first we determined that no noticeable changes in absorption spectrum were observed upon 24h storage of a diluted solution of **BDP1** in toluene, DMSO, and PBS (pH = 7.4). Then, we assessed the stability of **BDP1** under both basic and acidic conditions, in the presence of NaOH (aqueous 2M) in THF/MeOH (2:1) solution and TFA in CH_2Cl_2 solution (4:1 v/v), respectively. In both cases significant changes in UV−vis absorption were observed, specifically disappearance of the BODIPY band, and formation of a new broad band at shorter wavelength, indicating decomposition of **BDP1** under these conditions. These observations have led to the conclusion, that **BDP1**-containing compounds should be sufficiently stable for bioimaging applications in biological media, but their reactivity toward acids and bases limits the number of synthetic transformations, available for modification of this and similar compounds.

Absorption and Emission Properties. Absorption and emission properties of arrays and monomers were determined in organic solvents (toluene and DMF), PBS (for water-soluble BODIPY), and in micelles (i.e., aqueous Triton X-100 and Tween 20 solutions). The key aspects that we intended to determine are (1) the fluorescence properties of water-soluble BODIPY in aqueous media; (2) the influence of solvent dielectric constants on the fluorescence quantum yield of BODIPY-hydroporphyrin dyads, specifically on the efficiency of energy

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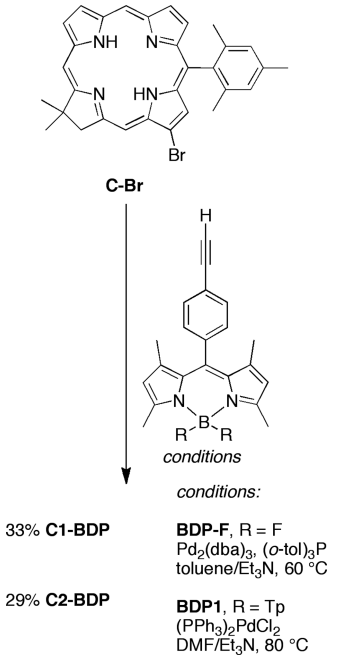
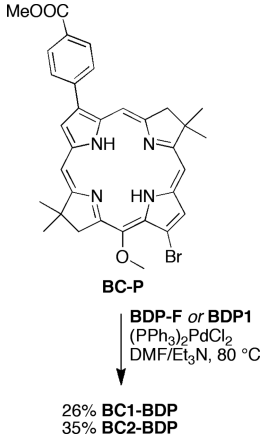
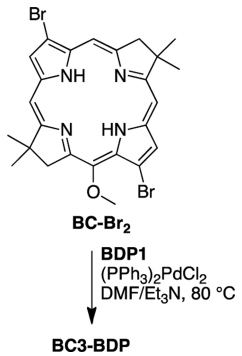
Scheme 5. Synthesis of Dyads C1-BDP and C2-BDP



Scheme 6. Synthesis of Dyads BC1-BDP and BC2-BDP



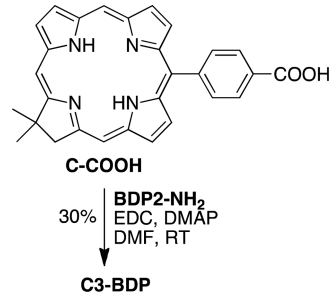
Scheme 7. Synthesis of Dyad BC3-BDP



and electron transfer between BODIPY and hydroporphyrins; and (3) whether amphiphilic BODIPY-hydroporphyrin arrays retain their fluorescence properties in aqueous micelles.

BODIPY. Absorption spectra of **BDP1**−**3** were determined in both PBS (pH = 7.4) and toluene (Figure 1 and Table 1). The spectra in PBS are of a similar width as in toluene, which

Scheme 8. Synthesis of Dyad C3-BDP



indicates, that at least at the concentration of 10 μM there is no aggregation. The absorption maxima for all three dyads in PBS are nearly identical, and the maxima of absorption are slightly bathochromically shifted (2−5 nm) in toluene. Installation of the aryl ring at the 3-position of BODIPY causes a red shift of absorption maxima of roughly 15 nm (Table 1, Figure 1).

The emission properties of water-soluble BODIPY were determined in both organic solvents (toluene and DMF) and aqueous media (PBS). Results are given in Table 1. All BODIPY show a strong emission band with Stokes' shift of 10−15 nm, and the maxima of emission bands for each compound are nearly independent of solvent. All examined water-soluble BODIPY, except **BDP2**, show a very high fluorescence quantum yield Φ_f, exceeding 0.75 in most cases, regardless of solvent. Two features are worth commenting on. First, Φ_f of **BDP1** in PBS is remarkably higher than in organic solvents (0.77 vs 0.56). Second, the BODIPY derivatives, possessing electron-rich trialkoxyphenyl substituents at the *meso* positions (**BDP2**, **BDP3**, **BDP3′**, and **BDP3-COOMe**) show comparable Φ_f in nonpolar toluene and polar solvents (DMF, PBS). It is well-known that BODIPY with electron-rich substituents at the *meso* position exhibit a significant reduction of the Φ_f in polar solvents, due to photoinduced electron transfer from *meso*-substituent to the BODIPY.[52] It is possible, that the four methyl substituents on the BODIPY core increase the reduction potential of BODIPY to a level where PET is not energetically feasible. The only exception is **BDP2**, which shows a significant reduction of Φ_f in PBS (0.25), compared to that observed in toluene (0.89). The reason for the observed quenching is unknown. Attachment of the aryl group to the BODIPY core, as in **BDP3-COOMe** does not impact Φ_f, which is still >0.80 in both organic and aqueous solutions. Overall, these results indicate that both the **BDP1** and **BDP3** series of compound exhibit excellent fluorescence properties in aqueous media, and as such may be useful for fluorescence imaging applications.

Arrays. Absorption spectra of amphiphilic arrays in toluene (Figure 2, Table 2) are essentially the sum of the absorption spectra of the corresponding monomers: BODIPY and hydroporphyrins (for the absorption maxima of corresponding hydroporphyrin monomers see Table S1). Interestingly, the absorption maximum for BODIPY moiety in **BC5-BDP** varies noticeably compared to **BDP3-COOMe** (527 nm vs 518 nm, respectively).

The absorption spectra of dyads in PBS/Triton X-100, at the array concentration of approximately 10 μM (assuming average extinction coefficient at the *B* band of chlorin[53] 150 000 $M^{-1}\cdot cm^{-1}$ and of bacteriochlorin[54] 100 000 $M^{-1}\cdot cm^{-1}$) are nearly identical to that in toluene for each array, with no noticeable broadening of the absorption bands. Apparently, there is no aggregation at

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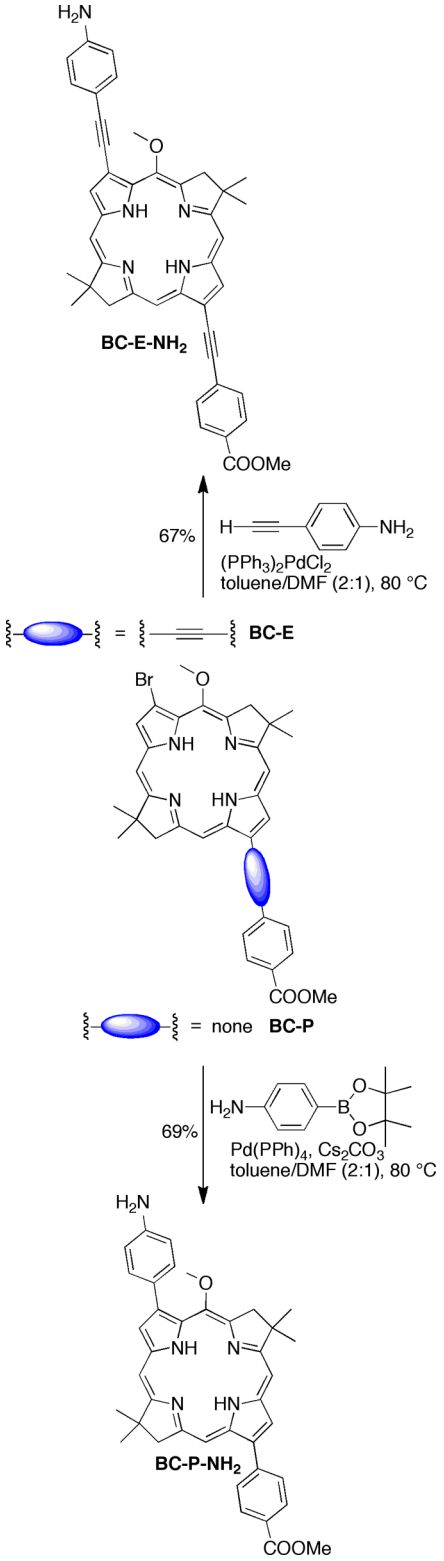
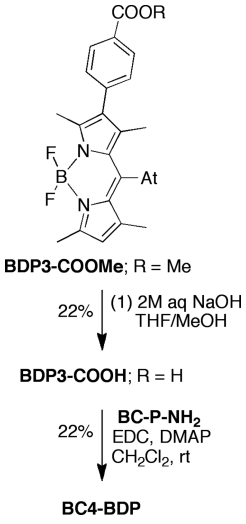
Scheme 9. Synthesis of Intermediates BC-P-NH_2 and BC-E-NH_2



this concentration. In case of Tween 20 we observed a different behavior. For dyads **C2-BDP**, **BC2-BDP**, and **BC3-BDP** an effective concentration of 10 μM of array can be achieved (based on the intensity of hydroporphyrin *B*-band). In case of **BC2-BDP** dyads, there are no significant differences in absorption spectra compared to those observed in toluene and

Scheme 10. Synthesis of Dyad BC4-BDP through EDC-Mediated Coupling



Triton X-100, besides a small alteration of the bands relative intensities. For **BC3-BDP** however, a new band at λ = 794 nm is observed, together with a significant reduction of bacteriochlorin Q_y band intensity. The presence of distinctive, long-wavelength absorption band in micellar solution was previously reported for chlorophyll derivatives, and is indicative of the formation of discrete assemblies.[36,55] For **C3-BDP** and **BC4/5-BDP** dyads the dissolution of respective dyads in aqueous Tween 20 results in a severe broadening of absorption features, which suggests extensive aggregation of the dyads. Absorption spectra obtained upon filtration of the resulting mixture through a 20 μm membrane are similar to that obtained in toluene and Triton X-100 solution (i.e., with nonbroadened bands) albeit at much lower concentration (e.g., absorption of the B band <0.1, which implies concentration below 1 μM), and with markedly altered band ratios (Figure S3, Supporting Information). No significant broadening or shifting of the BODIPY band was observed for any of examined arrays. To summarize (1) all arrays examined here show better solubility in aqueous Triton X-100 solution than in Tween 20 solution. (2) Arrays where PEG substituents are presented on the boron of BODIPY are better soluble in aqueous Tween 20 micelles, and are less prone to aggregation than those possessing PEG substituents at the *meso*-aryl ring of BODIPY.

Next we examined the fluorescence properties of BODIPY-hydroporphyrin arrays. As expected, emission spectrum of each dyad is dominated by the emission of the hydroporphyrin moiety, regardless of wavelength of excitation, while emission of BODIPY subunit at around 500 nm is significantly diminished (Figure 3). Excitation fluorescence spectra, monitored at wavelength where hydroporphyrins emit exclusively (>650 nm), resemble corresponding absorption spectra. These observations indicate efficient energy transfer from BODIPY to hydroporphyrin chromophore. Quantitatively, the energy transfer efficiency (ETE)[2,4] was expressed as a ratio of fluorescence quantum yield Φ_f of hydroporphyrin subunit upon excitation at the maximum of BODIPY absorbance (500 nm) to the same Φ_f upon direct excitation of hydroporphyrin subunit at the maximum of the *B* absorption band. ETE for all dyads in toluene exceeds 0.90. The relatively high ETE for all dyads is probably driven by the overlap of the BODIPY emission band with the Q_x band of hydroporphyrins, however,

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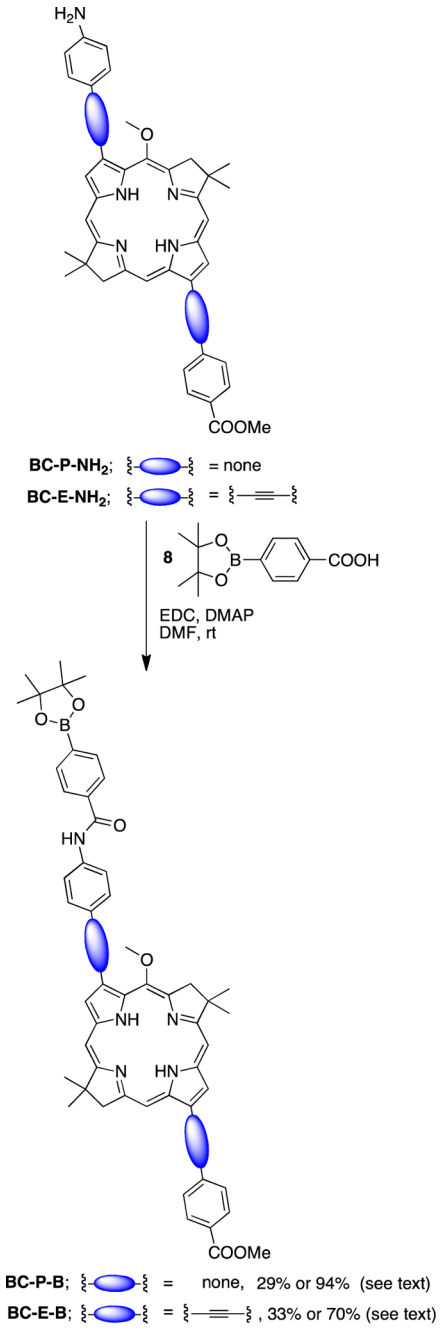
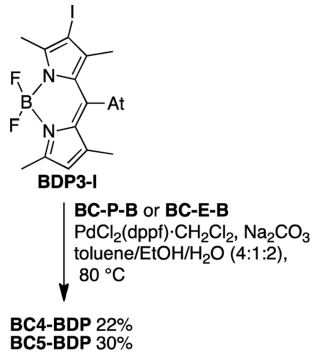
Scheme 11. Synthesis of Boronic Esters BC−P-B and BC-E-B



Scheme 12. Synthesis of Dyads BC4-BDP and BC5-BDP through Suzuki Cross-Coupling



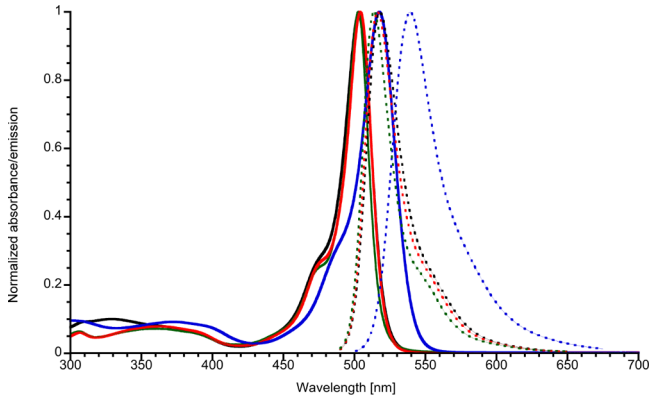


Figure 1. Absorption (solid, c ∼ 10 μM) and emission (dotted, c ∼ 1 μM) spectra of BODIPY monomers in PBS (pH = 7.4): **BDP1** (black), **BDP2** (green), **BDP3** (red), and **BDP3-COOMe** (blue). All spectra were taken at room temperature.

Table 1. Absorption and Emission Properties of BODIPY

compound	λ_{abs} PBS (toluene)	λ_{em} PBS (toluene)	Φ_f[a] PBS	Φ_f[a] toluene	Φ_f[a] DMF
BDP1	503 (505)	518 (519)	0.77	0.56	0.56
BDP2	503 (508)	514 (518)	0.25	0.89	0.80
BDP3	504 (507)	517 (520)	1.0	0.97	1.0
BDP3-COOMe	518 (521)	539 (539)	0.82	0.89	0.91
BDP3′	(509)	(520)	nd[b]	1.0	1.0

[a]Fluorescence quantum yield was determined using rhodamine 6G in EtOH (Φ_f = 0.88), upon excitation at blue edge of the absorption band (λ = 480−490 nm). [b]Not determined.

the contribution via through-bond energy transfer mechanism cannot be ruled out, as either the conjugated phenylene or phenylacetylene linker is used in all cases, both of which promote through-bond ET in both porphyrin-BODIPY[56] and other BODIPY[14] arrays. The fluorescence quantum yields Φ_f of hydroporphyrin components in toluene are comparable with that observed for analogous monomers (see Table S1), which indicates that in toluene attachment of BODIPY does not affect emission properties of hydroporphyrins.

Next we determined the Φ_f of hydroporphyrin component in DMF, to examine the influence of solvent dielectric constants on the emission properties of arrays. Particularly, we intended to evaluate the influence of putative PET on the Φ_f, as PET is expected to be more efficient in solvents of high dielectric constants.[57] For chlorin arrays Φ_f in DMF is comparable to that in toluene, with the exception of **C1-BDP** for which 1.7-fold reduction of Φ_f is observed (Table 2). On the other hand, bacteriochlorin arrays exhibit reduction of Φ_f in DMF, ranging from 3.6-fold (for **BC1-BDP**) to 1.2-fold (for **BC5-BDP**), compared to those in toluene. The ETE in both toluene and DMF are fairly comparable for nearly all arrays, except for **BC4-BDP**, (0.70 in DMF vs 0.90 in toluene). Greater reduction of Φ_f in DMF, which is observed for bacteriochlorin arrays than for the analogous chlorin arrays, can be explained by the lower oxidation potential of bacteriochlorins, compared to that of chlorins,[58] and therefore bacteriochlorins should be more prone to oxidative PET. Next, we analyzed the effect of substitution at the boron moiety on the Φ_f in DMF. Thus, Φ_f of **C1-BDP** in DMF is reduced 1.7-fold, compared to that in toluene (0.36 vs 0.21, respectively), while for **C2-BDP** Φ_f is identical in both solvents (0.35). A similar trend is observed for

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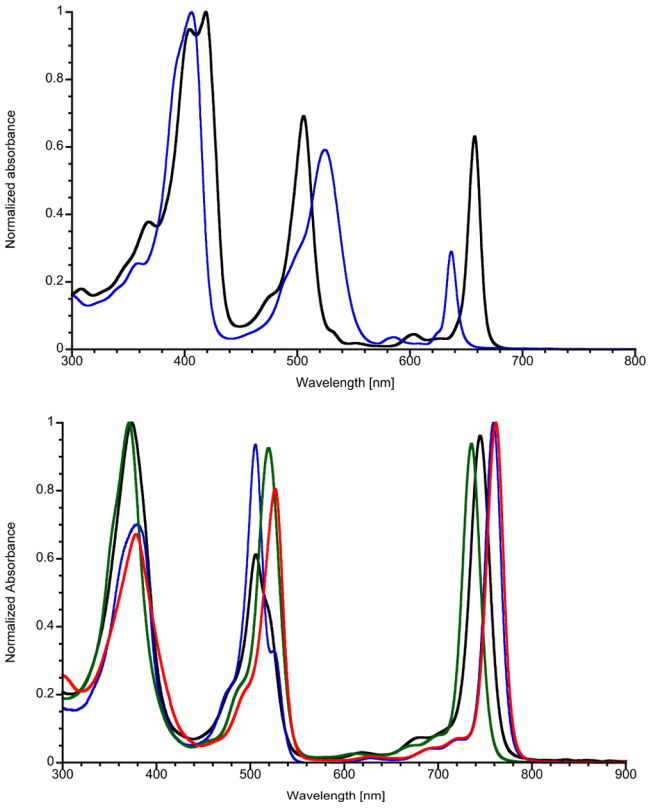

Figure 2. Upper panel: absorption spectra of chlorin-BODIPY dyads: **C2-BDP** (black), **C3-BDP** (blue). Lower panel: absorption spectra of bacteriochlorin-BODIPY arrays: **BC2-BDP** (black), **BC3-BDP** (blue), **BC4-BDP** (green), and **BC5-BDP** (red). All spectra were taken in toluene (c ~ 10 μM) at room temperature and normalized at the highest band.

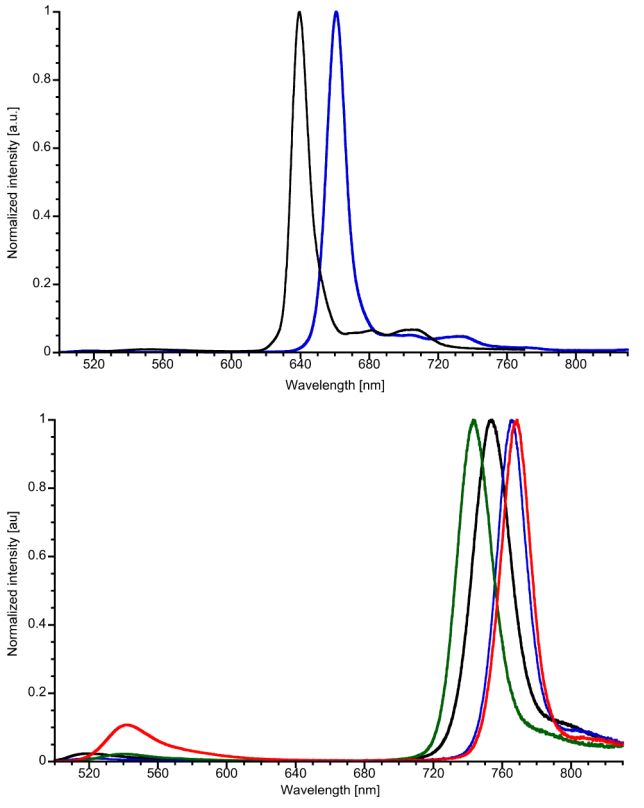

Figure 3. Upper panel: emission spectra of chlorin-BODIPY dyads: **C2-BDP** (black), **C3-BDP** (blue). Lower panel: emission spectra of bacteriochlorin-BODIPY arrays: **BC2-BDP** (black), **BC3-BDP** (blue), **BC4-BDP** (green), and **BC5-BDP** (red). All spectra were taken in toluene (c ~ 1 μM) at room temperature, upon excitation at the onset of BODIPY absorption (~475 nm).

BC1-BDP and **BC2-BDP**. Φ_f for **BC1-BDP** in DMF is significantly (3.6-fold) reduced, compared to that in toluene (0.07 vs. 0.22, respectively), whereas **BC2-BDP** and **BC3-BDP** shows 1.2-fold reduction in DMF (0.19/0.20 in DMF, respectively compared to 0.24 in toluene). Since all above-discussed arrays exhibit a comparable ETE in DMF and toluene, the lesser reduction of Φ_f in polar solvent for arrays containing alkoxy-substituted BODIPY compared to fluorine-substituted one, must be due to less efficient PET in the former. We attribute this effect to the increased electron density on the BODIPY subunit upon replacement of fluoride by alkoxide, which makes resulting BODIPY harder to reduce. This assumption is confirmed by DFT calculations, which shows, that upon substitution of −F with methoxide, the energy of HOMO and LUMO increase from by 0.15 and 0.19 eV, which is an indirect

Table 2. Absorption and Emission Properties of BODIPY-Hydroporphyrin Arrays[a]

compound	λ_{BODIPY}	λ_{Qy}	λ_{em}	Φ_{tol} (ETE)[c]	Φ_{DMF} (ETE)[c]	Φ_{triton}[b] (ETE)[c]	$\Phi_{Tween\text{-}20}$[b] (ETE)[c]
C1-BDP	503 nm	658 nm	661 nm	0.36 (0.96)	0.21 (0.98)		
C2-BDP	507 nm	658 nm	661 nm	0.35 (0.96)	0.35 (0.95)	0.31 (1.04)[d]	0.33 (1.04)[d]
C3-BDP	523 nm	637 nm	639 nm	0.22 (0.97)	0.22 (0.94)	0.16 (0.95)	0.12 (0.78)
BC1-BDP	505 nm	745 nm	754 nm	0.25 (0.96)	0.07 (0.97)		
BC2-BDP	505 nm	745 nm	754 nm	0.24 (1.00)	0.19 (0.93)	0.20 (1.2)[d]	0.19 (1.12)[d]
BC3-BDP	505 nm	759 nm	766 nm	0.24 (0.99)	0.20 (0.96)	0.19 (1.07)[d]	0.10 (0.84)
BC4-BDP	519 nm	736 nm	744 nm	0.22 (0.90)	0.12 (0.70)	0.12 (0.92)	0.069 (0.80)
BC5-BDP	527 nm	761 nm	767 nm	0.23 (0.91)	0.20 (0.82)	0.14 (1.0)	0.10 (0.83)

[a]All wavelength maxima given for measurements in toluene. Quantum yield of fluorescence measured upon excitation at the maxima of BODIPY absorbance, with absorbance at the highest absorption band ~0.1 (which corresponds to c.a. 1 μM concentration of dyad). [b]Measurements performed in 3 mM Triton X-100 and 0.1% (v/v) of Tween-20 all in PBS (pH = 7.4). Φ_f (±10%) was determined in air-equilibrated solvents, using tetraphenylporphyrin in toluene as a standard (Φ = 0.070[11]) and corrected for refractive index n of the medium. For all measurements done in aqueous surfactant value n = 1.45 was used,[18] as an average between that for pure hydrocarbons (1.49) and pure water (1.39). [c]Efficiency of energy transfer (ETE) is defined as ratio of the Φ_f measured upon excitation at the maximum of BODIPY absorbance to the Φ_f measured upon excitation at the maximum of *B* band of hydroporphyrin. [d]In some cases ETE in aqueous micelles exceed 1.00, which may be a result of experimental uncertainty. Alternatively, it is possible, that due to localization of BODIPY and hydroporphyrin in environment of different refractive index, the intensity of light was slightly different for excitation of both components, despite identical illumination of bulk sample.

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indication for the decrease in the reduction potential (see Table S2, Supporting Information).

Then, we analyzed the results for arrays, where linker is connected to the BODIPY through the 3-position. For **C3-BDP** dyad no reduction of Φ_f in DMF compared to toluene is observed. This result is consistent with those observed previously for analogous dyads, with BODIPY attached at the 10-position of chlorin.[7] For **BC4-BDP**, however, a quite significant reduction of Φ_f is observed (0.12 in DMF vs 0.22 in toluene), while for **BC5-BDP** this reduction is less pronounced (0.20 in DMF vs 0.23 in toluene). Note that for **BC5-BDP** the reduction of Φ_f in DMF is mainly due to lower ETE (0.82 in DMF vs 0.91 in toluene). Negligible PET for **BC5-BDP** can be explained by the likely higher oxidation potential of the phenylacetylene-substituted bacteriochlorin compared to the phenyl-substituted one.[30,59]

Finally, we determined the emission properties of dyads in aqueous micellar environment. Initially, we examined **BC2-BDP** in a variety of aqueous media, including PBS/DMSO (95:5 v/v) and PBS solutions of Triton X-100, Pluronic F127, Tween 20, and poly(ethylene glycol) methyl ether-*block*-poly(ε-caprolactone) diblock polymer (PEG−PCL, Figure S2). Since in PBS/DMSO, Pluronics F127 and PEG−PCL **BC2-BDP** showed a significant reduction of fluorescence (>10-fold compared to these observed in organic solvents), these surfactants were ruled out from further examination. All other amphiphilic arrays were examined in Triton X-100 and Tween 20 solutions in PBS (pH 7.4) at the concentration of surfactant above CMC (Table 2). In Triton X-100 all examined arrays exhibit Φ_f comparable with that observed for DMF, with the exception of **C3-BDP** and **BC5-BDP**, for which Φ_f in Triton X-100 is markedly lower than in DMF (0.16 vs 0.22 and 0.14 vs 0.20, respectively), despite a nearly quantitative ETE in both cases.

On the other hand, Φ_f for arrays in Tween 20 is reduced, compared to that observed in DMF and Triton X-100, with the exception of dyads with alkoxyboron BODIPY, **C2-BDP** and **BC2-BDP**, where Φ_f is comparable to that in DMF.

Although broader and more detailed studies on the structure−property relationship in hydroporphyrin arrays need to be conducted to draw accurate conclusions, several findings are important. (1) Very efficient ETE from BODIPY to chlorin and bacteriochlorin has been observed for all examined arrays; ETE generally exceeds 0.9 in organic solvents and varies from 0.8 to 1 in aqueous surfactants. (2) The reduction of Φ_f for hydroporphyrin component in polar solvent and in aqueous surfactant solution is generally greater for bacteriochlorin arrays. (3) The substitution of electron-withdrawing fluorine on boron by electron-donating alkoxy-substituents leads to the higher Φ_f in both DMF and in aqueous surfactants. (4) Placement of water-solubilizing PEG groups on the boron in BODIPY moiety lead to arrays with superior optical properties in aqueous media than for arrays with PEG groups at the BODIPY *meso* position.

Stability of Arrays in Aqueous Solutions. Stability of novel arrays in aqueous solution was evaluated both in the dark as well as upon exposure to light. Thus, solution of each array in PBS/Triton X-100, with comparable absorbance at the maxima of bacteriochlorin *B* band band (0.1) were exposed to continuous irradiation with monochromatic light at the wavelength corresponding to the maximum absorbance of BODIPY, and the absorbance of the solution was monitored (Figures 4 and S4, see the Supporting Information for the experimental details). In each case a gradual decrease in the absorption of hydroporphyrin has been observed, whereas absorption band of BODIPY shows much slower bleaching, except for **C3-BDP**, where bleaching of BODIPY band was observed, whereas bands of chlorin remain unchanged (Figure S4). The rate of photobleaching for BODIPY-hydroporphyrin arrays is fairly independent from wavelength of excitation (i.e., whether BODIPY or bacteriochlorin is excited, data not shown). No change in absorption was observed for the same solutions stored in the dark for 24 h.

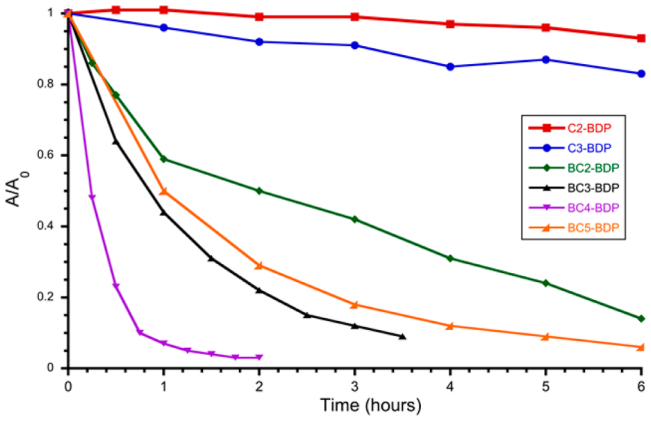

Figure 4. Rate of photobleaching measured as the decay of absorbance for BODIPY-hydroporphyrin arrays upon irradiation at the wavelength corresponding to the BODIPY absorption maxima. *A*: absorbance measured at the maximum of Q_y band upon irradiation, A_0: initial Q_y band absorbance. For details of measurement see Supporting Information.

The photostability of the BODIPY-hydroporphyrin arrays is comparable with that of other hydropoprhyrin energy transfer arrays, reported previously for *in vivo* imaging,[6] and thus should not prevent application of arrays in bioimaging. The mechanism responsible for photobleaching of BODIPY-hydroporphyrin arrays is unknown, it might be associated with the singlet oxygen production by hydroporphyrins,[6] or putative PET which leads to the oxidative degradation of hydroporphyrins.

In conclusion, we have synthesized novel water-soluble BODIPY derivatives, which retain a high Φ_f in aqueous media. A series of hydrophobic and ampiphilic BODIPY-chlorin and BODIPY-bacteriochlorin arrays have been synthesized, that featured a high ETE from BODIPY to hydroporphyrin. Significant reduction of Φ_f for BODIPY-hydroporphyrin arrays in polar solvents can be prevented by proper molecular design, particularly by placing electron-donating alkoxy substituents at the boron in BODIPY. BODIPY-hydroporphyrin arrays allow development of a series of fluorophores with a common excitation wavelength in the visible spectral window (e.g., arrays **C2-BDP**, **BC2-BDP**, and **BC3-BDP** have a common excitation wavelength at 505 nm) and a large pseudo-Stokes shift (150−240 nm for arrays reported here). Amphiphilic BODIPY-hydroporphyrin arrays show high Φ_f in aqueous surfactant, and thereby are potentially suitable for a variety of biomedical applications. The ultimate application in intracellular or *in vivo* imaging is contingent upon their low toxicity, cell permeability, etc., all these aspects are currently investigated in our laboratory.

EXPERIMENTAL SECTION

General. All commercially available reagents and solvents were used as received. Commercially available anhydrous solvents were used for palladium coupling reactions. THF was distilled from

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Na/benzophenone as required. Commercially available surfactants: Triton X-100, Tween 20, Pluronic F127, and PEG−PCL (PEG M_n ~ 5000, PCl M_n ~ 13000), were used as received. All reactions (except microwave-assisted click reactions) were performed under nitrogen atmosphere.

General Procedure for Palladium Catalyzed Reactions. All reagents with exception of palladium catalyst are transferred to Schlenk flask, dissolved in given solvent, and content of the flask was degassed by two cycles of freeze−pump−thaw. At this time palladium catalyst is added and a third cycle of free-pump-thaw is performed, and the reaction is stirred under N_2 at indicated temperature.

General Procedure for Microwave-assisted Reactions. Microwave-assisted reactions were performed in closed vessels (80 or 10 mL) equipped with a pressure sensor and stir bar, in a microwave reactor (CEM, Discover, Matthews, NC). Temperature of the reaction mixture was monitored by a built-in IR sensor. The reaction cycle includes (1) irradiation of a sample with 150 W for 2−3 min, upon which reaction temperature reaches 65−70 °C, (2) 30 min, "hold time" when reaction mixture was irradiated to keep the temperature at 65 °C, and (3) 10 min "cooling time" when reaction mixture was kept without irradiation in the closed vessel, until it reaches temperature of about 50 °C.

Purification. All column chromatographic purifications were performed using silica (32−63 μm), typically on 3.5 × 17 cm columns.

Characterization. All NMR spectra (400 or 500 MHz) were acquired at the room temperature. Chemical shift were referenced against the signals of residual protons from chloroform (7.26 ppm for ^{1}H NMR) and for carbon from $CDCl_3$ (77.0 ppm). The FT-ICR analyzer was used for ESI HRMS.

Spectroscopic Studies. Fluorescence measurements were performed with a sample absorbance A < 0.1, and were corrected for the instrument response. Solutions of arrays in aqueous surfactants were prepared in the following ways: Triton X-100: A solid sample of array (~0.1 mg) was dissolved in 5.6 mg of Triton X-100 and diluted to total volume of 3 mL using PBS solution (this provides 3 mM TX-100, which is then diluted by 3 mM solution of Triton X-100 in PBS to achieve array concentration suitable for measurements. Other surfactant: A solution of given surfactant in PBS at indicated concentration (~3 mL) was mixed vigorously with solution of array (~0.1−0.3 mg) in dichloromethane (~1 mL) under a gentle stream of air until dichloromethane completely evaporated. The resulting solution was diluted to an array concentration suitable for measurement.

DFT calculations were performed using Spartan 10 for Windows (Wave function Inc., Irvine, CA).

Synthesis. Known compounds: **1**,[42] **C−Br**,[48] **BC-P**,[3] **BC-Br$_2$**,[49] **BC-E**,[50] **C−COOH**,[7] **BDP-4**,[7] and **BDP-F**[7] were prepared following reported procedures.

BDP5. A solution of **BDP4** (50.0 mg, 119 μmol) and aluminum chloride (79.3 mg, 595 μmol) in freshly distilled THF (15 mL), was stirred vigorously at 40 °C. After 30 min, the reaction mixture was cooled to room temperature and treated with propargyl alcohol (1.00 mL, 17.8 mmol) and stirred for an additional 10 min. At this time TLC [silica, CH_2Cl_2/EtOAc (9:1)] indicated all starting material and intermediate were consumed. Crude reaction mixture was concentrated, and the residue was dissolved in EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Flash column chromatography [silica, CH_2Cl_2/EtOAc (5:1)] yielded a red-orange foam (50.5 mg, 86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.28 (s, 9H), 1.40 (s, 6H), 2.06 (t, J =2.2 Hz, 2H), 2.58 (s, 6H), 3.81−3.83 (m, 4H), 5.96 (s, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 0.04, 14.8, 15.2, 50.0, 70.8, 83.2, 95.9, 104.5, 121.7, 124.0, 128.5, 132.6, 132.8, 135.9, 140.5, 142.1, 157.0; HRMS (ESI-TOF) m/z [2M+Na]$^+$ Calcd for $C_{60}H_{66}B_2N_4O_4Si_2Na$ 1007.4720; Found 1007.4718.

BDP6. A 80 mL microwave reaction vessel was charged with samples of **BDP5** (134.0 mg, 0.272 mmol), azide terminated tetraethylene glycol **1** (171.3 mg, 0.734 mmol), copper(II) sulfate pentahydrate (34.0 mg, 0.136 mmol), L-ascorbic acid sodium salt (26.9 mg, 0.136 mmol), and acetone/water (5:1, 24 mL). The solution was then exposed to microwave irradiation as described in General Procedure. Once the vessel cooled, the product was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Flash column chromatography [silica, dichloromethane/methanol (100:0) → (40:1) → (20:1)] yielded a viscous red oil (third fraction, green): 151 mg, 58%. It is worth noting that TLC suggests the reaction is incomplete after a single cycle of microwave exposure, however, a second exposure results in both decrease of product yield and introduction of a new impurity that elutes closely following the product, making purification difficult. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.24 (s, 9H), 1.36 (s, 6H), 2.50 (s, 6H), 3.32 (s, 6H), 3.46−3.51 (m, 4H), 3.56−3.64 (m, 20H), 3.76−3.84 (m, 4H), 4.25 (s, 4H), 4.37−4.46 (m, 4H), 5.90 (s, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.56 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ −0.1, 14.7, 15.0, 50.0, 56.7, 59.0, 69.6, 70.6, 70.7, 72.0, 95.7, 104.4, 121.5, 122.6, 123.9, 128.4, 132.6, 132.7, 135.7, 141.0, 141.9, 148.6, 155.9; HRMS (ESI-TOF) m/z [M+Na]$^+$ Calcd for $C_{48}H_{71}BN_8O_{10}SiNa$ 981.5056; Found 981.5073.

BDP1. A solution of **BDP6** (151.3 mg, 0.158 mmol) in THF/methanol (1:1, 30 mL), was treated with K_2CO_3 (28.4 mg, 0.205 mmol) and stirred vigorously for 30 min. The reaction mixture was diluted with EtOAC, washed (water and brine), dried (Na_2SO_4), and concentrated to afford a viscous red oil (113.0 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.35 (s, 6H), 2.49 (s, 6H), 3.16 (s, 1H), 3.31 (s, 6H), 3.46−3.50 (m, 4H), 3.56−3.60 (m, 20H), 3.78 (t, J = 5.3 Hz, 4H), 4.24 (s, 4H), 4.41 (t, J = 5.3 Hz, 4H), 5.90 (s, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.55 (s, 2H), 7.60 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.8, 15.0, 50.1, 56.7, 59.1, 69.7, 70.54, 70.56, 70.64, 72.0, 78.5, 83.1, 121.6, 122.77, 122.84, 128.5, 132.5, 132.9, 136.1, 140.8, 141.9, 148.6, 156.0; HRMS (ESI-TOF) m/z [M+Na]$^+$ Calcd for $C_{45}H_{63}BN_8O_{10}Na$ 909.4660; Found 909.4652.

Aldehyde 4. A solution of aldehyde **2** (1.30 g, 8.43 mmol) and tosylate **3** (8.86 g, 27.8 mmol) in DMF (55 mL) was treated with K_2CO_3 (7.46 g, 54.0 mmol) and stirred at 100 °C for 21 h. Reaction mixture was diluted with CH_2Cl_2, washed (water and brine), dried (Na_2SO_4), and concentrated. Flash column chromatography [silica, CH_2Cl_2/MeOH (50:1)] yielded a viscous, pale brown oil (1.80 g, 47%). ^{1}H NMR ($CDCl_3$, 500 MHz): d 3.22−3.26 (m, 17H), 3.39−3.43 (m, 13H), 3.45−3.65 (m, 43H), 3.71−3.78 (m, 7H), 4.01−4.05 (m, 6H), 6.00 (s, 2H), 10.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 58.73, 58.76, 61.4, 67.5, 68.6, 69.1, 69.2, 70.1, 70.2, 70.3, 70.35, 70.41, 70.43, 70.6, 70.8, 71.67, 71.68, 72.3, 92.2, 109.2, 162.8, 164.9, 187.1; HRMS (ESI-TOF) m/z [M+Na]$^+$ Calcd for $C_{28}H_{48}O_{13}Na$ 615.2987; Found 615.2993.

BDP2. A solution of aldehyde **4** (2.29 g, 3.86 mmol) and 2,4-dimethylpyrrole (0.80 mL, 7.73 mmol) in CH_2Cl_2 (40 mL) was treated with trifluoroacetic acid (5 drops) and stirred vigorously at room temperature. After 5 h, aldehyde (**4**) appeared fully consumed based upon TLC analysis (silica/CH_2Cl_2). DDQ (0.876 g, 3.86 mmol) was added, and the reaction mixture was stirred for an additional 30 min. Then triethylamine (7.5 mL, 54.0 mmol) and BF_3·OEt_3 (7.6 mL, 61.8 mmol) were added, and the reaction mixture was stirred for an additional 30 min. The reaction mixture was concentrated and dried under vacuum, to afford a purple-black residue. Purification required extensive column chromatography. The first column utilized flash chromatography [silica, EtOAc/acetone (9:1)] separating the proper BODIPY from the bulk material. The second column [silica, EtOAc] performed was a gravity column that separated out product from a blue colored, red fluorescent impurity. NMR suggested that a BODIPY-like impurity coeluted with the desired product. A final gravity column [silica (3.5 × 13 cm), EtOAc], afforded the product as a red-orange, highly viscous oil (270.9 mg, 9%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.52 (s, 6H), 2.47 (s, 6H), 3.23−3.75 (m, 49H), 3.80−3.98 (m, 10H), 5.87 (s, 2H), 6.18 (s, 2H);^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.7, 14.5, 58.9, 59.00, 59.04, 61.7, 67.6, 69.0, 69.4, 69.7, 70.1, 70.3, 70.47, 70.54, 70.6, 70.66, 70.9, 71.0, 71.8, 71.89, 71.93, 72.5, 92.6, 105.5, 120.3, 132.2, 136.2, 142.2, 154.0, 157.2, 161.6; HRMS (ESI-TOF) m/z [M+Na]$^+$ Calcd for $C_{40}H_{61}BF_2N_2O_{12}Na$ 833.4185; Found 833.4175.

BDP2-I. In the first flask a solution of **BDP2** (93.2 mg, 0.115 mmol) and iodine (14.6 mg, 0.057 mmol) in ethanol/CH_2Cl_2 (2:1, 30 mL)

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were prepared. In a second flask, iodic acid (10.0 mg, 0.057 mmol) was dissolved in deionized water (10 mL), then added dropwise to the flask containing **BDP2**. The reaction solution was then stirred vigorously at 50 °C for 45 min. The crude reaction mixture was diluted with CH_2Cl_2, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, EtOAc/acetone (8:1) → (4:1) → (2:1)] yielded a highly viscous pink/light red oil (59.8 mg, 56%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.57 (s, 3H), 1.59 (s, 3H), 2.52 (s, 3H), 2.58 (s, 3H), 3.31−3.42 (m, 18H), 3.47−3.58 (m, 12H), 3.62−3.78 (m, 11H), 3.87−3.91 (m, 2H), 3.98−4.03 (m, 4H), 4.12−4.17 (m, 2H), 5.98 (s, 1H), 6.22 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.0, 14.8, 15.8, 29.8, 59.1, 59.2, 67.8, 69.1, 69.5, 69.8, 70.4, 70.73, 70.74, 70.8, 71.0, 71.1, 71.9, 72.1, 83.3, 92.7, 105.4, 121.6, 131.6, 132.9, 136.5, 142.2, 144.6, 152.94, 156.7, 157.3, 162.0; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{40}H_{60}BF_2IN_2O_{12}Na$ 959.3151; Found 959.3134.

BDP2-NH$_2$. Following the general procedure for palladium catalyzed cross coupling reactions, a solution of **BDP2-I** (70.9 mg, 0.0757 mmol) and 4-aminophenylboronic acid pinacol ester **5** (49.6 mg, 0.227 mmol), Na_2CO_3 (80.2 mg, 0.757 mmol), and $PdCl_2$(dppf)·CH_2Cl_2 (3.1 mg, 3.79 μmol) in toluene/ethanol/water (7 mL, 4:1:2) was stirred at 80 °C for 18 h. Crude reaction mixture was concentrated, and the residue was dissolved in CH_2Cl_2, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, EtOAc/acetone (5:1) → (4:1) → (3:1) → (2:1)] yielded a red-pink film that is orange fluorescent (51.6 mg, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.48 (s, 3H), 1.56 (s, 3H), 2.47 (s, 3H), 2.51 (s, 3H), 3.29−3.57 (m, 32H), 3.63−3.77 (m, 14H), 3.85−3.90 (m, 2H), 3.99−4.05 (m, 4H), 4.10−4.16 (m, 2H), 5.29 (s, 1H), 6.21 (s, 2H), 6.68 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 7.9 Hz, 2H);^{13}C NMR ($CDCl_3$, 125 MHz): δ 12.0, 13.4, 13.8, 14.6, 53.5, 59.0, 59.2, 67.7, 69.2, 69.5, 69.8, 70.2, 70.7, 70.8, 71.0, 71.1, 71.9, 72.0, 92.7, 106.0, 115.0, 120.2, 123.8, 131.2, 132.1, 132.2, 133.1, 136.1, 138.4, 141.7, 145.4, 153.5, 153.6, 157.3, 161.7; HRMS (ESI-TOF) m/z $[M+Cs]^+$ Calcd for $C_{46}H_{66}BF_2N_3O_{12}Cs$ 1034.3765; Found 1034.3742.

*2,4,6-Tris(prop-2-yn-1-yloxy)benzaldehyde (**6**).* A solution of 2,4,6-trihydroxybenzaldehyde (1.00 g, 6.49 mmol) in anhydrous DMF (21 mL) was added to flask charged with K_2CO_3 (8.90 g, 64.3 mmol, dried under high vacuum, overnight). The resulting mixture was stirred at 60 °C for 30 min. A sample of propargyl bromide (2.87 mL, 25.8 mmol, 80% in toluene) was added dropwise. The resulting mixture was stirred at 80 °C for 1 h. The resulting mixture was diluted with ethyl acetate and washed (water and brine), dried (Na_2SO_4), and concentrated. The resulting solid was suspended in diethyl ether (10 mL), sonicated, and filtered to yield a light-brown solid (0.960 g, 55%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.56 (t, J = 2.4 Hz, 1H), 2.60 (t, J = 2.4 Hz, 1H), 4.76 (d, J = 2.4 Hz, 2H), 4.78 (d, J = 2.4 Hz, 4H), 6.39 (s, 2H), 10.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.3, 56.9, 76.8, 76.9, 77.5, 77.7, 94.1, 110.6, 161.8, 163.5; HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{16}H_{13}O_4$ 269.0808; Found 269.0809.

BDP3′. A solution of aldehyde **6** (3.00 g, 11.2 mmol) and 2,4-dimethylpyrrole (2.30 mL, 22.4 mmol) in CH_2Cl_2 (110 mL) was treated with trifluoroacetic acid (5 drops) and stirred vigorously. After 30 min, **2** appeared fully consumed based upon TLC [silica/CH_2Cl_2]. A sample of DDQ (2.53 g, 11.2 mmol) was added, and stirring was continued for an additional 30 min. Then, triethylamine (22.0 mL, 157 mmol) and BF_3·OEt_2 (22.0 mL, 179 mmol) were added, and the resulting mixture was stirred for an additional 30 min. The crude reaction mixture was filtered through silica (6.5 × 10 cm column), all green fluorescent material was collected and concentrated. The resultant viscous oil was dissolved in 30 mL EtOAc and washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/hexanes (3:1)] yielded a nearly pure product, with a minor pink-red impurity. To remove the impurity, product was dissolved in dichloromethane (40 mL), diluted with hexanes (20 mL), and then dichloromethane was removed via rotary evaporator, being cautious to avoid removing the hexanes. The resulting precipitate was filtered and dried over vacuum to afford a red-orange solid (1.23 g, 23%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.58 (s, 6H), 2.44 (t, J = 2.3 Hz, 2H), 2.54 (s, 6H), 2.58 (t, J = 2.4 Hz, 1H), 4.62 (d, J = 2.3 Hz, 4H) 4.77 (d, J = 2.4 Hz, 2H), 5.94 (s, 2H), 6.52 (s, 2H);^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.8, 14.8, 55.9, 56.5, 76.17, 76.21, 78.1, 78.4, 94.4, 106.9, 120.7, 132.1, 134.9, 142.4, 154.6, 155.9, 160.0; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{25}BF_2N_2O_3Na$ 509.1823; Found 509.1818.

BDP3. A 10 mL microwave reaction vessel was charged with **BDP3′** (40.0 mg, 0.0823 mmol), azide terminated tetraethylene glycol **1** (76.7 mg, 0.329 mmol), copper(II) sulfate pentahydrate (10.3 mg, 0.0412 mmol), L-ascorbic acid sodium salt (8.2 mg, 0.0412 mmol), and acetone/water (6 mL, 5:1). The resulting mixture was irradiated in the microwave reactor as described in General Procedure. Crude reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Note that the product exhibits water solubility and it may be necessary to wash aqueous layer with EtOAc in a back extraction to recover all product. Column chromatography [silica, CH_2Cl_2/methanol (25:1)] afforded a highly viscous red-orange oil (60.5 mg, 62%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.45 (s, 6H), 2.50 (s, 6H), 3.31 (s, 6H), 3.32 (s, 3H), 3.46−3.57 (m, 27H), 3.59−3.64 (m, 11H), 3.78 (t, J = 5.4 Hz, 4H), 3.88 (t, J = 5.1 Hz, 2H), 4.40 (t, J = 5.4 Hz, 4H), 4.57 (t, J = 5.2 Hz, 2H), 5.11 (s, 4H), 5.21 (s, 2H), 5.89 (s, 2H), 6.58 (s, 2H), 7.33 (s, 2H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.6, 14.6, 50.2, 50.4, 59.0, 59.1, 62.2, 63.4, 69.3, 69.5, 70.5, 70.55, 70.62, 70.65, 71.9, 72.0, 94.6, 106.6, 120.6, 123.8, 124.5, 132.2, 136.1, 142.3, 143.0, 144.0, 154.2, 156.7, 161.3; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{55}H_{82}BF_2N_{11}O_{15}Na$ 1208.5954; Found 1208.5973.

BDP3′-I. In a first flask a solution of **BDP3′** (500 mg, 1.03 mmol) and iodine (131 mg, 0.517 mmol) in CH_2Cl_2 (80 mL) and ethanol (160 mL) was prepared. In a second flask, a solution of iodic acid (90.9 mg, 0.517 mmol) in deionized water (80 mL) was prepared. Once homogeneous, the iodic acid solution (contents of the second flask) was added slowly to the BDP solution (first flask). The reaction mixture was then stirred at 50 °C for 20 min. The reaction mixture was cooled, diluted with CH_2Cl_2, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/hexane (1:1)] yielded the desired product (the second to last compound to elute, appearing bright orange on TLC). Bright orange solid (313.0 mg, 50%). Note that the desired product is the major product, however, there is a distribution of other iodo-BDP products. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.58 (s, 3H), 1.59 (s, 3H), 2.45 (t, J = 2.3 Hz, 2H), 2.55 (s, 3H), 2.59 (t, J = 2.4 Hz, 1H), 2.62 (s, 3H), 4.62 (d, J = 2.2 Hz, 4H), 4.77 (d, J = 2.4 Hz, 2H), 6.00 (s, 1H), 6.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.1, 15.0, 15.9, 55.9, 56.5, 76.30, 76.34, 78.0, 78.2, 83.8, 94.4, 106.6, 121.8, 131.5, 132.7, 134.9, 142.3, 144.6, 153.5, 155.8, 157.1, 160.2; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{28}H_{24}BF_2IN_2O_3Na$ 635.0799; Found 635.0786.

BDP3-I. A microwave reaction vessel (80 mL) was charged with **BDP3′-I** (300.0 mg, 0.499 mmol), azide terminated tetraethylene glycol **1** (465.6 mg, 2.00 mmol), copper(II)sulfate pentahydrate (62.4 mg, 0.250 mmol), L-ascorbic acid sodium salt (49.5 mg, 0.250 mmol), and acetone/water (44 mL, 5:1). Contents of microwave vessel were then irradiated in the microwave reactor as described in the General Procedure. Crude reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Note that product exhibits water solubility and it may be necessary to wash aqueous layer with EtOAc in a back extraction to recover all product. Column chromatography [silica, CH_2Cl_2/methanol (40:1) → (30:1) → (20:1) → (15:1)] yielded a highly viscous red-orange oil (515.4 mg, 80%). Note that product began eluting with the CH_2Cl_2/methanol (30:1) solvent system, however, product stuck to the silica and eluent polarity was increased to (20:1) with addition of pressure and eventual increase in polarity to (15:1) to force remaining product to elute. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.44 (s, 3H), 1.48 (s, 3H), 2.54 (s, 3H), 2.60 (s, 3H), 3.33 (s, 6H), 3.35 (s, 3H), 3.48−3.51 (m, 4H), 3.52−3.60 (m, 23H), 3.62−3.66 (m 10H), 3.81 (t, J = 5.4 Hz, 4H), 3.91 (t, J = 5.1 Hz, 2H), 4.43 (t, J = 5.4 Hz, 4H), 4.59 (t, J = 5.1 Hz, 2H), 5.10−5.16 (m, 4H) 5.23 (s, 2H), 5.98 (s, 1H), 6.62 (s, 2H), 7.36 (s, 2H), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 13.7, 14.6, 15.4, 15.6, 50.0, 50.2, 58.8, 58.9, 62.0, 62.9, 69.1, 69.3, 70.26, 70.30,

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70.35, 70.41, 70.44, 71.7, 71.8, 83.2, 94.5, 105.9, 121.6, 123.7, 124.4, 131.4, 132.7, 136.1, 141.9, 142.7, 143.6, 144.6, 152.6, 156.4, 156.7, 161.3; HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{55}H_{82}BF_2IN_{11}O_{15}$ 1312.5101; Found 1312.5124.

BDP3-COOMe. Following the general procedure for palladium catalyzed cross coupling reactions, **BDP3-I** (100.0 mg, 0.0764 mmol), *p*-methylbenzoateboronic acid pinacol ester **7** (60.0 mg, 0.229 mmol), Na_2CO_3 (81.0 mg, 0.764 mmol), and $PdCl_2(dppf)\cdot CH_2Cl_2$ (6.2 mg, 7.63 μmol) in toluene/ethanol/water (7 mL, 4:1:2) were stirred at 80 °C for 15 h. Crude reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/methanol (30:1) → (20:1)] yielded a viscous pink oil (70.3 mg, 70%). Note that as with **BDP3-I** the product stuck to silica and increased polarity was necessitated to remove all product from column. It is quite challenging to distinguish product from starting material based solely on TLC, however the product is highly fluorescent in comparison to starting material. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.43 (s, 3H), 1.47 (s, 3H), 2.50 (s, 3H), 2.56 (s, 3H) 3.33 (s, 6H), 3.35 (s, 3H), 3.47−3.59 (m, 31H), 3.61−3.66 (m, 11H), 3.80 (t, J = 5.3 Hz, 4H), 3.92 (t, J = 5.1 Hz, 2H), 3.93 (s, 3H), 4.35−4.46 (m, 4H), 4.58 (t, J = 5.2 Hz, 2H), 5.16 (s, 2H), 5.17 (s, 2H), 5.22 (s, 2H), 5.96 (s, 1H), 6.61 (s, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.41 (s, 2H), 7.94 (s, 1H), 8.04 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 11.8, 13.3, 13.8, 14.7, 50.2, 50.4, 52.1, 58.96, 59.01, 62.1, 63.3, 70.45, 70.52, 70.59, 70.61, 71.89, 71.94, 94.6, 106.5, 121.1, 123.8, 124.5, 128.6, 129.6, 130.2, 131.6, 131.8, 132.8, 136.7, 138.1, 138.9, 142.9, 143.1, 143.9, 151.8, 155.3, 156.7, 161.4, 166.9; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{63}H_{88}BF_2N_{11}O_{17}Na$ 1342.6323; Found 1342.6353.

Dyad C1-BDP. Following the general procedure for palladium catalyzed cross coupling reactions, samples of **C−Br** (46 mg, 0.090 mmol), **BDP-F** (31 mg, 0.090 mmol), and P(o-tolyl)$_3$ (33 mg, 0.108 mmol), and $Pd_2(dba)_3$ (0.016 g, 0.018 mmol) in toluene/triethylamine (5:1, 62 mL) were reacted as described in General Procedure. The progress of the reaction was monitored using absorption spectroscopy. After 4h a second batch of $Pd_2(dba)_3$ (0.016 g, 0.018 mmol) and P(o-tolyl)$_3$ (0.033 g, 0.108 mmol) was added and the reaction mixture was stirred at 60 °C. After 15 h absorption spectroscopy showed disappearance of the Q_y band of starting chlorin at 650 nm. The reaction mixture was concentrated, and remaining solid was dried under high vacuum. Column chromatography [silica, hexane/CH_2Cl_2 (1:1), second fraction (green) was collected] provided a semipure product, which was further purified by washing with methanol and methanol/CH_2Cl_2 (4:1), and column chromatography [silica, hexane/CH_2Cl_2 (2:1)] to obtain a green solid (0.023 g, 33%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ: −1.89 (br, 1H), −1.55 (br, 1H), 1.54 (s, 6H), 1.87 (s, 6H), 2.07 (s, 6H), 2.61 (apparent s, two overlapped singlets, 9H), 4.68 (s, 2H), 6.04 (s, 2H), 7.26 (s, 4H), 7.43 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 7.8 Hz, 2H), 8.46 (d, J = 3.7 Hz, 2H), 8.78 (s, 1H), 8.85 (s overlapped with a doublet), 8.92 (d, J = 4.6 Hz, 1H), 9.18 (d, J = 4.2 Hz, 2H), 9.30 (s, 1H), 9.72 (s, 1H); ^{13}C NMR δ (100 MHz): 14.8, 21.4, 21.6, 29.85, 31.2, 46.8, 52, 94.6, 95, 95.7, 106.9, 116.3, 121.0, 121.6, 124.2, 124.6, 127.9, 128.6, 128.7, 128.9, 131.4, 131.8, 132.6, 133.02, 133.05, 135.3, 135.4, 139.2, 139.7, 143.2, 152.3, 152.7, 156, 163.2, 176.3; HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{52}H_{48}BF_2N_6$ 805.4004; Found 805.4005.

Dyad C2-BDP. Following the general procedure for palladium catalyzed cross coupling reactions, samples of **C1−Br** (15.0 mg, 27.9 μmol), **BDP1** (26.0 mg, 29.3 μmol), $(PPh_3)_2PdCl_2$ (2.9 mg, 4.2 μmol) in DMF/Et_3N (2:1, 6 mL) were stirred at 80 °C for 15 h. The crude reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Flash column chromatography [silica, CH_2Cl_2/methanol (1:0) → (50:1) → (30:1) → (25:1) → (15:1) → (11:1)] followed by a second gravity column chromatography [silica, CH_2Cl_2/methanol (1:0) → (25:1) → (15:1)] afforded target dyad as a green solid (10.8 mg, 29%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ −1.90 (s, 1H), −1.57 (s, 1H), 1.55 (s, 6H), 1.87 (s, 6H), 2.08 (s, 6H), 2.58 (s, 6H), 2.62 (s, 3H), 3.38 (s, 6H), 3.53−3.57 (m, 5H), 3.61−3.67 (m, 23H), 3.86 (t, J = 5.2 Hz, 4H), 4.36 (s, 4H), 4.49 (t, J = 5.2 Hz, 4H), 4.71 (s, 2H), 6.01 (s, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.64 (s, 1H), 8.02 (d, J = 7.9 Hz, 2H), 8.47 (d, J = 4.2 Hz, 1H), 8.78 (s, 1H), 8.86 (s, 2H), 8.92 (d, J = 4.4 Hz, 1H), 9.18 (d, J = 4.4 Hz, 1H), 9.32 (s, 1H), 9.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 15.0, 15.1, 21.4, 21.6, 29.8, 31.2, 46.8, 50.2, 52.0, 56.8, 59.2, 69.8, 70.66, 70.74, 72.1, 86.2, 94.6, 95.0, 95.8, 106.9, 116.4, 121.0, 121.7, 122.9, 124.1, 124.4, 127.9, 128.8, 128.9, 131.8, 132.6, 132.8, 133.0, 133.1, 135.3, 135.8, 137.5, 137.9, 139.2, 139.7, 141.2, 141.8, 142.1, 148.7, 152.3, 152.8, 156.1, 163.3, 176.3; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{76}H_{91}BN_{12}O_{10}Na$ 1365.6978; Found 1365.6953.

BC1-BDP. Following the general procedure for palladium catalyzed cross coupling reactions, samples of **BC1** (20.0 mg, 32.6 μmol), **BDP-F** (17.0 mg, 48.9 μmol), $(PPh_3)_2PdCl_2$ (4.6 mg, 6.5 μmol) in DMF/Et_3N (2:1, 9 mL) were reacted at 80 °C for 16 h. The crude reaction mixture was diluted with EtOAC, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/hexanes (1:1) → (2:1)] yielded a red-brown solid (7.4 mg, 26%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ −1.47 (s, 1H), −1/26 (s, 1H), 1.57 (s, 6H), 1.93 (s, 6H), 1.96 (s, 6H), 2.60 (s, 6H), 4.06 (s, 3H), 4.34 (s, 2H), 4.43 (s, 2H), 4.55 (s, 3H), 6.04 (s, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H), 8.23 (d, J = 8.2 Hz, 2H), 8.42 (d, J = 8.2 Hz, 2H), 8.53 (s, 1H), 8.57 (s, 1H), 8.67 (s, 1H) 8.77 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.5, 14.9, 30.9, 31.2, 45.3, 46.2, 47.2, 52.4, 52.5, 64.6, 89.2, 92.5, 97.0, 97.1, 97.6, 110.7, 121.5, 123.5, 123.6, 125.5, 128.5, 129.3, 130.4, 131.0, 131.2, 131.5, 132.4, 133.7, 134.7, 135.6, 136.1, 136.5, 136.8, 140.8, 141.3, 143.3, 153.9, 155.9, 162.2, 167.3, 169.0, 171.5; HRMS (ESI-TOF) m/z $[M]^+$ Calcd for $C_{54}H_{51}BF_2N_6O_3$ 880.4087; Found 880.4079.

Dyad BC2-BDP. Following the general procedure for palladium catalyzed cross coupling reactions, samples of **BC1** (20.0 mg, 32.6 μmol), **BDP1** (43.4 mg, 48.9 μmol), $(PPh_3)_2PdCl_2$ (4.6 mg, 6.5 μmol) in DMF/Et_3N (2:1, 9 mL) were reacted at 80 °C for 4 h. The crude reaction was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/methanol (100:0) → (20:1)] yielded a red-brown solid (13.4 mg, 29%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ −1.49 (s, 1H), −1.28 (s, 1H), 1.56 (s, 6H), 1.66 (s, 6H), 1.94 (s, 6H), 1.97 (s, 6H), 2.59 (s, 6H), 3.38 (s, 6H), 3.54−3.57 (m, 5H), 3.61−3.66 (m, 23H), 3.86 (t, J = 5.4 Hz, 4H), 4.06 (s, 3H), 4.34−4.36 (m, 6H), 4.47 (t, J = 5.4 Hz, 4H), 4.57 (s, 3H), 7.50 (d, J = 8.3 Hz, 2H), 7.64 (s, 2H), 8.01 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 8.5 Hz, 2H), 8.41 (d, J = 8.5 Hz, 2H), 8.53 (s, 1H), 8.58 (s, 1H), 8.67 (s, 1H), 8.76−8.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 15.0, 15.2, 30.9, 31.2, 45.3, 46.1, 47.2, 50.2, 52.4, 52.5, 56.8, 59.2, 64.6, 69.8, 70.7, 70.67, 70.74, 72.1, 89.0, 92.7, 97.0, 97.1, 97.6, 110.9, 121.7, 122.9, 123.5, 123.7, 125.3, 128.6, 128.69, 128.72, 129.3, 130.6, 131.0, 131.2, 132.2, 132.3, 132.4, 132.8, 133.8, 135.2, 135.7, 136.0, 136.4, 136.7, 140.8, 141.4, 142.2, 148.8, 154.0, 155.9, 162.1, 167.3, 169.0, 171.4; HRMS (ESI-TOF) m/z $[M+Na]^+$ Calcd for $C_{78}H_{95}BN_{12}O_{13}$ 1441.7139; Found 1441.7142.

Triad BC3-BDP. Following the general procedure for palladium catalyzed cross coupling reactions, samples of **BC1** (10.0 mg, 17.9 μmol), **BDP1** (39.7 mg, 44.8 μmol), $(PPh_3)_2PdCl_2$ (2.6 mg, 3.6 μmol) were reacted in DMF/Et_3N (2:1, 9 mL) at 80 °C for 2.5 h. The crude reaction was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4) and concentrated. During extraction a precipitate was observed in the aqueous phase, this was extracted using CH_2Cl_2, which was subsequently washed with brine, dried (Na_2SO_4) and combined with the first extract (TLC indicated the two mixtures were nearly identical). Two size exclusion chromatography columns [Bio-Beads S-X1 Support#152−2151 (2.5 × 57 cm), THF] were performed to remove byproduct, followed with column chromatography [silica, CH_2Cl_2/methanol (100:0) → (20:1) → (10:1) → (5:1)] yielded a red-brown solid (13.0 mg, 33%). ^{1}H NMR shows impurities in the aromatic region which was identified on the basis of HRMS data {[obsd 1794.9300 $(M+Na)^+$ calcd 1794.9300 $(M+Na)^+$ [$(M+Na)^+$, M = $C_{90}H_{124}B_2N_{16}O_{20}$]} as a product of homocoupling of **BDP1**. This impurity can be removed through rigorous, iterative crystallization, however, the yield of highly pure **BC3-BDP** is negligible. Relative integration suggests this impurity is present in ∼5−10%, however, it does not appear to have an impact on the photochemical properties of the sample (Φ_F and Φ_{ETE} recrystallized and nonrecrystallized samples

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are the same within experimental uncertainty). ^{1}H NMR ($CDCl_3$, 500 MHz): δ −1.65 (s, 1H), −1.45 (s, 1H), 1.56 (s, 6H), 1.57 (s, 6H), 1.97 (s, 12H), 2.59 (s, 12H), 3.38 (s, 12H), 3.54−3.57 (m, 10H), 3.60−3.67 (m, 50H), 3.86 (t, J = 5.2 Hz, 9H), 4.34−4.36 (m, 10H), 4.46 (s, 3H), 4.49 (t, J = 5.0 Hz, 4H), 4.56 (s, 3H), 6.01 (s, 2H), 6.02 (s,2H), 7.51 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.63 (s, 2H), 7.64 (s, 2H), 8.02 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 8.57 (d, J = 8.5 Hz, 2H), 8.82−8.84 (m, 2H), 8.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 15.0, 15.2, 31.0, 31.1, 45.7, 45.8, 50.2, 52.0, 56.8, 59.2, 64.7, 69.8, 70.7, 70.8, 72.1, 121.69, 121.74, 122.9, 124.4, 124.7, 128.8, 128.9, 132.4, 132.6, 132.8, 134.7, 135.7, 135.9, 138.4, 141.2, 141.4, 142.1, 142.2, 148.8, 156.0, 156.1, 170.2; HRMS (ESI-TOF) m/z $[M+2Na]^{2+}$ Calcd for $C_{115}H_{150}B_2N_{20}O_{21}Na_2$ 1107.0650; Found 1107.0677.

Dyad C3-BDP. A solution of **BDP2-NH$_2$** (35.0 mg, 0.0388 mmol), **C1-COOH** (15.0 mg, 0.0326 mmol), EDC·HCl (12.5 mg, 0.0652 mmol) and DMAP (8.0 mg, 0.0652 mmol) in DMF (3 mL) was stirred at room temperature for 4 days. The crude reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, EtOAc/acetone (6:1) → (4:1)] yielded a red-purple solid (12.9 mg, 30%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ −2.36 (s, 1H), −1.97 (s, 1H), 1.59 (s, 3H), 1.62 (s, 3H), 2.08 (s, 6H), 2.58 (s, 6H), 3.37 (s, 6H), 3.39 (s, 3H), 3.47−3.54 (m, 4H), 3.47−3.54 (m, 8H), 3.54−3.59 (m, 6H), 3.66−3.70 (m, 2H), 3.70−3.76 (m, 6H), 3.76−3.79 (m, 2H), 3.89−3.92 (m, 2H), 4.05−4.10 (m, 4H), 4.15−4.19 (m, 2H), 4.76 (s, 2H), 5.97 (s, 1H), 6.27 (s, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 8.20 (s, 1H), 8.24 (d, J = 8.1 Hz, 2H), 8.30 (d, J = 8.1 Hz, 2H), 8.62 (d, J = 4.3 Hz, 1H), 8.79 (d, J = 4.7 Hz, 1H), 8.87 (d, J = 4.7 Hz, 1H), 8.96 (s, 1H), 8.99 (d, J = 4.5 Hz, 1H), 9.01 (d, J = 4.3 Hz, 1H), 9.08 (s, 1H), 9.27 (d, J = 4.4 Hz, 1H), 9.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 12.0, 13.5, 13.9, 14.8, 29.8, 31.3, 46.6, 52.2, 59.1, 59.2, 67.8, 69.3, 69.5, 69.8, 70.4, 70.7, 70.78, 70.81, 71.0, 71.2, 72.0, 72.1, 92.8, 94.7, 97.3, 105.9, 107.5, 119.8, 120.3, 120.7, 123.6, 124.1, 125.7, 127.9, 128.6, 130.5, 131.2, 131.8, 132.0, 132.2, 132.7, 132.8, 134.3, 134.5, 134.6, 134.9, 136.7, 137.0, 138.4, 139.6, 141.2, 142.6, 145.8, 151.1, 152.0, 152.6, 154.5, 157.4, 161.8, 163.3, 166.0, 175.6; HRMS (ESI-TOF) m/z $[M]^+$ Calcd for $C_{75}H_{88}BF_2N_7O_{13}$ 1343.6508; Found 1343.6494.

***Dyad BC4-BDP** (Prepared through Suzuki Cross-Coupling).* Following the general procedure for palladium coupling reactions, **BC2-B** (90% pure, 22.7 mg, 0.0239 mmol), **BDP3-I** (37.6 mg, 0.0286 mmol), Na_2CO_3 (25.3 mg, 0.239 mmol) and $PdCl_2$(dppf)·CH_2Cl_2 (3.9 mg, 4.78 μmol) in toluene/ethanol/water (7 mL, 4:1:2) were reacted at 80 °C for 2 h. Crude reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4) and concentrated. Size exclusion chromatography [Bio-Beads S-X1 Support#152−2151 (2.5 × 57 cm), THF], followed with chromatography column [silica, CH_2Cl_2/methanol (35:1) → (30:1) → (25:1)] yielded a purple solid (10.0 mg, 22%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.46 (s, 3H), 1.53 (s, 3H), 1.96 (s, 6H), 1.98 (s, 6H), 2.59 (s, 3H), 2.60 (2, 3H), 3.33−3.37 (m, 10H), 3.51−3.67 (m, 43H), 3.71 (s, 3H), 3.82 (t, J = 5.3 Hz, 4H), 3.91 (t, J = 5.0 Hz, 2H), 4.06 (s, 3H), 4.40 (s, 4H), 4.43 (t, J = 5.3 Hz, 4H), 4.60 (t, J = 5.0 Hz, 2H), 5.20 (s, 2H), 5.21 (s, 2H), 5.26 (s, 2H), 6.00 (s, 1H), 6.65 (s, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.44 (s, 2H), 7.97 (s, 1H), 7.98 (d, J = 8.3 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 8.2 Hz, 2H), 8.27 (d, J = 8.0 Hz, 2H), 8.41 (d, J = 8.1 Hz, 2H), 8.51 (s, 1H), 8.63−8.70 (m, 3H), 8.80 (s, 1H), 8.82 (s, 1H);^{13}C NMR ($CDCl_3$, 125 MHz): δ 11.9, 13.9, 14.9, 29.8, 31.18, 31.23, 45.6, 45.8, 48.0, 50.3, 50.5, 51.9, 52.4, 59.08, 59.14, 62.2, 63.4, 63.5, 69.4, 69.6, 70.5, 70.57, 70.64, 70.67, 70.70, 70.72, 72.02, 72.05, 94.8, 96.7, 97.3, 106.6, 119.6, 121.9, 123.0, 124.0, 124.7, 127.5, 127.9, 128.9, 130.3, 130.7, 131.0, 131.9, 134.3, 134.5, 134.6, 134.9, 136.3, 136.8, 143.1, 144.0, 154.9, 155.6, 156.8, 160.2, 161.5, 165.9, 167.4, 169.4, 169.9; HRMS (ESI-TOF) m/z $[M+2Na]^{2+}$ Calcd for $C_{101}H_{123}BF_2N_{16}O_{19}Na_2$ 979.4506; Found 979.4524.

***Dyad BC4-BDP** (Prepared through EDC-Mediated Coupling).* A solution of **BDP3-COOMe** (63.2 mg, 0.0479 mmol) in THF/methanol (1:1, 6 mL) was treated with aqueous NaOH (1 mL, 3M) and stirred vigorously at room temperature for 1 h. Crude reaction mixture was diluted with EtOAc, washed (5% HCl and brine), and dried (Na_2SO_4). Note that considerable nonfluorescent color was observed in aqueous phase suggesting decomposition of BODIPY during reaction. Residue was then purified by column chromatography [silica, CH_2Cl_2/MeOH (20:1) → (15:1) → (5:1)] yielding **BDP3-COOH** as a pink film (13.5 mg, 22%). [^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.38 (s, 3H), 1.49 (s, 3H), 2.51 (s, 3H), 2.57 (s, 3H) 3.34 (s, 6H), 3.35 (s, 3H), 3.48−3.66 (m, 48H), 3.77 (t, J = 5.4 Hz, 4H), 3.90 (t, J = 5.2 Hz, 2H), 4.40 (t, J = 5.4 Hz, 4H), 4.59 (t, J = 5.2 Hz, 2H), 5.16 (s, 2H), 5.17 (s, 2H), 5.23 (s, 2H), 5.97 (s, 1H), 6.61 (s, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.40 (s, 2H), 7.95 (s, 1H), 8.09 (d, J = 8.2 Hz, 2H)] **BDP3-COOH** was then immediately used in the subsequent reaction without further characterization. **BC-P-NH$_2$** (7.5 mg, 12 μmol), **BDP3-COOH** (13.0 mg, 9.96 μmol), EDC·HCl (3.8 mg, 20 μmol), and DMAP (2.4 mg, 20 μmol) were dissolved in 3 mL of CH_2Cl_2 and stirred at room temperature, in darkness, for 18 h. Crude reaction mixture was purified by column chromatography [silica, CH_2Cl_2/MeOH (30:1)], to afford a purple film (5.0 mg, 22% from **BDP3-COOH**). Characterization data (^{1}H NMR, absorption, emission) are consistent with those obtained for the sample prepared via Suzuki cross-coupling.

Dyad BC5-BDP. Following the general procedure for palladium coupling reactions, **BC3-B** (95% pure, 32.0 mg, 0.035 mmol), **BDP3-I** (55.7 mg, 0.042 mmol), sodium carbonate (37.1 mg, 0.35 mmol), and $PdCl_2$(dppf)·CH_2Cl_2 (5.7 mg, 7.0 μmol) in toluene/ethanol/water (7 mL, 4:1:2) were reacted at 80 °C for 2 h. Crude reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/methanol (25:1)] yielded a purple-brown solid (28.5 mg, 41%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ −1.80 (s, 1H), −1.55 (s. 1H), 1.43 (s, 3H), 1.53 (s, 3H), 1.95 (s, 12H), 2.56 (s, 3H), 2.59 (s, 3H), 3.33 (s, 6H), 3.36 (s, 3H), 3.48−3.66 (m, 41H), 3.79 (t, J = 5.2 Hz, 4H), 3.90 (t, J = 5.0 Hz, 2H), 3.99 (s, 3H), 4.38−4.46 (m, 8H), 4.50 (s, 3H), 4.59 (t, J = 4.9 Hz, 2H), 5.19 (s, 2H), 5.20 (s, 2H), 5.25 (s, 2H), 6.60 (s, 1H), 6.64 (s, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.43 (s, 2H), 7.85 (s, 3H), 7.91 (d, J = 8.1 Hz, 2H), 7.96 (s, 1H), 8.03 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 8.1 Hz, 2H), 8.54 (s, 1H), 8.57 (s, 1H), 8.65 (s, 1H), 8.79−8.83 (m, 2H), 8.91 (s, 1H);^{13}C NMR ($CDCl_3$, 125 MHz): δ 11.9, 13.5, 13.9, 14.9, 31.0, 31.1, 45.6, 45.8, 47.8, 50.3, 50.5, 51.7, 52.5, 59.06, 59.13, 62.1, 63.3, 64.7, 69.3, 69.6, 70.4, 70.5, 70.59, 70.61, 70.66, 70.69, 71.96, 72.01, 94.7, 97.1, 97.8, 106.5, 113.3, 115.5, 120.3, 124.0, 124.7, 124.9, 125.0, 127.6, 128.5, 129.6, 129.8, 130.6, 131.70, 131.73, 132.6, 133.4, 135.0, 135.4, 135.7, 137.9, 138.0, 143.0, 144.0, 155.7, 156.7, 161.1, 161.5, 165.8, 166.8, 170.2, 170.6; HRMS (ESI-TOF) m/z $[M+2Na]^{2+}$ Calcd for $C_{105}H_{123}BF_2N_{16}O_{19}Na_2$ 1003.9518; Found 1003.9541.

*3-(4-Aminophenyl)-5-methoxy-8,8,18,18-tetramethyl-13-(4-methoxycarbonylphenyl)-bacteriochlorin **(BC-P-NH$_2$)**.* A mixture of **BC-P** (30.0 mg, 0.0489 mmol), 4-aminophenylboronic pinacolate (11.6 mg, 0.0528 mmol), Cs_2CO_3 (161 mg, 0.0489 mmol), and $Pd(PPh_3)_4$ (9.1 mg, 0.0079 mmol) in toluene (6 mL) and DMF (3 mL) was stirred at 85 °C under nitrogen atmosphere. After approximately 17 h, the mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. The residue was purified with column chromatography (silica, CH_2Cl_2→ CH_2Cl_2/2% MeOH) to afford a dirty green solid (26 mg, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ −2.06 (s, 1H), −1.68 (s, 1H), 1.96 (s, 6H), 1.98 (s, 6H), 3.73 (s, 3H), 3.89 (brs, 2H), 4.07 (s, 3H), 4.40 (s, 2H), 4.42 (s, 2H), 6.98 (d, J = 8.44 Hz, 2H), 7.94 (d, J = 8.44 Hz, 2H), 8.28 (d, J = 8.44 Hz, 2H), 8.42 (d, J = 8.44 Hz, 2H), 8.62 (s, 1H), 8.63 (s, 1H), 8.70 (s, 1H), 8.82 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.4, 31.5, 45.6, 46.2, 48.4, 51.9, 52.6, 63.8, 96.5, 96.8, 97.6, 114.9, 121.5, 123.3, 128.5, 128.6, 128.9, 130.5, 131.2, 132.4, 133.9, 134.1, 134.5, 135.3, 136.5, 141.8, 145.9, 155.7, 159.8, 167.7, 168.9, 170.3; HRMS (ESI-TOF) m/z $[M]^+$ Calcd for $C_{39}H_{39}N_5O_3$ 625.3047; Found 625.3047.

*3-(4-Aminophenylethynyl)-5-methoxy-8,8,18,18-tetramethyl-13-(4-methoxycarbonylphenylethynyl)bacteriochlorin **(BC-E-NH$_2$)**.* A mixture of **BC-E** (20 mg, 0.031 mmol), 4-ethynylaniline (4.3 mg, 0.037 mmol), and $PdCl_2(PPh_3)_2$ (3.5 mg, 0.0050 mmol) in Et_3N (2 mL) and DMF (4 mL) was stirred at 80 °C under nitrogen

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atmosphere. After approximately 2 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 [silica, hexane/CH_2Cl_2 (1:3)] to afford a dark reddish powder (14 mg, 67%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ −1.87 (s, 1H), −1.57 (s, 1H), 1.95 (s, 12H), 3.93 (brs, 2H), 3.99 (s, 3H), 4.43 (s, 2H), 4.45 (s, 2H), 4.50 (s, 3H), 6.79 (d, J = 8.45 Hz, 1H), 7.68 (d, J = 8.45 Hz, 1H), 7.94 (d, J = 8.40 Hz, 1H), 8.19 (d, J = 8.40 Hz, 1H), 8.53 (s, 1H), 8.58 (s, 1H), 8.78 (d, J = 2.2 Hz, 1H), 8.81 (d, J = 1.9 Hz, 1H), 8.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.3, 41.7, 46.2, 48.2, 51.8, 52.7, 64.9, 85.4, 88.4, 95.3, 95.8, 96.6, 96.9, 98.1, 114.0, 114.8, 115.1, 115.3, 124.6, 125.3, 128.8, 129.9, 130.1, 131.9, 132.1, 133.5, 135.2, 135.7, 135.9, 137.9, 147.1, 156.4, 160.9, 167.0, 169.8, 171.1; HRMS (ESI-TOF) m/z $[M]^+$ Calcd for $C_{43}H_{39}N_5O_3$ 673.3047; Found 673.3052.

BC-P-B. A solution of **BC-P-NH$_2$** (17.6 mg, 0.0281 mmol), 4-carboxylphenylboronic acid pinacol ester **8** (14.0 mg, 0.0562 mmol), EDC·HCl (10.8 mg, 0.0562 mmol), and DMAP (6.9 mg, 0.0562 mmol) in DMF (2 mL) was treated with hydroxybenzotriazole monohydrate (8.8 mg, 0.0562 mmol) and stirred for 64 h. The reaction crude was diluted with EtOAc, washed (saturated aqueous $NaHCO_3$ (3×), water, and brine), dried (Na_2SO_4), and concentrated, yielding a green solid (22.7 mg, 94%). Proton NMR indicates a product with approximately 90% purity, which was deemed acceptable for subsequent reactions. Column chromatography of this compound leads to significantly lower yields (20−30% overall), streaking observed during TLC suggests this diminished yield is due to product adhering to silica. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −1.97 (s, 1H), −1.66 (s, 1H), 1.39 (s, 3H), 1.40 (s, 12H), 1.96 (s, 6H), 1.98 (s, 6H), 3.71 (s, 2H), 4.06 (s, 2H), 7.95−8.05 (m, 6H), 8.10 (s, 1H), 8.16 (d, J = 8.5 Hz, 2H), 8.25−8.30 (m, 3H), 8.42 (d, J = 8.3 Hz, 2H), 8.66 (s, 1H), 8.69 (s, 1H), 8.80 (s, 1H), 8.82 (s, 1H); HRMS (ESI-TOF) m/z $[M]^+$ Calcd for $C_{52}H_{54}BN_5O_6$ 855.4170; Found 855.4172.

BC-E-B. A solution of **BC-E-NH$_2$** (35.0 mg, 0.0519 mmol), 4-carboxylphenylboronic acid pinacol ester **8** (25.8 mg, 0.104 mmol), EDC·HCl (19.9 mg, 0.104 mmol), and DMAP (12.7 mg, 0.104 mmol) in DMF (3 mL) was stirred for 46 h. The crude reaction mixture was diluted with EtOAc, washed (saturated aqueous $NaHCO_3$ (3×), water, and brine), dried (Na_2SO_4), and concentrated, yielding a red-brown solid (32.9 mg, 70%). Proton NMR indicates a product with greater than 95% purity, and was used for the next step without purification. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −1.80 (s, 1H), −1.55 (s, 1H), 1.39 (s, 12H), 1.96 (s, 12H), 3.99 (s, 3H), 4.44 (s, 2H), 4.45 (s, 2H), 4.51 (s, 3H), 7.79 (d, J = 8.7 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 8.07 (s, 1H), 8.14 (d, J = 8.5 Hz, 2H), 8.55 (s, 1H), 8.57 (s, 1H), 8.81 (s, 1H), 8.82 (s, 1H), 8.91 (s, 1H); HRMS (ESI-TOF) m/z $[M]^+$ Calcd for $C_{56}H_{54}BN_5O_6$ 903.4171; Found 903.4164.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00357.

Additional absorption and emission spectra, spectroscopic data for benchmark monomers, and computational results (PDF)

Copies of ^{1}H and ^{13}C spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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