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Energy Transfer in BODIPY-Bacteriochlorin Arrays: Towards Near-IR Emitters with Broadly Tunable, Multiple Absorption Bands

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Abstract

A series of energy transfer arrays, comprising of a near-IR absorbing and emitting bacteriochlorin, and BODIPY derivatives with different absorption bands in the visible region (503 – 668 nm) have been synthesized. Absorption band of BODIPY was tuned by installation of 0, 1, or 2 styryl substituents [2-(2,4,6-trimethoxyphenyl)ethenyl], which leads to derivatives with absorption maxima at 503 nm, 587 nm, and 668 nm, respectively. Efficient energy transfer (>0.90) is observed for each dyad, which is manifested by nearly exclusive emission from bacteriochlorin moiety upon BODIPY excitation. Fluorescence quantum yield of each dyad in non-polar solvent (toluene) is comparable with that observed for corresponding bacteriochlorin monomer, and is significantly reduced in solvent of high dielectric constants (DMF), most likely by photoinduced electron transfer. Given the availability of diverse BODIPY derivatives, with absorption in 500–700 nm, BODIPY-bacteriochlorin arrays should allow for construction of near-IR emitting agents with multiple and broadly tunable absorption bands. Solvent-dielectric constants dependence of Φ_f in dyads gives an opportunity to construct environmentally-sensitive fluorophores and probes.

Graphical Abstract

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Supporting Information Available. Additional absorption and emission spectra and copies of ^1H and ^{13}C spectra for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>

Introduction

Photonic materials with multiple absorption bands which can be tuned across the visible and near-IR spectral windows are valuable for a variety of applications, ranging from solar energy conversion^{1–7} to fluorescence imaging.^{8–12} In regards to energy-related applications, such arrays are used for the development of panchromatic absorbers, capable of harvesting light at multiple wavelengths and transferring the excited state energy to the designated site.^{1–7} For biomedical applications, such arrays are utilized, for example, for construction of fluorophores with tunable pseudo-Stokes shift, or fluorophores with multiple excitation wavelengths.^{8–11}

One of the main approaches for systems with multiple excitation bands entails an assembly of multiple individual chromophores into energy transfer (ET) arrays, where each chromophore absorbs at a distinct wavelength and transfers the excited state energy to the terminal chromophore (that with the lowest excited state energy).¹ High efficiency of ET between auxiliary and terminal chromophores is a prerequisite to the desired function of the array, which imposes certain limitations on the selection of the ET arrays components. Förster resonance energy transfer requires huge spectral overlap between energy donor and acceptor for efficient ET,^{12,13} whereas through-bond ET requires appreciable electronic conjugation between donor and acceptor, which is typically achieved by connecting array's components through a conjugated linker.¹² For biomedical fluorescence application, ET arrays with donor and terminal acceptor with absorption and emission in deep-red (650 – 700 nm) or near infrared (near-IR) regions are of particular importance, since near-IR emission enables their application in deep-tissue.¹⁴ However, there are only a handful of ET arrays with both donor and acceptor absorbing in these spectral windows.^{15–18}

Our long-term goal is to develop energy transfer arrays with near-IR emission and broadly tunable absorption, which ultimately can function as fluorophores for a variety of biomedical applications. As energy acceptors we have utilized hydroporphyrins, i.e. chlorins¹⁹ and bacteriochlorins.^{17,20} In particular, bacteriochlorins absorb strongly at 350–380 nm (*B* bands), and pass 700 nm (*Q_y* band), and moderately between 500–550 nm (*Q_x* band),^{21–23} Bacteriochlorins also have a relatively intensive emission band in near-IR (>700 nm)^{22,23} which is exceptionally narrow (with full-width-at-half-of-maximum FWHM ~20–25 nm), and which maximum position can be broadly tuned (700–800 nm) by relatively simple structural modifications.^{22,23} Therefore, bacteriochlorins are well-suited for *in vivo* photonic applications,^{10,11,16,24} particularly multicolor imaging.¹¹

Towards this goal, we recently prepared a series of BODIPY-hydroporphyrin arrays where a common BODIPY absorbing at 500 nm is attached to long-wavelength absorbing chlorins¹⁹ or bacteriochlorins.²⁰ Highly efficient (> 0.90 in non-polar solvent, > 0.80 in polar solvents) energy transfer from BODIPY to hydroporphyrin was observed for each array, so that excitation of BODIPY moiety results in nearly exclusive emission of hydroporphyrin unit. Such arrays constitute a platform for development of fluorophores with a common excitation wavelength at 500 nm, and tunable, huge Stokes' shift > 150 nm. The success of this approach motivated us to further expand the properties of BODIPY-hydroporphyrin arrays, by incorporation of BODIPY with different absorption characteristics. Specifically, we are

interested in arrays with tunable excitation wavelengths in the visible region, because of potential applications of resulting fluorophores in various biomedical settings, such as fluorescence-guided surgery.^{10,11}

BODIPY are very versatile chromophores, with a broadly tunable absorption band.^{24,25} One of the established ways to shift BODIPY absorption towards longer wavelength is installation of styryl substituents at the pyrrolic positions.^{324,25–29} Position of absorption maximum can be tuned by the number of styryl substituents and the electronic properties of the aryl moiety in each styryl substituent, thus while unsubstituted BODIPY absorbs around 500 nm, monostyryl at ~550–600 nm, and distyryl at ~630–700 nm, depending on the aryl group of the styryl substituent.^{24–29} Mono- and distyryl BODIPY can be conveniently synthesized from the corresponding, common methyl derivatives (Scheme 1).²⁵ Styryl BODIPY derivatives have been utilized as fluorophores for bioimaging,³⁰ singlet oxygen photosensitizers for photodynamic therapy,³¹ and have been incorporated into energy transfer arrays, where monostyryl BODIPY functions either as an energy donor,^{5,32–36} or acceptor,^{6,37} while distyryl BODIPY functions predominantly as an energy acceptor,^{6,33–35,38–41} while only in very few cases functions as energy donor.^{38,40} Although covalent²⁰ and non-covalent⁴² BODIPY-bacteriochlorin ET arrays have been previously examined, we are not aware of any prior example of covalently-linked styryl-BODIPY – bacteriochlorin arrays.

Here, we synthesize a series of BODIPY-bacteriochlorin arrays, containing BODIPY substituted with 0, 1, and 2 styryl substituents, since mono- and di-styryl BODIPY will complement the intrinsic bacteriochlorin absorbance. The key question which we intend to answer here is how efficient is the energy transfer between BODIPY and bacteriochlorin, when there is a limited spectral overlap between donor and acceptor. Additionally, we intended to determine how installation of various BODIPY derivatives in a close proximity of bacteriochlorin affects the fluorescence properties of the latter. It is known that bacteriochlorins are relatively potent electron donors,⁴³ while BODIPY,⁴⁴ and di-styryl-BODIPY³⁹ are relatively good electron acceptors. Therefore, there is potential for photoinduced electron transfer, either from bacteriochlorin to excited BODIPY, or from photoexcited bacteriochlorin to BODIPY, in both cases producing non-emissive radical pairs. Such a process is obviously devastating for fluorescence properties of such arrays, since it would greatly reduce Φ_f , particularly in polar solvents. On the other hand, intensively absorbing systems, undergoing photoinduced electron separation can be beneficial for other applications, such as artificial photosynthesis.²

Results and Discussion

The target dyads are presented in Chart 1. In each dyad BODIPY is attached to a common bacteriochlorin through an aryl moiety. As BODIPY donor we employed 3-[2-(2,4,6-trimethoxyphenyl)ethenyl]-BODIPY **BC-BDP2** or 3,5-bis[2-(2,4,6-trimethoxyphenyl)ethenyl]-BODIPY **BC-BDP3**. The choice of this particular substituent is motivated by the known fact, that electron rich aryl groups provide a larger bathochromic shift in resulting styryl-BODIPY derivatives.^{25–29} For comparison, we also examined the **BC-BDP1**, where tetramethyl BODIPY was employed as an energy donor. As a benchmark

energy acceptor, we included bacteriochlorin **BC**, whereas BODIPY boron pinacolates **BDP1-3** (Chart 1) have also been used here as benchmark energy donors.

BDP2 and **BDP3** were synthesized from known **BDP1** (prepared by Miyaura reaction of corresponding 8-(4-bromophenyl)-BODIPY),⁴⁵ by well established protocol²⁵ with assistance of microwave irradiation⁴⁶ (Scheme 2). Thus, reaction of **BDP1** with 2,4,6-trimethoxybenzaldehyde, in the presence of AcOH/piperidine in DMF provides **BDP2** and **BDP3** albeit in quite low yields (13% and 9%, respectively). Attempts to improve the yields, by either using of conventional heating, or different solvents, were unsuccessful. The low yield is partially due to the formation of the other styryl-BODIPY derivatives, and decomposition of the starting material during the reaction. We also anticipate that the steric hindrance imposed by methoxy substituents, affects the outcome of these reactions.

The target dyads **BC-BDP1-3** were prepared by Suzuki reaction of boronic esters **BC1-3** with known bromobacteriochlorin **BC1**¹⁷ under reported conditions (Scheme 3).⁴⁷ The desired dyads were obtained in moderate yields (46–56%). The target dyads were easily isolated by column chromatography.

Benchmark **BC** was obtained in non-optimized synthesis, as a side-product in synthesis of **BC1** in 37% yield (Scheme 4).

Characterization

All new compounds were characterized by ¹H and ¹³C NMR spectroscopy, as well as HRMS. The data are consistent with the expected structures. In particular, formation of the mono- and distyryl substituted BODIPY was confirmed by the presence of new sets of doublets (7.60 ppm and 7.20 ppm), due to the formation of a vinyl part of a styryl substituent, and disappearance of resonances of methyl groups at 2.35 ppm in ¹H NMR. Vicinal coupling constants between vinyl protons $J = 16.6$ Hz confirms *E* stereochemistry of newly formed styryl substituents. The presence of resonances of bacteriochlorin and BODIPY protons in 1:1 ratio in ¹H NMR spectra of **BC-BDP1-3** confirms the formation of dyads.

Absorption and emission properties

Monomers—Absorption and emission spectra of **BDP1-3** in toluene are presented in Figure 1, and absorption and emission data in toluene and DMF are given in Table 1. Each derivative features an intensive $S_0 \rightarrow S_1$ absorption band, which is bathochromically shifted by approximately 80 nm upon addition of each styryl substituent. Installation of the styryl substituents also causes significant broadening of the main absorption band, with a distinctive shoulder at the blue edge of the main band. Increasing the number of styryl substituents also leads to intensification of the second, short wavelength $S_0 \rightarrow S_2$ absorption at about 350 nm (**BDP2**) and 380 nm (**BDP3**). Each BODIPY derivative exhibits an intense emission, with a Stokes' shift of 12–15 nm, and fluorescence quantum yield (Φ_f) of 0.56–0.84. Interestingly, Φ_f only moderately depends on the solvent dielectric constants, and in DMF is reduced only by 10–25%, compared to toluene.

Bacteriochlorin-BDP dyads

Absorption spectra of bacteriochlorin-BODIPY dyads (Figure 2, Table 1) are essentially the sum of the absorption of corresponding BODIPY and bacteriochlorin, with nearly identical absorption maxima. This indicates a negligible electronic conjugation between BODIPY and bacteriochlorin in dyads, as expected, given that the phenyl linker is twisted in respect of both chromophores, and thus provides a little direct conjugation. Excitation of each dyad in toluene, at the wavelength where BODIPY component absorbs predominantly, results in nearly exclusive emission of bacteriochlorin component (at 744 nm), while emission of the BODIPY component is negligible (Figure 3). Excitation spectra, monitored at a wavelength where bacteriochlorin emits exclusively, closely resemble absorption (Figure S2). All these indicate efficient energy transfer, from BODIPY to bacteriochlorin. Energy transfer efficiency (ETE), defined as the ratio of Φ_f of bacteriochlorin component upon excitation at the BODIPY maximum relative to the Φ_f upon direct excitation of bacteriochlorin at the maximum of the *B* band, exceeds 0.90 for each dyad. Since, there is minute overlap of **BDP-2** emissions and bacteriochlorin absorption (Figure S3, Supporting Information), the energy transfer likely occurs (at least in part) by through-bond mechanism.¹²

Contrary to toluene, fluorescence of both components (BODIPY and bacteriochlorin) is severely reduced in DMF (~10 times for bacteriochlorin component), regardless of wavelength of excitation. Φ_f for benchmark monomer **BC** in DMF is comparable to that observed in toluene (Table 1). To get further insight into processes responsible for fluorescence quenching, Φ_f and ETE were determined for **BC-BDP3** in solvents with a broad range of dielectric constants (ϵ , Table 2). Both Φ_f and ETE are consistently high in solvents of low ϵ , while Φ_f is dramatically reduced for solvents with $\epsilon > 9$. The only exception is *i*-PrOH, for which Φ_f is comparable to that determined in low-dielectric constant solvents. For each solvent examined, a nearly quantitative ETE is observed, which means that essentially the same degree of fluorescence quenching is observed when bacteriochlorin or BODIPY is excited. The wavelength of emission is nearly independent on solvent polarity. These observations are consistent with photoinduced electron transfer between dyad components, which produces a non-emissive ion-radical pair and thus competes with the fluorescence of locally excited bacteriochlorin.

The most probable PET in bacteriochlorin-BODIPY arrays is electron transfer from the photoexcited bacteriochlorin to the ground-state BODIPY. This direction is consistent with that previously reported for porphyrin-BODIPY arrays,³⁹ and with fluorescence excitation spectra, which indicate that the degree of fluorescence quenching is nearly identical regardless of whether BODIPY or bacteriochlorin component is excited.

Conclusion and Outlook

Very efficient energy transfer (with ETE > 0.9) is observed from BODIPY to near-IR absorbing bacteriochlorin, for different BODIPY with absorption spanning 505 – 668 nm. This enables, in principle, construction of near-IR emitting agents with broadly tunable excitation profile. Particularly, arrays of bacteriochlorins with distyryl-BODIPY, with deep-red absorption (670–700 nm) appear to be a valuable platform for a variety of biomedical applications, since both absorption and emission of arrays are localized in the physiological

window. Such arrays are rather rare.^{15–18} For example, we¹⁷ and others^{15,16} previously studied chlorin-bacteriochlorin arrays as fluorophores with absorption and emission in deep red and emission in near-IR windows. Distyryl-BODIPYs usually possess comparable or higher absorption coefficient than chlorins ($\sim 100,000 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for distyryl-BODIPY²⁵ vs. $75,000 - 80,000 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for chlorin¹⁵) comparable, or longer wavelength absorption bands, are significantly easier to synthesize than chlorins, and, similarly to chlorins, are efficient energy donors to bacteriochlorins. Therefore, distyryl-BODIPY-bacteriochlorin arrays may provide an attractive alternative for chlorin-bacteriochlorin arrays. Other possible applications for (di)styryl-BODIPY-bacteriochlorin arrays include a construction of panchromatic absorbers, absorbing across a wide range of UV-vis and near-IR windows, for light harvesting applications.

The solvent-polarity dependence of the Φ_f of BODIPY-bacteriochlorin dyads is the factor which certainly may affect their applications and performance in biomedical settings, as their fluorescence is highly reduced in polar media. One plausible solution for this problem is an encapsulation of hydrophobic dyads in the hydrophobic part of water-soluble nanostructures, such as micelles or vesicles, an approach which was broadly utilized for biological applications of tetrapyrrolic and related structures.⁴⁹ On the other hand, the biological environment is highly heterogeneous, with structures of low polarity/dielectric constants (such as lipid bilayers, proteins, etc),⁵⁰ which gives an opportunity to construct fluorescent probes, which have fluorescence activated upon localization inside such structures. Finally, further optimization of arrays structure, i.e. tuning the linker length and redox properties of both BODIPY and bacteriochlorin is a potential way to mitigate the influence of the solvent polarity on the emission properties of BODIPY-bacteriochlorin dyads. This research is currently ongoing in our laboratory.

Experimental Section

Synthesis

All reagents, solvents, etc. not prepared in house were purchased through either Sigma-Aldrich or Fisher Scientific and used without further purification.

General procedure for palladium cross-coupling reactions—All reagents and solvents with exception of palladium catalyst were placed in a Schlenk flask, and contents was degassed by two cycles of freeze-pump-thaw. At which time catalyst is added and a third cycle of freeze-pump-thaw is performed, and the reaction mixture was stirred under N_2 at indicated temperature.

Microwave Reactions—Microwave reactions were performed in CEM Discover CEM, Mathew, NC) microwave instrument. All reactions were performed in 10 mL closed tube, with continuous monitoring of pressure and temperature. Temperature was monitored using built-in IR sensor. Microwave reactions involves three stages: (1) “Run time” - reaction mixture was irradiated with 150 W until it reaches 120 °C (30–60 sec); (2) “Hold time” – reaction mixture was maintained at 120 °C for 10 minutes, (3) “Cooling time” – reaction mixture was kept in closed reaction vials until reaches about 50 °C (approximately 10 min).

Characterization—All NMR spectra were acquired on either 400 MHz NMR or 500 MHz NMR. ¹³C NMR Data for dyads 1–3 collected as combination of pure product isolated from two separate syntheses. All HRMS data acquired on Bruker 12T FT-ICR MS.

Spectroscopic Studies—Fluorescence measurements were performed with a sample absorbance of < 0.1. All measurements were performed in HPLC grade solvents.

Known compounds **BDP1**,⁴⁵ **BC1**,¹⁷ and **BC-Br₂**⁵¹ were prepared following published procedures.

BDP2: A mixture of **BDP1** (106 mg, 0.235 mmol), 2,4,6-trimethoxybenzaldehyde **1** (46.2 mg, 0.235 mmol), acetic acid (6 drops) and piperidine (6 drops) in DMF (5 mL) were reacted under microwave irradiation as described in *General Procedure*. Crude reaction mixture was diluted with EtOAc, washed (water and brine) and concentrated. Flash column chromatography [silica, CH₂Cl₂/hexanes (5:1)] yielded a blue/pink solid (19.6 mg, 13%). ¹H NMR (CDCl₃, 400 MHz): δ 1.36 (s, 3H), 1.39 (s, 12H), 1.41 (s, 3H), 2.57 (s, 3H), 3.84 (s, 3H), 3.91 (s, 6H), 5.93 (s, 1H), 6.12 (s, 2H), 6.65 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 16.5 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 8.12 (d, *J* = 16.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.6, 14.7, 15.1, 25.1, 55.5, 56.0, 84.2, 90.7, 108.3, 117.8, 120.1, 120.3, 128.0, 128.9, 130.9, 133.1, 135.3, 138.6, 138.9, 140.6, 143.0, 152.8, 157.0, 160.7, 162.0; HRMS (ESI-TOF) *m/z* [M+Cs]⁺ Calcd for C₃₅H₄₀B₂F₂N₂O₅Cs 761.2152; Found 761.2154.

BDP3: A mixture of **BDP1** (106 mg, 0.200 mmol), 2,4,6-trimethoxybenzaldehyde **1** (156 mg, 0.8 mmol), acetic acid (6 drops) and piperidine (6 drops) in DMF (5 mL) were placed in a 10 mL microwave tube. The mixture was irradiated for 10 min under the following conditions: 120 °C, 150 W, max PSI 250. After a single microwave exposure TLC indicated that **BDP2** was present, however, further irradiation leads to increased decomposition rather than increased yield. Crude reaction mixture was diluted with EtOAc, washed with water (2x), brine (1x) and concentrated. Flash column chromatography [silica, CH₂Cl₂/hexanes (5:1)] yielded a teal solid (14.5 mg, 9%). ¹H NMR (CDCl₃, 400MHz): δ 1.39 (s, 12H), 1.41 (s, 6H), 3.84 (s, 6H), 3.92 (s, 12H), 6.13 (s, 4H), 6.64 (s, 2H), 7.36 (d, *J* = 7.9Hz, 2H), 7.59 (d, *J* = 16.6 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 16.6 Hz, 2H); ¹³C NMR (CDCl₃, 100MHz): δ 15.0, 25.1, 55.5, 55.9, 84.2, 90.8, 108.7, 117.1, 120.8, 127.0, 128.4, 132.9, 135.2, 136.5, 139.0, 140.9, 154.7, 160.5, 161.5; HRMS (ESI-TOF) *m/z* [M]⁺ Calcd for C₄₅H₅₀B₂F₂N₂O₈ 806.3731; Found 806.3708.

BC-BDP1: Following the general procedure, a mixture of **BC1** (10.0 mg, 0.0163 mmol), **BDP1** (8.8 mg, 0.0196 mmol), sodium carbonate (17.3 mg, 0.163 mmol) and PdCl₂(dppf)·CH₂Cl₂ (2.7 mg, 3.26 μmol) in toluene/ethanol/water (4:1:2, 7 mL) was stirred under N₂ at 80°C for 20 hours. The reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na₂SO₄) and concentrated. Column chromatography [silica (2.5 × 18 cm, hexanes/CH₂Cl₂ (1:3)], followed up with trituration of solid product with hexanes (performed until filtrate was no longer fluorescent) yielded a red-brown solid (6.8 mg, 49%). ¹H NMR (CDCl₃, 500 MHz): δ -1.83 (s, 1H), -1.57 (s, 1H), 1.74 (s, 6H), 1.96 (s, 6H), 1.99 (s, 6H), 2.63 (s, 6H), 3.73 (s, 3H), 4.07 (s, 3H), 4.40 (s, 4H), 6.09 (s, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 8.25–8.30 (m, 4H), 8.42 (d, *J* = 8.0 Hz, 2H), 8.65–8.70 (m, 3H), 8.79 (s, 1H), 8.83

(s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 14.8, 15.0, 31.2, 31.3, 45.7, 45.8, 47.8, 52.0, 52.5, 63.7, 96.8, 97.0, 97.3, 121.4, 122.5, 123.0, 127.2, 127.6, 129.1, 130.4, 131.0, 131.8, 132.0, 133.0, 133.6, 134.1, 135.0, 135.2, 135.5, 136.2, 139.2, 141.2, 142.3, 143.3, 154.4, 155.6, 160.8, 167.4, 169.6, 170.1; HRMS (ESI-TOF) m/z $[\text{M}]^+$ Calcd for $\text{C}_{52}\text{H}_{51}\text{BF}_2\text{N}_6\text{O}_3$ 856.4087; Found 856.4074.

BC-BDP2: Following the General Procedure, a mixture of **BC1** (10.0 mg, 0.0163 mmol), **BDP2** (12.3 mg, 0.0196 mmol), sodium carbonate (17.3 mg, 0.163 mmol) and $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (2.7 mg, 3.26 μmol) in toluene/ethanol/water (4:1:2, 7 mL) was stirred under N_2 at 80°C for 17 hours. The reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na_2SO_4) and concentrated. Column chromatography [silica (2.5 $\times$ 16 cm, hexanes/ CH_2Cl_2 (1:3))] yielded a dark blue solid, which contained a minor red fluorescent impurity. This impurity was removed by trituration of solid product with hexanes until filtrate was no longer orange-red fluorescent, resulting in an overall yield of 9.5 mg (56%). ^1H NMR (CDCl_3 , 500 MHz): δ -1.86 (s, 1H), -1.59 (s, 1H), 1.73 (s, 3H), 1.78 (s, 3H), 1.96 (s, 6H), 2.00 (s, 6H), 2.65 (s, 3H), 3.74 (s, 3H), 3.87 (s, 3H), 3.96 (s, 6H), 4.06 (s, 3H), 4.40 (s, 2H), 4.41 (s, 2H), 6.06 (s, 1H), 6.16 (s, 2H), 6.77 (s, 1H), 7.58 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 16.5 Hz, 1H), 8.21 (d, J = 16.6 Hz, 1H), 8.24–8.29 (m, 4H), 8.42 (d, J = 8.1 Hz, 2H), 8.66–8.70 (m, 2H), 8.79 (s, 1H), 8.83 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 14.8, 14.9, 15.4, 31.2, 31.2, 45.7, 45.8, 47.8, 52.0, 52.5, 55.5, 56.0, 63.7, 90.8, 96.8, 96.9, 97.3, 108.3, 117.9, 120.2, 120.4, 122.4, 123.2, 127.3, 128.1, 128.9, 129.0, 130.3, 131.0, 131.4, 131.8, 133.4, 133.6, 134.15, 134.23, 134.9, 135.0, 135.3, 136.2, 138.9, 139.4, 140.6, 141.3, 142.9, 152.8, 154.5, 157.0, 160.68, 160.72, 162.0, 167.4, 169.6, 169.9; HRMS (ESI-TOF) m/z $[\text{M}]^+$ Calcd for $\text{C}_{62}\text{H}_{61}\text{BF}_2\text{N}_6\text{O}_6$ 1,034.4718; Found 1034.4706.

BC-BDP3: Following the general procedure, a mixture of **BC1** (8.9 mg, 14.5 μmol), **BDP3** (14.0 mg, 17.4 μmol), potassium carbonate (20.0 mg, 145 μmol) and $\text{Pd}(\text{PPh}_3)_4$ (4.0 mg, 3.5 μmol) in toluene/DMF (2:1, 6 mL) was stirred under N_2 at 80°C for 14 hours. The reaction mixture was diluted with EtOAc, washed with water, brine, dried (Na_2SO_4) and concentrated. Flash column chromatography [silica (2.5 $\times$ 17 cm, CH_2Cl_2)] yielded a teal green solid, 9.9 mg (56%). ^1H NMR (CDCl_3 , 500 MHz): δ -1.88 (s, 1H), -1.60 (s, 1H), 1.78 (s, 6H), 1.96 (s, 6H), 2.00 (s, 6H), 3.76 (s, 3H), 3.87 (s, 6H), 3.97 (s, 12H), 4.06 (s, 3H), 4.40 (s, 2H), 4.42 (s, 2H), 6.17 (s, 4H), 6.76 (s, 2H), 7.61 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 16.6 Hz, 2H), 8.23–8.30 (m, 6H), 8.42 (d, J = 8.1 Hz, 2H), 8.67–8.71 (m, 3H), 8.80 (s, 1H), 8.83 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 15.3, 25.1, 29.8, 31.2, 45.8, 51.9, 55.5, 55.87, 55.91, 63.8, 90.9, 96.9, 97.3, 108.7, 117.2, 120.9, 122.3, 123.3, 127.1, 127.4, 128.5, 129.0, 130.3, 131.0, 131.7, 131.7, 133.4, 133.7, 134.3, 134.6, 134.8, 134.9, 135.19, 135.23, 136.3, 137.0, 138.7, 140.89, 140.91, 141.3, 154.7, 160.5, 160.6, 161.5, 167.4, 169.8; HRMS (ESI-TOF) m/z $[\text{2M} + \text{2H}]^{2+}$ Calcd for $\text{C}_{144}\text{H}_{144}\text{B}_2\text{F}_4\text{N}_{12}\text{O}_{18}$ 1213.0365; Found 1213.0357.

5-Methoxy-3,13-bis(4-methoxycarbonylphenyl)-8,8,18,18-tetramethyl BC: This compound was prepared in non-optimized reaction, as a side product in synthesis of **BC1**.¹⁷ Following the general procedure, a mixture of **BC-Br₂** (100.0 mg, 0.179 mmol), 4-methoxycarbonylphenylboronic acid pinacol ester (**2**) (56.3 mg, 0.215 mmol), potassium carbonate (247.4 mg, 1.79 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (41.4 mg, 0.0358 mmol) in toluene/DMF

(2:1, 21 mL) was stirred at 80°C, under N₂ for 15 hours. The reaction mixture was diluted with EtOAc, washed (water and brine), dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/CH₂Cl₂ (1:2) → EtOAc] yielded **BC1** (54.5 mg, 50%) as a green solid, and **BC** (second fraction, green). **BC** was further purified by flash column chromatography [silica, CH₂Cl₂ → CH₂Cl₂/EtOAc (20:1)] to remove residual pinacol ester **2**. **BC2** was obtained as a green solid (26.6 mg, 37%). ¹H NMR (CDCl₃, 400 MHz): δ -1.82 (s, 1H), -1.57 (s, 1H), 1.95 (s, 6H), 1.98 (s, 6H), 3.64 (s, 3H), 4.05 (s, 3H), 4.06 (s, 3H), 4.37 (s, 2H), 4.39 (s, 2H), 8.20 (d, *J* = 8.5 Hz, 2H), 8.27 (d, *J* = 8.5 Hz, 2H), 8.32 (d, *J* = 8.5 Hz, 2H), 8.42 (d, *J* = 8.5 Hz, 2H), 8.64 (s, 1H), 8.65 (d, *J* = 2.8 Hz, 1H), 8.67 (s, 1H), 8.77 (s, 1H), 8.82 (d, *J* = 2.1 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ 31.16, 31.23, 45.7, 45.8, 47.7, 52.1, 52.3, 52.5, 63.4, 96.8, 97.1, 97.3, 122.5, 122.6, 127.4, 128.6, 129.08, 129.14, 130.4, 131.0, 131.4, 132.9, 134.2, 135.1, 135.2, 135.6, 136.3, 141.20, 143.23, 154.5, 160.9, 167.4, 167.7, 169.5, 170.1. HRMS (ESI-TOF) *m/z* [M]⁺ Calcd for C₄₁H₄₀N₄O₅ 668.2993; Found 668.2997.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Absorption (solid) and emission (dotted) spectra of **BDP1** (black), **BDP2** (blue), and **BDP3** (red). All spectra were taken in toluene, at room temperature and are normalized at their highest absorption/emission peaks. Emission spectra were taken upon excitation at the blue edge of main absorption peak.

Figure 2. Absorption spectra of BODIPY-bacteriochlorin dyads: **BC-BDP1** (black), **BC-BDP2** (blue), and **BC-BDP3** (red). All spectra were taken in toluene at room temperature and are normalized at the *B* bands.

Figure 3.

Emission spectra of BODIPY-bacteriochlorin dyads: **BC-BDP1** (black), **BC-BDP2** (blue), and **BC-BDP3** (red). All spectra were taken in toluene at room temperature upon excitation at the onset of BODIPY absorption.

Scheme 1.

General scheme for reaction of tetramethyl-BODIPY with aldehydes.

Scheme 2.
Synthesis of **BDP2-3** monomers.

<i>Starting BODIPY</i>	<i>Conditions</i>	<i>Product</i>	<i>Yield</i>
BDP1	a)	BC-BDP1	49%
BDP2	a)	BC-BDP2	56%
BDP3	b)	BC-BDP3	56%

a) Na_2CO_3 , $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$, toluene/EtOH/ H_2O (4:1:2), 80 °C
 b) K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, toluene/DMF (2:1), 80 °C

Scheme 3.
 Synthesis of dyads **BC-BDP1-3**.

Scheme 4.
Synthesis of benchmark monomer **BC**.

Chart 1.

Structures of dyads and BODIPY derivatives reported here.

Table 1

Absorption and emission properties of BODIPY and bacteriochlorin monomers and bacteriochlorin-BODIPY dyads.

Compound	λ_B	λ_{BODIPY}	λ_{Oy}	λ_{em}	Φ_f^a (toluene)	Φ_f^a (DMF)	E^{TE^b} (toluene)
BODIPY monomers							
BDP1	-	503	-	515	0.69	0.54	-
BDP2	-	587	-	602	0.84	0.75	-
BDP3	-	668	-	683	0.56	0.45	-
Bacteriochlorin monomer							
BC	369	514 ^{c)}	735	744	0.25	0.23	-
Dyads							
BC-BDP1	371	504	735	744	0.23	0.026	0.93
BC-BDP2	370	588	735	743	0.24	0.018	0.92
BC-BDP3	373	669	736	744	0.24	<0.005	0.96

^{a)} Fluorescence quantum yields were determined using Rhodamine 6G in non-degassed MeOH ($\Phi_f = 0.88$, for BODIPY derivatives), and tetraphenylporphyrin in non-degassed toluene ($\Phi_f = 0.070$,⁴⁸ for dyads). Samples were excited at the blue edge of absorption band (BODIPY derivatives), at the maximum of BODIPY absorbance (dyads) or maximum of the B band (BC). For dyads, only emission of bacteriochlorin component was integrated.

^{b)} Energy transfer efficiency determined as a ratio of Φ_f upon excitation at the maximum of BODIPY absorption relative to the Φ_f upon excitation at the maximum of B band of bacteriochlorin. ETE in DMF was not determined due to weak emission intensities.

^{c)} Wavelength of Q_X band of bacteriochlorin.

Table 2

Fluorescence quantum yields for **BC-BDP3** in solvents of different dielectric constants.

Solvent (<i>e</i>)	toluene (2.38)	CHCl ₃ (4.81)	C ₆ H ₅ -Cl (5.62)	THF (7.58)	CH ₂ Cl ₂ (8.93)	<i>i</i> -PrOH ^a (17.9)	Acetone (20.7)	PhCN (26.0)	DMF (36.7)
Φ_F	0.25	0.21	0.26	0.22	0.059	0.19	0.03	0.033	<0.005
ETE	0.97	0.99	0.96	0.95	1.0	1.0	^b	^b	^b

^a) Contains THF (2.5% v/v) to facilitate solubilization.

^b) ETE could not be accurately determined, due to weak emission from bacteriochlorin and its overlap with residual emission from BODIPY.