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Deep-red Emissive BODIPY-Chlorin Arrays Excitable with Green and Red Wavelengths

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Abstract

We report here synthesis and characterization of BODIPY-chlorin arrays containing a chlorin subunit, with tunable deep-red (641–685 nm) emission, and one or two BODIPY moieties, absorbing at 504 nm. Two types of arrays were examined: one where BODIPY moieties are attached through phenylacetylene linker at the 13- or 3,13-positions of chlorin, and a second type where BODIPY is attached at the 10-position of chlorin through an amide linker. Each of the examined arrays exhibits an efficient (0.80) energy transfer from BODIPY to chlorin moiety in both toluene and DMF and exhibits intense fluorescence of chlorin upon excitation of BODIPY at ~ 500 nm. Therefore, the effective Stokes shift in such arrays is in the range of 140–180 nm. Dyads with BODIPY attached at the 10-position of chlorin exhibit a bright fluorescence in a range of solvents with different polarities (i.e. toluene, MeOH, DMF, and DMSO). In contrast to this, some of the arrays in which BODIPY is attached at the 3- or at both 3,13-positions of chlorin exhibit significant reduction of fluorescence in polar solvents. Overall, dyads where BODIPY is attached at the 10-position of chlorin exhibit ~5-fold brighter fluorescence than corresponding chlorin monomers, upon excitation at 500 nm.

Introduction

Hydroporphyrins (chlorins and bacteriochlorins) are tetrapyrrolic macrocycles, which offer unique benefits for *in vivo* fluorescence imaging. They possess multiple absorption bands; e.g. the deep-red or near-IR Q_y band (650–700 nm for chlorins, 700–800 nm for bacteriochlorins), Q_x band which is located in the green range (500–520 nm), and B bands, which are located in the violet or UV spectral windows (400–430 nm for chlorins, 360–380 nm for bacteriochlorins).^{1–4} Excitation at each of these absorption bands results in an emission in the deep-red (chlorin, 630–700 nm) or the near-IR (bacteriochlorin 720–800 nm) spectral windows. Another beneficial feature of hydroporphyrins are their narrow (with full-width-at-half-of-maximum ~12–20 nm) emission bands. Additionally, wavelengths of

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Supporting Information Available. Absorption and emission spectra for benchmark monomers, fluorescence data for selected dyads in different solvents, copies of ¹H, ¹³C, and ¹⁹F NMR spectra for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>

absorption and emission maxima for hydroporphyrins can be precisely tuned by substitution on the periphery of the macrocycles.^{2–5} Both the latter properties should greatly facilitate applications of hydroporphyrins as fluorophores for multicolor imaging. Recently, our collaborative efforts have demonstrated that unique properties of hydroporphyrins are highly beneficial for construction of fluorescent probes for anti-cancer fluorescence-guided surgery.^{6,7} It has been shown that upon excitation with the green light (~510 nm) a probe containing bacteriochlorin as a fluorophore, results in near-IR emission (760 nm) with a large pseudo-Stokes shift (250 nm), and produces a very sharp near-IR image of target tumors located on tissue surface, with high tumor-to-background ratio.⁶ This is apparently due to the large Stokes shift, which enables detection of a near-IR emission far from the excitation beam. As a result, both background fluorescence and detection of scattered light from excitation source are diminished. Due to very shallow tissue penetration, green light is unable to excite fluorophores localized deeper in tissue, these can be only detected and visualized upon excitation with the near-IR wavelengths. However, near-IR excitation, due to the small Stokes shift (~10 nm) and tissue autofluorescence, produces blurred images with a tumor-to-background ratio lower than observed for green excitation. Nevertheless, near-IR excitation can instead be used for detection of tumors localized below tissue surface (or hidden behind mesentery or intestines), while green excitation can be used for precise determination of tumor margins. This “double-excitation” approach is not possible with fluorophores typically used for near-IR imaging (such as cyanines), since the latter does not possess an appreciable absorbance in the green spectral window.⁶ Typical organic near-IR fluorophores usually exhibit a single, relatively narrow absorption band in the near-IR spectral window, due to their $S_0 - S_1$ absorption, and their band corresponding to $S_0 - S_2$ absorption is located in the UV spectral window (with $\lambda < 400$ nm).⁸

Subsequently, it has also been demonstrated that hydroporphyrins can be used for simultaneous visualization of two different cancer cells *in vivo* due to their narrow and tunable emission bands.⁷ Chlorins and bacteriochlorins have also been utilized by other groups for intracellular and *in vivo* fluorescence or photoacoustic imaging.^{9,10}

One of the limitations, which potentially might hamper the full exploitation of hydroporphyrins' properties in fluorescence-guided surgery, is the relatively low extinction coefficient for the Q_x band (~500 nm) which is in the range of ~8,000 – 13,000 $M^{-1}\cdot cm^{-1}$ for chlorins,¹¹ and 35,000 – 39,000 $M^{-1}\cdot cm^{-1}$ for bacteriochlorins.¹² These values are substantially lower in comparison to typical fluorophores used in fluorescence imaging (> 100,000 $M^{-1}\cdot cm^{-1}$) and results in substantially lower fluorescence brightness upon visible excitation (for a compilation of brightness of typical near-IR fluorophores see, for example, ref 13).

We propose to increase the fluorescence brightness of hydroporphyrins, upon excitation at ~500 nm, by utilizing an auxiliary chromophore, strongly absorbing in the green region, and capable of transferring excitation energy to hydroporphyrins. Hydroporphyrins in energy transfer arrays might function as both energy donors and acceptors, which was utilized in the construction of arrays with potential biomedical or energy-related applications.^{9,14–22} Dyad containing green light-absorbing rhodamine as an energy donor and a chlorophyll *a* derivative as an energy acceptor has been reported, and efficient energy transfer from

rhodamine to chlorin moiety has been determined.⁹ We anticipated that positively-charged rhodamine might be an efficient electron acceptor for a photoexcited chlorin, and thus might significantly quench the chlorin fluorescence in resulting arrays constructs (as it was reported for analogous porphyrinrhodamine arrays).^{23,24} Therefore, as an auxiliary chromophore we have chosen a boron complex of dipyrin (often referred to as BODIPY).^{25–28} BODIPY is a class of neutral molecules, broadly utilized as fluorescent labels and probes, with molar excitation coefficients up to $100,000 \text{ M}^{-1}\cdot\text{cm}^{-1}$, and usually possessing high fluorescence quantum yields. There are numerous examples of energy transfer dyads where BODIPY derivatives have been employed as energy donor,^{25,26} including these with red or near-IR emitting acceptors,²⁷ and a wide range of BODIPY-porphyrin dyads.²⁸ To the best of our knowledge, the only examples of BODIPY-hydroporphyrin arrays are the aza-BODIPY-chlorin dyads reported by Tamiaki, where a chlorophyll-type moiety functions as energy donor, and aza-BODIPY as an energy acceptor.²²

In this paper we describe synthesis and evaluation of optical properties of BODIPY-chlorin arrays. Our goal was to establish a molecular architecture for arrays which assures bright emission of chlorin acceptor upon excitation of BODIPY donor, regardless of polarity of environment. This requires efficient energy transfer, and a lack of competitive processes, which might quench fluorescence of chlorin. The latter processes can be potentially devastating for the emission properties of dyad, as significant quenching of fluorescence of both donor and acceptor has been reported (for example in BODIPY-phthalocyanine dyads²⁹). One such process could be photoinduced electron transfer (PET), from photoexcited chlorin to BODIPY. Chlorins are known as a potent electron donor in their excited state,^{18,30} and quenching of BODIPY fluorescence by PET is a well-known phenomenon.³¹ Indeed, significant quenching of fluorescence in aza-BODIPY-chlorin dyads in polar solvents due to PET has been reported.²²

Additionally, we have been searching for the BODIPY-chlorin dyad architecture which would provide versatility in tuning the absorption/emission wavelengths of chlorin. The wavelength of absorption and emission can be tuned by substitution of chlorins at the 3 and 13 positions,^{3,4} therefore our construct should allow placing different substituents at these positions.

Towards these goals we designed two types of arrays (Chart 1). In the first type [arrays **1-BDP**, **2-(BDP)₂**, and **Zn2-(BDP)₂**] a BODIPY unit is attached at the 13 and 3,13-positions, through phenylethynyl linker. In these constructs the linker functions also as an auxochrome which tunes emission properties of chlorin. In the second type (dyads **3-BDP**, **4-BDP**, and **Zn4-BDP**) a BODIPY unit is attached to a phenyl group localized at the 10-position of chlorin through an amide bond, while auxochromes (phenylethynyl groups) are placed independently at the 3- and 13-positions. Two corresponding Zn(II) chelates of some arrays were prepared [i.e. **Zn2-(BDP)₂** and **Zn4-BDP**] to evaluate the influence of metal complexation of chlorin on optical properties of resulting arrays. This selection of arrays enables us to examine properties of architectures for which the chlorin acceptor possesses a broad range of optical and redox properties, since both substitution at the 3,13-positions and zinc metalation markedly alter absorption/emission maxima, and redox properties of

chlorins.^{3,4,18} As benchmark donors we investigated corresponding BODIPY derivatives – **BDP-TMS** and **BDP-NHBz**, and as benchmark acceptors – chlorin derivatives – **1-3** and **Zn2** (Chart 1).

Results and Discussion

Synthesis

Syntheses of target BODIPY-chlorin arrays required two different strategies. The key reaction for synthesis of **1-BDP** and **2-(BDP)₂** is Sonogashira coupling of bromosubstituted chlorins with BODIPY derivative with 4-ethynylphenyl substituent at the *meso* position (**BDP-H**). For synthesis of **3-BDP** and **4-BDP** we employed amide bond formation between chlorin derivatives possessing carboxylic acid function and amine-functionalized BODIPY (**BDP-NH₂**). Both strategies utilize similar chlorin building blocks: chlorins **1-Br**, **2-Br₂** and **3**, each possessing a 4-(methoxycarbonyl)phenyl substituent at the 10-position. Synthesis of 13-bromochlorin **1-Br** has been previously reported.²⁰ Chlorins **2-Br₂** and **3** were synthesized using reported procedures for analogous derivatives (Scheme 1).^{32,33} Thus, bromination of known formyldipyrromethane **5₂₀** with one or two equivalents of NBS provides 1-bromo-9-formyldipyrromethane **6-Br** (94% yield) or 1,2-dibromo-9-formyldipyrromethane **6-Br₂** (67% yield), respectively. Subsequent condensation of **6-Br** with tetrahydrodipyrin **7**, and **6-Br₂** with 8-bromotetrahydrodipyrin **7-Br**, followed by zinc-mediated oxidative cyclization, and demetalation provides **3** (25% yield), and **2-Br₂** (17% yield).

The synthesis of requisite **BDP-H** and **BDP-TMS** has been reported numerous times,³⁴ but here we prepared it in a slightly different manner. We synthesized **BDP-H** following established procedure for *meso*-substituted BODIPY, in one-pot, three step reaction of 2,4-dimethylpyrrole with 4-[(trimethylsilyl)ethynyl]benzaldehyde, catalyzed by trace amount of TFA, followed by oxidation of resulting dipyrromethane with DDQ, and complexation of resulting dipyrin by BF₃·OEt₂ in the presence of Et₃N (Scheme 2), to afford **BDP-TMS** in 23% yield. Resulting **BDP-TMS** with TMS-protected ethynyl functionality were deprotected using previously reported procedure³⁴ (K₂CO₃ in MeOH/THF), to afford a target **BDP-H** in 60%.

Two different sets of copper-free Sonogashira cross-coupling conditions, reported previously for hydroporphyrins, were examined for reaction of **BDP-H** with chlorins **1-Br** and **2-Br₂**: Pd₂(dba)₃ in the presence of (*o*-tol)₃P in toluene/Et₃N,³³ and (PPh₃)₂PdCl₂ in DMF/Et₃N.³⁵ We found, that the latter conditions provided desired products with better yields (52% and 47% for **1-BDP** and **2-(BDP)₂**, respectively, Scheme 3), and the target arrays were easier to purify. It is worth noting that reaction of analogous BODIPY, without methyl groups at pyrrole units led to decomposition of starting BODIPY, and no dyad was isolated.

Benchmark monomers **1** and **2** were obtained in analogous reactions of **1-Br** and **2-Br₂** with phenylacetylene in 84% and 60% yield, respectively (Scheme 4)

Dyads **3-BDP** and **4-BDP** were synthesized through the EDC-mediated coupling of known, amine-functionalized **BDP-NH₂**³⁶ with carboxylic acid functionalized chlorins (Scheme 5). Ester functions in **2** and **3** were quantitatively hydrolyzed to obtain respective chlorins, equipped with free carboxylic acid moiety (**2-COOH** and **3-COOH**, structures not shown). The crude chlorin acids were reacted with **BDP-NH₂** in the presence of EDC hydrochloride and DMAP in DMF, to provide **3-BDP** and **4-BDP** in 53% and 25% yield, respectively. Zn(II) chelates (**Zn2-(BDP)₂**, **Zn4-BDP**, and **Zn2**) were obtained in reaction of corresponding free bases with Zn(OAc)₂ in CHCl₃/MeOH (5:1) mixture, in 50%, 57%, and 71% yield, respectively.

Benchmark monomer **BDP-NHBz** was obtained by reaction of **BDP-NH₂** with benzoic acid, under analogous conditions as for **3-BDP** and **4-BDP**, to provide the desired product in 80% yield (Scheme 6).

Characterization

Target arrays were characterized by ¹H, ¹³C, and ¹⁹F NMR, LD-MS and high resolution MS. Triad **2-(BDP)₂** shows a low solubility in common organic solvents, which prevents recording of a good quality ¹³C NMR and ¹⁹F NMR spectra. The NMR spectra for all arrays are consistent with expected structures. In particular, ¹H NMR spectra for dyads **1-BDP**, **3-BDP**, and **4-BDP** show resonances of protons from both chlorin macrocycle and BODIPY unit, with integration indicating 1 to 1 ratio of chlorin to BODIPY. ¹H NMR spectrum of **2-(BDP)₂** shows resonances from two, slightly non-equivalent BODIPY units.

Zinc complexation of **2** and **2-(BDP)₂** causes an extensive aggregation of resulting **Zn2** and **Zn2-(BDP)₂**, which results in a low solubility of both complexes in common solvents, and makes the NMR characterization of these chelates problematic. We were able to obtain the ¹H NMR spectrum only for a crude sample of **Zn2-(BDP)₂**. After chromatographic purification and washing with MeOH and hexanes, the sample became insoluble, and no ¹H NMR spectra could be recorded. Nevertheless, the ¹H NMR spectrum of crude **Zn2-(BDP)₂** showed a single chlorin, with chlorin and BODIPY resonances as expected, and HRMS shows *m/z* consistent with expected structures.

Absorption and emission properties

Absorption and emission properties of BODIPY-chlorin arrays as well as benchmark monomers are listed in Table 1, and spectra of arrays are presented in Figures 1 and 2 (absorption and emission spectra of monomers are presented in Figures S1 and S2, Supporting Information). Absorption spectra for chlorin derivatives are consistent with the one reported in the literature for analogous chlorins.^{4,16} Chlorin monomers **1–3** and **Zn2** exhibit strong *B* bands in the range of 403–430 nm, *Q_x* bands in the range of 499–514 nm, and *Q_y* bands progressively shifted with number of substituents at 3,13-positions: 636 nm (**3**), 656 nm (**1**), and 675 nm (**2**). For **Zn2** absorption maximum of the *Q_y* band is shifted 24 nm, compared to the corresponding free base.

Absorption spectra for arrays are essentially the sum of absorption spectra of their components (Figure 1, Table 1). For dyads **3-BDP**, **4-BDP**, and **Zn4-BDP** the absorption

maxima are identical to corresponding benchmark monomers **3**, **2**, and **Zn2**, respectively, while for **1-BDP**, **2-(BDP)₂**, and **Zn2-(BDP)₂** absorption bands for chlorin components are slightly shifted bathochromically by 1–7 nm compared to monomers **1**, **2**, and **Zn2**, respectively.

Emission spectra of chlorin benchmarks contain a narrow band, with relatively small Stokes shifts (1–6 nm). **BDP-TMS** and **BDP-NHBz** show a strong emission band at 517 nm and 516 nm, respectively. Emission spectra of all BODIPY-chlorin arrays are dominated by emission of the chlorin component. The maxima of chlorin emission in dyads **1-BDP**, **2-(BDP)₂**, and **Zn2-(BDP)₂** are shifted bathochromically by 2–5 nm, compared to benchmark monomers, while emission maxima for **3-BDP**, **4-BDP**, and **Zn4-BDP** appears exactly at the same wavelengths as for corresponding monomers. For each array significant quenching of BODIPY fluorescence and almost exclusive emission from chlorin components are observed, even when BODIPY is directly excited at the wavelength where chlorins show a negligible absorbance (Figure 2). Excitation spectra, monitored at the wavelengths where chlorin components emit exclusively (not shown) closely resemble the corresponding absorption spectra. These indicate an efficient excitation energy transfer from BODIPY to chlorin chromophore.

In order to quantitatively assess the energy transfer efficiency and presence of putative quenching processes in dyads we determined the quantum yields of fluorescence of chlorin components for dyads and benchmark monomers in toluene and DMF (Table 1). We determined the relevant quantum yields in polar solvent to evaluate the possible quenching of chlorin fluorescence via PET, which is facilitated in polar solvents.

The fluorescence quantum yields in toluene for chlorin monomers increases with the number of conjugated substituents at the 3,13-positions: 0.21 for **3** (no substituents), 0.33 for **1** (one substituent), and 0.37 for **2**, (two substituents). Quantum yield of emission for **Zn2** in toluene is 0.33. These data are consistent with those reported for analogous chlorin derivatives.^{3,16} Quantum yields of fluorescence for monomers only slightly depend on solvent polarity, and values are nearly identical in DMF as in toluene (Table 1). Only for **Zn2** we observed increase in DMF (1.12-fold vs. toluene). This increase we attributed to coordination of DMF to zinc, since such coordination has been reported to increase the fluorescence quantum yields for porphyrins.³⁷

Quantum yields of fluorescence of chlorin components in dyads were determined by direct excitation of a given chlorin at the maxima of the *B* bands (410–430 nm), where the BODIPY component has a negligible absorbance. In non-polar solvent (toluene) quantum yields for dyads are comparable (**3-BDP** and **4-BDP**), or even slightly higher (**1-BDP** and **2-BDP**) than for the corresponding benchmark monomers (Table 1). This indicates, that in non-polar solvents, the presence of BODIPY unit does not quench the emission from chlorin.

In highly polar DMF, fluorescence of **1-BDP** is 0.71-fold of that in toluene, while for **2-BDP** is 0.93-fold. Fluorescence quantum yields for **3-BDP** and **4-BDP** in DMF are nearly the same as in toluene.

Fluorescence quantum yield for zinc complex **Zn2-(BDP)₂** in toluene ($\Phi_f = 0.37$), is markedly higher than for the corresponding chlorin benchmark **Zn2** ($\Phi_f = 0.33$). However, fluorescence is reduced ~30 times ($\Phi_f = 0.011$) in DMF. On the contrary, fluorescence quantum yields for **Zn4-BDP** in both toluene and DMF are nearly identical.

The efficiency of energy transfer (ETE)³⁸ for BODIPY-chlorin arrays has been determined by comparison of fluorescence quantum yields of chlorin acceptor upon excitation at the donor absorption maxima (504 nm, where chlorin absorbs much less than BODIPY), with fluorescence quantum yield obtained upon direct chlorin excitation at the maximum of the *B* band (Table 1). The ETE is relatively high (>0.90) in toluene, and is rather independent on solvent polarity for **1-BDP** and **2-(BDP)₂**. For amide-linked **3-BDP** and **4-BDP** ETE in DMF is slightly lower than in toluene, however, still exceeds 0.85. ETE for **Zn4-BDP** (0.87 and 0.80 in toluene and DMF respectively), is noticeably lower than for the corresponding free base, this also appears to be true for **Zn2-(BDP)₂** (0.87 in toluene, ETE for **Zn2-BDP** in DMF cannot be determined accurately, due to the low fluorescence intensity for excitations at both BODIPY and *B* bands maxima).

The efficient energy transfer between BODIPY and chlorin is likely driven by the overlap of BODIPY emission band with *Q_x* band of chlorin. The lower ETE for dyads containing chlorin zinc complexes can be explained by the lower oscillator strength of the *Q_x* band for zinc chlorin complexes, compared with free bases,^{4,11} which results in lower spectral overlap. Despite the high and comparable ETE, both classes of arrays reported here exhibit a different behavior in polar solvent. The fluorescence quantum yields for amide-linked dyads are nearly the same in toluene and DMF. However, for arrays where BODIPY is attached through phenylacetylene linker at the 3- and 3,13-positions, quantum yields depend on the solvent, and fluorescence is diminished in DMF, compared to toluene. While reduction of fluorescence in case of **2-(BDP)₂** (0.93-fold in DMF, compared to toluene) is comparable with these observed for amide-linker dyads, more pronounced reduction in intensity is observed for **1-BDP**, (0.71-fold intensity in DMF of that in toluene), and almost complete quenching (~30 times) for **Zn2-(BDP)₂**. The observed reduction of fluorescence in polar DMF is most likely due to photoinduced electron transfer (PET) from excited chlorin to BODIPY. Such PET would be more favorable in polar solvents, due to the stabilization of resulting ion-radical pair. The much more extensive quenching of fluorescence observed for **Zn2-(BDP)₂** can be explained by the lower oxidation potential for zinc complexes of chlorins, compared to the corresponding free bases,¹⁸ hence chlorin moiety in **Zn2-(BDP)₂** is likely more prone to oxidation than in **2-(BDP)₂**. Similarly, it has been reported, that installation of (phenyl)ethynyl substituents at the 3,13-positions of chlorin leads to the increase of the oxidation potential of chlorin,^{4,18} thus this explains the lower fluorescence for **1-BDP** vs. **2-(BDP)₂** in DMF.

The important observation is that fluorescence quantum yields for amide-linked dyads are nearly identical in DMF and toluene. Particularly striking is the difference between **Zn2-(BDP)₂** and **Zn4-BDP**, where chlorin macrocycles should possess comparable redox properties. The nearly-complete quenching of fluorescence for **Zn2-(BDP)₂** in DMF, and no quenching for **Zn4-BDP** indicate that the type of linker connecting the chlorin and BODIPY and perhaps position of BODIPY attachment play a critical role in photochemical properties

of resulting arrays. A possible reason for observed differences might be the stronger electronic coupling between chlorin and BODIPY in phenylethynyl-linked dyads **1-BDP** and **(Zn)2-(BDP)₂**, which facilitates electron transfer from photoexcited chlorin to BODIPY. It is known that phenylethynyl-type linkers provide strong electronic coupling between dyads' components and promote ultrafast PET.³⁹ Electronic communication between BODIPY and chlorin can be inferred from absorption and emission spectra of **1-BDP** and **(Zn)2-(BDP)₂**, which show slight bathochromic shift of both absorption Q_y and emission bands, and increased fluorescence quantum yields (in toluene) of chlorin components, compared to the benchmark monomers (see Table 1). For **3-BDP** and **4-BDP** both absorption and emission maxima and fluorescence quantum yields are identical to the corresponding benchmark monomers, which suggest that there is a negligible conjugation between chlorin and BODIPY, which in turn may lead to an attenuation of photoinduced electron transfer. However, further systematic time-resolved spectroscopic and electrochemical measurements are necessary to elucidate the exact mechanism of quenching of fluorescence for chlorin components in arrays.

In order to further evaluate the applicability of amide-linked BODIPY-chlorin dyads for bioimaging, we compared the quantum yields of fluorescence for chlorin component in arrays upon excitation at the maximum of the BODIPY absorption, in various solvents (toluene, MeOH, DMSO, DMF, Table S1, Supporting Information). The data show, that the dyads **3-BDP**, **4-BDP**, and **Zn4-BDP** retain relatively high fluorescence quantum yields in solvents of different polarities. Fluorescence for these arrays is comparable in toluene, DMF and DMSO, and modestly reduced in MeOH (on average fluorescence quantum yields in MeOH are 0.71-fold of that in toluene). Finally, we compared the fluorescence intensity for dyads vs. monomers upon excitation at ~ 500 nm, at the same concentration. We observed 5.2-fold and 4.7-fold increase for **3-BDP** and 5.5-fold and 5.2-fold for **4-BDP** in toluene and DMF, respectively.

Conclusion and Outlook

We identified molecular architecture for BODIPY-chlorin arrays with bright fluorescence of chlorin upon excitation at ~500 nm in various solvents of different polarity. While all examined arrays exhibit an efficient energy transfer from BODIPY to chlorin moiety, the dyads where BODIPY is attached at 13- or 3,13-positions of chlorin exhibit diminished fluorescence in polar solvent, compared to that observed for toluene. The reduction of fluorescence is the most pronounced in the case of dyad comprising a Zn(II) complex of chlorin. On the contrary, dyads where BODIPY is attached through an amide bond at the 10-position of chlorin exhibit relatively high fluorescence quantum yield in various solvents of different polarities, for all three dyads examined. Therefore, the construct, represented by dyads **3-BDP** and **(Zn)4-BDP** constitutes an attractive platform for development of deep red or near-IR fluorophores excitable with green (and near-IR) light. In that architecture the wavelength of chlorin emission can be tuned by placing different substituents at 3,13-positions of chlorin, or by insertion of Zn(II) into the chlorin macrocycle. Obviously, application of reported dyads in fluorescence imaging requires modification of their structure to provide water solubility, installation of bioconjugatable group, etc. These are the subjects of ongoing research in our laboratory.

Experimental Section

General experimental section

^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were collected at room temperature in CDCl_3 , unless noted otherwise. Chemical shifts (δ) were calibrated using solvent peaks (^1H signals: residual proton signals: 7.26 ppm for chloroform, 2.50 ppm for DMSO; ^{13}C signals: 77.0 ppm for CDCl_3 , 39.5 ppm for DMSO- d_6). All solvents and commercially available reagents were used as received. Palladium coupling reactions was performed using commercially available anhydrous solvents (toluene and DMF). Low-resolution LD-MS analyses were performed without matrix. The FT-ICR analyzer was used for ESI and MALDI HRMS.

Known compounds: **1-Br**,²⁰ **5**,²⁰ **7**,⁴⁰ **BDP-NH₂**,³⁶ and **7-Br**⁴¹ were prepared following reported procedures. Known compound **6-Br₂**,²⁰ was prepared by a slightly modified procedure.

3,13-Dibromo-18,18-dimethyl-10-(4-methoxycarbonylphenyl)chlorin (**2-Br₂**)

Following a reported procedure,^{32,33} a solution of **5** (610 mg, 2.00 mmol) in THF (20 mL) and treated with NBS (696 mg, 4.00 mmol) under nitrogen at -78°C . The resulting reaction mixture was stirred for 1 h at -78°C . The cooling bath was removed, the reaction mixture was warmed up to -20°C , and hexanes/water mixture (~ 10 mL, 1:1) was added. Organic layer was separated, dried (Na_2SO_4) and concentrated. Column chromatography (silica [hexanes/dichloromethane/ethyl acetate, 7:3:2]) provided a white/pale yellow solid (0.62 g, 67%). The resulting **6-Br₂** was immediately used in the next step without further characterization.

Following a reported procedure,^{32,33} a mixture of **6-Br₂** (0.516 g, 1.14 mmol) and **7-Br₄₀** (0.315 g, 1.14 mmol) in CH_2Cl_2 (30 mL) was treated with solution of *p*-toluenesulfonic acid (1.26 g, 6.65 mmol) in MeOH (10 mL). The resulting mixture was stirred at room temperature for 30 min. A sample of TMP (6.65 mL, 38.6 mmol) was added to the reaction flask, and resulting mixture was concentrated. The resulting orange-red solid was suspended in acetonitrile (100 mL) and treated with $\text{Zn}(\text{AOc})_2$ (3.66 g, 20.0 mmol) AgOTf (1.0 g, 4.0 mmol) and (TMP (6.78 mL, 39.9 mmol)). The resulting mixture was refluxed overnight and then concentrated. Crude zinc complex of chlorin was filtered through silica (CH_2Cl_2) and all green fractions containing chlorin were collected and concentrated. Resulting solid was dissolved in dichloromethane (10 mL), treated with TFA (1.00 mL), and stirred for 4 hours. Saturated aqueous NaHCO_3 was added, and stirred for 5 minutes. Organic layer was separated, washed (water and brine), dried (Na_2SO_4), and concentrated, to give red-brown solid. Column chromatography (silica, hexane/ CH_2Cl_2 (1:1)) provided a dark-green solid (125 mg, 17%). ^1H NMR δ -2.17 (s, 1H), -1.78 (s, 1H), 2.04 (s, 6H), 4.13 (s, 3H), 4.63 (s, 2H), 8.18 (d, $J = 8.0$ Hz, 2H), 8.43 (d, $J = 8.0$ Hz, 2H), 8.50 (d, $J = 4.0$ Hz, 1H), 8.76 (s, 1H), 8.78 (s, 1H), 8.94 (d, $J = 4.0$ Hz, 1H), 8.96 (s, 1H), 9.15 (s, 1H), 9.85 (s, 1H); ^{13}C NMR δ 31.2, 46.5, 52.1, 52.6, 94.8, 95.7, 105.9, 113.8, 118.8, 120.2, 124.7, 128.3, 128.7, 129.9, 132.2, 132.4, 133.3, 134.0, 134.1, 137.2, 140.2, 145.9, 151.2, 152.4, 163.7, 167.4, 176.0; MS m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{25}\text{N}_4\text{O}_2\text{Br}_2$ 631.0339; Found (HRMS-ESI) 631.03117.

9-Bromo-1-formyl-5-(4-methoxycarbonylphenyl)dipyrromethane (6-Br)

Following a reported procedure,³² a solution of 1-formyl-5-(4-methoxycarbonylphenyl)dipyrromethane **5**₂₀ (1.08 g, 3.51 mmol) in THF (60 mL) was treated with NBS (0.640 g, 3.60 mmol) at -78 °C. After 40 minutes the cooling bath was removed, and a mixture of hexane and water (1:1, 10 mL) was added. The resulting mixture was diluted with ethyl acetate, washed with brine and dried (Na₂SO₄) and concentrated. Column chromatography [hexane/ethyl acetate (2:1)] provides the desired product as a white powder (1.27 g, 94%): ¹H NMR (DMSO-*d*₆) δ 3.83 (s, 3 H), 5.54 (s, 1H), 5.67 (app t, *J* = 3.0 Hz, 1H), 6.01-5.93 (m, 2H), 6.91 (app t, *J* = 3.0 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 9.39 (s, 1H), 11.46 (br, 1H), 12.09 (br, 1H). The product was used immediately in the next step without further characterization.

10-(4-Methoxycarbonylphenyl)-18,18-dimethylchlorin (3)

Following a reported procedure,³² a suspension of 3,4,5,6-tetrahydro-1,3,3-trimethyldipyrin **7**⁴⁰ (0.620 g, 3.26 mmol) and **6-Br** (1.27 g, 3.28 mmol) in dichloromethane (80 mL) was treated with a solution of *p*-toluenesulfonic acid (3.04 g, 16.0 mmol) in methanol (20 mL) and stirred at room temperature for 40 minutes. The resulting mixture was treated with 2,2,6,6-tetramethylpiperidine (6.60 mL, 38.9 mmol). The reaction mixture was concentrated, and resulting brown solid was suspended in acetonitrile (300 mL) and treated with zinc acetate (8.78 g, 48.0 mmol), 2,2,6,6-tetramethylpiperidine (13.5 mL, 79.5 mmol) and silver trifluoromethanesulfonate (2.50 g, 9.73 mmol). The resulting suspension was refluxed for 17 hours. The reaction mixture was cooled down, concentrated and the residue was purified by column chromatography [silica, hexane/dichloromethane (1:2)]. The resulting green solid (crude zinc chlorin) was treated with a solution of TFA (5.80 mL, 75.3 mmol) in CH₂Cl₂ (70 mL). The resulting mixture was stirred for 3 hours, then washed (saturated aqueous NaHCO₃ and brine), dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexane/CH₂Cl₂ (1:2)] provides a green solid (0.422 g, 25%): ¹H NMR δ -2.34 (s, 1H), -1.96 (s, 1H), 2.07 (s, 6H), 4.13 (s, 3H), 4.64 (s, 2H), 8.27 (d, *J* = 8.3 Hz, 2H), 8.45 (d, *J* = 8.3 Hz, 2H), 8.62 (d, *J* = 4.3 Hz, 1H), 8.78 (d, *J* = 4.9 Hz, 1H), 8.85 (d, *J* = 4.3 Hz, 1H), 8.96 (s, 1H), 8.98 (d, *J* = 4.9 Hz, 1H), 9.01 (d, *J* = 4.3 Hz, 1H), 9.05 (s, 1H), 9.26 (d, *J* = 4.9 Hz, 1H), 9.89 (s, 1H); ¹³C NMR δ 31.2, 46.4, 52.0, 52.4, 94.5, 97.1, 107.3, 119.9, 123.4, 123.8, 127.8, 128.0, 128.4, 129.4, 131.6, 132.6, 134.1, 134.3, 134.7, 139.4, 140.9, 146.6, 150.9, 151.8, 163.0, 167.4, 175.4; HRMS (ESI) *m/z* [M+H]⁺ Calcd for C₃₀H₂₆N₄O₂ 475.2129; Found 475.2118.

8-[4-(Trimethylsilyl)ethynylphenyl]-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (BDP-TMS).³⁴

A mixture of 4-[(trimethylsilyl)ethynyl]benzaldehyde (0.404 g, 2.00 mmol) and 2,4-dimethylpyrrole (0.440 g, 4.00 mmol) in anhydrous dichloromethane (100 mL) was treated with trifluoroacetic acid (15 μL, 0.2 mmol) and the reaction mixture was stirred at room temperature for 6 hours, under N₂ to obtain a deep red mixture. A sample of DDQ (0.454 g, 2.00 mmol) was added, and the resulting mixture was stirred for 1h. Samples of NEt₃ (3.40 g, 33.6 mmol), and BF₃·OEt₂ (5.20 g, 36.6 mmol) were then added and the resulting mixture was stirred overnight. The mixture was washed with saturated aqueous NaHCO₃, dried

(Na₂SO₄) and concentrated. A viscous oily liquid is obtained. Column chromatography [silica, hexane/ethylacetate (20:1)] provides an solid, which was washed with hexanes, and dried under vacuum to obtain an orange solid, (196 mg, 23%). ¹H NMR δ 0.28 (s, 9H), 1.40 (s, 6H), 2.56 (6H), 5.98 (s, 2H), 7.25 (d, *J* = 8.2 Hz, 2H, overlap with CHCl₃ peak), 7.61 (d, *J* = 8.2 Hz, 2H); ¹³C NMR δ (100 MHz): 0.01, 14.7, 95.9, 100.0, 104.3, 121.5, 124.0, 128.2, 131.3, 132.8, 135.3, 140.9, 143.1, 155.9; ¹⁹F NMR δ -146.1 (q, *J* = 34.0 Hz); MS *m/z* [M + H]⁺ Calcd for C₂₄H₂₇BF₂N₂Si 421.2082; Found (LD-MS) 421.6, (HRMS-ESI) 421.2094.

8-(4-Ethynylphenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene BDP-H.³⁶

A mixture of **BDP-TMS** (0.558 g, 1.33 mmol) and potassium carbonate (0.201 g, 1.459 mmol) in methanol /THF (1:1, 66 mL) was stirred for one hour after which water is added to the mixture. The compound is extracted thrice with dichloromethane. The organic extracts were concentrated and the remaining solid was dried under high vacuum. The dried compound was chromatographed [silica, hexane: ethyl acetate (15:1)] to obtain an orange solid (0.278 g, 60%). ¹H NMR δ 1.39 (s, 6H), 3.17 (s, 1H), 5.98 (s, 2H), 7.26 (d, *J* = 8.3 Hz, 2H, overlaps with CHCl₃ peak), 7.62 (d, *J* = 8.2 Hz, 2H); ¹³C NMR δ 14.65, 14.69, 78.7, 83.0, 121.5, 123.1, 128.3, 131.2, 133.0, 135.7, 140.7, 143.1, 155.9; MS *m/z* [M+H]⁺ Calcd for C₂₁H₁₉BF₂N₂ 349.1682; Found: (LD-MS) 349.2, (HRMS-ESI) 349.1683.

1-BDP

Following a reported procedure,³⁵ a mixture of **1-Br** (20 mg, 0.036 mmol) and **BDP-H** (15 mg, 0.043 mmol) in DMF/triethylamine (2:1, 6 mL) were degassed by freeze-thaw cycles (two times). A sample of (PPh₃)₂Cl₂ (3.8 mg, 0.0054 mmol) was added under nitrogen. The resulting mixture was degassed using freeze-thaw cycle under nitrogen. The reaction flask was placed in an oil bath preheated to 80 °C. After 2 hours TLC [silica, hexanes/CH₂Cl₂ (1:1)] showed a complete consumption of the starting chlorin. The reaction mixture was diluted with ethyl acetate, washed (water and brine), dried (Na₂CO₃), and concentrated. Column chromatography [silica, hexane/CH₂Cl₂ (1:2)], provide a brown solid (which appears green in solution and on the chromatography column). Yield: 15 mg, 52%. ¹H NMR δ -2.07 (br, 1H), -1.64 (br, 1H), 1.55 (s, 6H), 2.08 (s, 6H), 2.60 (s, 6H), 4.11 (s, 3H), 4.71 (s, 2H), 6.04 (s, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 8.24 (d, *J* = 8.7 Hz, 2H), 8.43 (d, *J* = 8.2 Hz, 2H), 8.58 (d, *J* = 4.1 Hz, 1H), 8.91 – 8.97 (m, 4H), 9.23 (d, *J* = 4.6 Hz, 1H), 9.37 (s, 1H), 9.80 (s, 1H); ¹³C NMR δ 14.3, 14.9, 31.2, 46.8, 52.1, 52.6, 86.0, 95.0, 95.5, 96.0, 107.3, 116.7, 124.4, 124.5, 128.3, 128.6, 129.2, 129.5, 129.8, 131.4, 132.5, 132.6, 133.0, 133.2, 134.2, 135.42, 135.44, 139.6, 141.9, 143.2, 146.3, 152.1, 152.2, 156.0, 163.6, 167.4, 176.7; ¹⁹F NMR δ -146.1 (q, *J* = 30.9 Hz); MS *m/z* [M+H]⁺ Calcd for C₅₁H₄₃BF₂N₆O₂ 821.3589; Found (LD-MS) 821.8, (HRMS-ESI) 821.3597.

2-BDP

Following a reported procedure,³⁵ a mixture of **2-Br₂** (10 mg, 0.016 mmol), **BDP-H** (14 mg, 0.040 mmol), in DMF/Et₃N (6 mL, 2:1), was degassed by freeze/thaw (2 cycles). Then a sample of (PPh₃)₂PdCl₂ (1.5 mg, 0.0021 mmol) was added, and the mixture was degassed by one more freeze/thaw cycle. The reaction mixture was placed in pre-heated oil bath, and

stirred at 80 °C for 3h. The resulting mixture was diluted with water, and extracted with ethyl acetate, organic phase was washed (water, brine), dried (Na₂SO₄), and concentrated. Column chromatography (hexanes/dichloromethane 1:1 → 1:10) provided brown solid which was washed with methanol and hexanes (9.1 mg, 47%). ¹H NMR δ -1.88 (br, 1H), -1.45 (br, 1H), 1.55, 1.58 (two singlets overlapped with water signal), 2.09 (s, 6H), 2.60–2.61 (broad, two overlapped singlets, 12H), 4.12 (s, 3H), 4.71 (s, 2H), 6.05, 6.06 (two overlapped singlets, 4H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 8.00 (d, *J* = 7.3 Hz, 2H), 8.12 (d, *J* = 7.3 Hz, 2H), 8.24 (d, *J* = 8.2 Hz, 2H), 8.44 (d, *J* = 8.2 Hz), 8.58 (d, *J* = 4.1 Hz, 1H), 8.87 (s, 1H), 8.89 (s, 1H), 9.02 (d, *J* = 4.1 Hz, 1H), 9.35 (s, 1H), 10.07 (s, 1H); MS *m/z* [M]⁺ Calcd for C₇₂H₆₀B₂F₄N₈O₂ 1167.49995; Found (HRMS-MALDI) 1167.5024.

Zn2-(BDP)₂

A mixture of **2-(BDP)₂** (3.5 mg, 0.0036 mmol) in CHCl₃/MeOH (1 mL, 5:1), was treated with Zn(OAc)₂ (10 mg, 0.055 mmol), and stirred at 50 °C for 1h. The reaction mixture was concentrated (¹H NMR was recorded at this point). The sample was then dissolved in CH₂Cl₂, washed (water and brine), dried (Na₂SO₄), and concentrated. Resulting solid was washed with MeOH and hexanes (with sonication), to provide a green solid (3.6 mg, 97%). Product after washing with water, MeOH and hexanes showed extremely low solubility in common organic solvents (CHCl₃, CH₂Cl₂, THF, DMSO), which prevents recording a ¹H NMR spectrum of pure sample. The ¹H NMR data reported here were taken on the semi-pure sample, before washing with water, MeOH, and hexanes. ¹H NMR δ 1.54 (s, 6H), 1.58 (s, 6H), 2.07 (s, 6H), 2.59 (broad, two overlapped singlets, 12H), 4.10 (s, 3H), 4.62 (s, 2H), 6.04 and 6.05 (two overlapped singlets, 4H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 8.1 Hz, 2H), 8.40 (d, *J* = 8.1 Hz, 2H), 8.50 (d, *J* = 4.2 Hz, 1H), 8.63 (s, 1H), 8.80 (s, 1H), 8.96 (s, 1H), 8.96 (d, *J* = 4.2 Hz, 1H), 9.10 (s, 1H), 9.93 (s, 1H); MS *m/z* [M]⁺ Calcd for C₇₂H₅₈B₂F₄N₈O₂Zn 1228.4113; Found (LD-MS) 1228.3 (HRMS MALDI) 1228.4092.

3-BDP

Following a reported procedure,²⁰ a solution of **3** (118 mg, 0.249 mmol) in THF (4 mL) and methanol (2 mL) was treated with NaOH (1 M aqueous solution, 2 mL) and stirred under nitrogen for 14 hours. The reaction mixture was treated with aqueous HCl solution (1M, 10 mL), and extracted with CH₂Cl₂. Combined organic layers was dried over anhydrous Na₂SO₄ and concentrated to afford an intermediate acid **3-COOH** as a green powder (112 mg, 98%) which was used in next step without further purification: ¹H NMR (DMSO-*d*₆) δ -2.56 (s, 1H), -2.12 (s, 1H), 2.02 (s, 6H), 4.63 (s, 2H), 8.24 (d, *J* = 8.3 Hz, 2H), 8.37 (d, *J* = 8.3 Hz, 2H), 8.49 (d, *J* = 4.3 Hz, 1H), 8.78 (d, *J* = 4.9 Hz, 1H), 9.13-9.06 (m, 2H), 9.28-9.20 (m, 3H), 9.50 (d, *J* = 4.2 Hz, 1H), 10.08 (s, 1H), 13.27 (br, 1H); ¹³C NMR (DMSO-*d*₆) δ 30.8, 46.2, 51.3, 94.8, 97.3, 107.4, 119.4, 124.1, 124.7, 127.7, 128.9, 129.1, 130.2, 131.2, 133.1, 133.8, 134.0, 134.1, 138.9, 140.7, 145.4, 150.3, 151.0, 163.6, 167.6, 175.7; HRMS (ESI) *m/z* [M+H]⁺ Calcd for C₂₉H₂₄N₄O₂ 461.1972; Found 461.1972.

A solution of **BDP-NH₂**³⁶ (14.7 mg, 0.0434 mmol) in DMF (5 mL) was treated with crude **3-COOH** (20.0 mg, 0.0434 mmol), EDC hydrochloride (83.0 mg 0.434 mmol) and DMAP (5.3 mg, 0.043 mmol) and was stirred at room temperature overnight. The resulting mixture

was diluted with ethyl acetate (20 mL), the organic layer was then washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography [silica, hexane/ CH_2Cl_2 (1:2)] provided a brown-green solid; 18.0 mg, 53%. ^1H NMR δ -2.37 (bs, 1H), -1.98 (bs, 1H), 1.54 (s, 6H), 2.09 (s, 6H), 2.59 (s, 6H), 4.68 (s, 2H), 6.03 (s, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4, 2H), 8.25 (s, 1H), 8.28 (d, J = 8.2 Hz, 2H), 8.33 (d, J = 8.2 Hz, 2H), 8.61 (d, J = 4.3 Hz, 1H), 8.79 (d, J = 4.7 Hz, 1H), 8.89 (d, J = 4.7 Hz, 1H), 9.00 (d, J = 4.3 Hz, 1H), 8.97 (s, 1H), 9.02 (d, J = 4.4 Hz, 1H), 9.10 (s, 1H), 9.29 (d, J = 4.3, 1H), 9.91 (s, 1H); ^{13}C NMR δ 14.6, 14.8, 31.2, 46.5, 52.0, 94.6, 97.2, 107.4, 119.5, 120.4, 121.3, 123.5, 123.9, 125.5, 127.7, 128.5, 129.0, 131.0, 131.5, 131.6, 132.7, 133.8, 134.3, 134.5, 134.7, 138.9, 139.4, 141.0, 141.2, 143.1, 146.0, 150.9, 151.8, 155.6, 163.2, 165.9, 175.5; ^{19}F NMR δ -146.1 (q, J = 33.4 Hz); HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{48}\text{H}_{42}\text{BF}_2\text{N}_7\text{O}$ 782.359; Found 782.3574.

4-BDP

Following a reported procedure,²⁰ a sample of **2** (0.0417 g, 0.0617 mmol) was dissolved in THF (4 mL) and methanol (3 mL), and treated with aqueous NaOH (3 mL, 1.0 M). After 20 hours TLC (dichloromethane) showed consumption of all starting material and a single, more polar, red fluorescent spot. The reaction mixture was diluted with dichloromethane (15 mL), quenched with HCl (~3 mL, 1M), washed with water and brine, dried (Na_2SO_4), and concentrated. ^1H NMR clearly indicated the loss of the methoxy group. The yield of hydrolysis was assumed to be quantitative, and resulting acid **2-COOH** was used in the next step without further purification. ^1H NMR δ 2.08 (s, 3H), 4.69 (s, 2H), 7.49–7.59 (m, 8H), 7.88–7.90 (m, 2H), 7.98–8.00 (m, 2H), 8.29 (d, J = 8.2 Hz, 2H), 8.53 (d, J = 8.2 Hz, 2H), 8.58 (d, J = 4.4 Hz, 1H), 8.86 (s, 1H), 8.88 (s, 1H), 9.02 (d, J = 4.4 Hz, 1H), 9.05 (s, 1H), 9.35 (s, 1H), 10.07 (s, 1H).

Following a reported procedure,²⁰ a solution of **BDP-NH₂**³⁶ (18.0 mg, 0.0530 mmol) in DMF (7 mL) was treated with **2-COOH** (35.0 mg, 0.0530 mmol), EDC hydrochloride (101 mg, 0.530 mmol) and DMAP (6.5 mg, 0.053 mmol) and was stirred at room temperature overnight. The resulting mixture was diluted with ethyl acetate (20 mL), the organic layer was then washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography [silica, hexane/ CH_2Cl_2 (1:2)] yielded of mixture of product and a green-fluorescent impurity. The resulting sample was dissolved in CH_2Cl_2 , mixed with silica (~2g), and concentrated. The resulting powder was loaded on the top of silica column, and eluted with MeOH (the green-fluorescent impurity was eluted, whereas insoluble **4-BDP** stayed on the top of the column). Elution with MeOH was continued until green-fluorescent impurity was completely eluted. The **4-BDP** was then eluted with CH_2Cl_2 . The resulting sample was washed with MeOH and hexanes to afford a brown solid. 13.1 mg, 25%. ^1H NMR δ -1.92 (bs 1H) -1.50 (bs, 1H), 1.55 (s, 6H), 2.08 (s, 6H), 2.59 (s, 6H), 4.69 (s, 2H), 6.03 (s, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.59-7.48 (m, 7H), 7.42-7.38 (m, 2H), 8.00-7.95 (m, 3H), 8.2 (s, 1H) 8.33-8.27 (m, 4H), 8.58 (d, J = 4.3 Hz, 1H), 8.86 (s, 1H), 8.87 (s, 1H), 9.02 (d, J = 4.4 Hz, 1H), 9.05 (s, 1H), 9.34 (s, 1H), 10.07 (s, 1H); ^{13}C NMR δ 14.6, 14.7, 31.1, 46.4, 52.1, 84.0, 84.1, 95.2, 95.8, 97.1, 98.1, 105.4, 118.2, 120.0, 120.4, 121.3, 122.9, 123.2, 123.3, 125.2, 125.7, 128.6, 128.7, 128.8, 128.9, 129.0, 129.4, 131.0, 131.6, 131.8, 132.0, 132.1, 133.4, 134.0, 134.1, 134.5, 135.4, 138.9, 140.0, 140.1, 141.2, 143.1, 145.3, 151.8,

152.6, 155.6, 164.1, 165.8, 176.1; ^{19}F NMR δ -146.1 (q, J = 33.1 Hz); HRMS (ESI) m/z [$\text{M} + \text{H}$] $^{+}$ Calcd for $\text{C}_{64}\text{H}_{50}\text{BF}_2\text{N}_7\text{O}$ 982.4221; Found 982.4193.

Zn4-BDP

A sample of **4-BDP** (4.7 mg, 0.048 mmol) was dissolved in chloroform (2.5 mL) and methanol (0.5 mL), and treated with zinc acetate (1.9 mg, 0.010 mmol). After 6 hours TLC indicated that all starting material had been consumed. The reaction mixture was then quenched with saturated aqueous NaHCO_3 , washed with water and brine, dried (Na_2SO_4) and concentrated. Column chromatography [silica, CH_2Cl_2] provided a green solid that became brown after extensive drying 3.0 mg, 57%. ^1H NMR δ 1.53 (s, 6H, overlapped with water signal), 2.06 (s, 6H), 2.59 (s, 6H), 4.59 (s, 2H), 6.03 (s, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.55-7.40 (m, 6H), 7.81 (d, J = 7.0 Hz, 2H), 7.85 (d, J = 7.7 Hz, 2H), 7.92 (d, J = 6.8 Hz, 2H), 8.10 (d, J = 7.5 Hz, 2H), 8.24-8.15 (m, 3H), 8.47 (d, J = 4.2 Hz, 1H), 8.60 (s, 1H), 8.77 (s, 1H), 8.91 (s, 1H), 8.92 (d, J = 4.0 Hz, 1H), 9.07 (s, 1H), 9.87 (s, 1H); MS m/z [$\text{M} + \text{H}$] $^{+}$ Calcd for $\text{C}_{64}\text{H}_{48}\text{BF}_2\text{N}_7\text{OZn}$ 1043.32777; Found (LD-MS) 1042.9 (HRMS-MALDI) 1043.3265.

18,18-Dimethyl-10-(4-methoxycarbonylphenyl)-13-phenylethynylchlorin (1)

Following a reported procedure,³⁵ a solution of **1-Br**²⁰ (15.2 mg, 0.0275 mmol), in DMF/ Et_3N (6 mL, 2:1) was degassed by freeze/thaw (2 cycles), and a sample of $(\text{PPh}_3)_2\text{PdCl}_2$ (3 mg, 0.004 mmol), and mixture was degassed by one more freeze/thaw cycle. A sample of phenylacetylene (5.6 μL , 0.052 mmol), and the resulting mixture was stirred at 80 $^\circ\text{C}$ for 3h. A reaction mixture was diluted with water and extracted with ethyl acetate. Organic phase was washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography (hexanes/dichloromethane, 1:2) provided a green solid; 13 mg, 84%: ^1H NMR δ -2.11 (br, 1H), -1.72 (br, 1H), 2.08 (s, 6H), 4.12 (s, 3H), 4.70 (s, 2H), 7.45-7.54 (m, 3H), 7.87-7.89 (m, 2H), 8.24 (d, J = 8.2 Hz, 2H), 8.43 (d, J = 8.2 Hz, 2H), 8.58 (d, J = 4.3 Hz, 1H), 8.88 (s, 1H), 8.91 (s, 1H), 8.94 (d, J = 4.4 Hz, 1H), 8.96 (d, J = 4.3 Hz, 1H), 9.22 (d, J = 4.4 Hz, 1H), 9.38 (s, 1H), 9.81 (s, 1H); ^{13}C NMR δ 31.2, 46.8, 52.2, 52.6, 95.0, 95.6, 96.8, 107.3, 117.5, 120.6, 123.6, 124.2, 128.3, 128.76, 128.81, 129.0, 129.3, 129.7, 132.0, 132.3, 132.9, 133.3, 134.2, 135.2, 139.7, 141.7, 146.3, 151.9, 152.1, 163.7, 167.5, 176.4; HRMS (MALDI) m/z [$\text{M} + \text{H}$] $^{+}$ Calcd for $\text{C}_{38}\text{H}_{30}\text{N}_4\text{O}_2$ 575.2442; Found 575.2451.

18,18-Dimethyl-10-(4-methoxycarbonylphenyl)-3,13-diphenylethynylchlorin (2)

Following a reported procedure,³⁵ a mixture of **2-Br**₂ (20 mg, 0.030 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (2.1 mg, 0.0030 mmol, 10 mol%) in DMF/ NEt_3 (9 mL, 2:1) was placed in a Schlenk flask. The mixture was deoxygenated by freeze-pump-thaw cycles (3 times), and a sample of phenylacetylene (0.013 mL, 0.012 mmol) was added to the reaction flask. Reaction mixture was stirred for 4 hours at 80 $^\circ\text{C}$. The resulting mixture was washed (water and brine), dried (Na_2SO_4), and concentrated to obtain a dark brown solid. Column chromatography [silica, hexane/ethyl acetate (5:1)] provided a brown solid (12 mg, 60%). ^1H NMR δ -1.93 (s, 1H), -1.50 (s, 1H), 2.07 (s, 6H), 4.11 (s, 3H), 4.68 (s, 2H), 7.52(m, 6H), 7.87 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 8.24 (d, J = 12 Hz, 2H), 8.43

(d, $J = 8$ Hz, 2H), 8.55 (d, $J = 4$ Hz, 1H), 8.85 (s, 2H, 2 signal overlap), 9.00 (d, $J = 4$ Hz, 1H), 9.04 (s, 1H), 9.33 (s, 1H); ^{13}C NMR δ 31.3, 46.6, 52.3, 52.6, 84.2, 84.4, 95.3, 95.9, 97.2, 98.2, 105.6, 118.3, 120.6, 123.0, 123.4, 123.4, 125.3, 128.4, 128.8, 128.9, 129.0, 129.2, 129.7, 129.8, 132.0, 132.2, 132.5, 133.6, 134.2, 134.3, 135.6, 140.2, 146.2, 152.0, 152.9, 164.2, 167.5, 176.2; MS m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{46}\text{H}_{35}\text{N}_4\text{O}_2$ 675.2754; Found (HRMS-ESI) 675.2780, (MALDI-MS) 674.7.

18,18-Dimethyl-10-(4-methoxycarbonylphenyl)-3,13-diphenylethynylchlorinato zinc(II) (Zn2)

A solution of **2** (15.0 mg, 0.0222 mmol) in $\text{CHCl}_3/\text{MeOH}$ (6 mL, 5:1) was treated with $\text{Zn}(\text{OAc})_2$ 8.2 mg, 0.045 mmol). The resulting mixture was stirred at 50 °C for 30 min. The reaction mixture was diluted with water, and resulting mixture was extracted with ethyl acetate. Combined organic phases were washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography (silica, hexanes/ CH_2Cl_2 1:3) provides a green solid, which was washed (with sonication) with hexanes and MeOH; 12.1 mg, 71%). ^1H NMR δ 2.05 (s, 6H), 4.08 (s, 3H), 4.58 (s, 2H), 7.55-7.43 (m, 6H), 7.82 (d, $J = 7.0$ Hz, 2H), 7.94 (d, $J = 7.0$ Hz, 2H), 8.16 (d, $J = 8.0$ Hz, 2H), 8.37 (d, $J = 8.0$, 2H), 8.46 (d, $J = 4.2$ Hz, 1H), 8.57 (s, 1H), 8.74 (s, 1H), 8.88 (s, 1H), 8.90 (d, $J = 4.2$ Hz, 1H), 9.05 (s, 1H), 9.85 (s, 1H); HRMS (MALDI) m/z $[\text{M}]^+$ Calcd for $\text{C}_{46}\text{H}_{32}\text{N}_4\text{O}_2\text{Zn}$ 736.1811; Found 736.1819.

8-(4-Benzyloxyaminophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (BDP-NHBz)

A solution of **BDP-NH₂**³⁶ (0.020 g, 0.059 mmol) in DMF (10 mL) was treated with benzoic acid (0.072 g, 0.590 mmol), EDC hydrochloride (0.0226 g, 0.118 mmol) and DMAP (0.0144 g, 0.118 mmol) and was stirred at room temperature. After 40 hours the resulting mixture was diluted with ethyl acetate (20 mL), the organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2 /hexane/ethyl acetate (20:1:1)] provided a semi-pure compound. Subsequent column chromatography (silica, CH_2Cl_2) provided a bright orange-red solid; 20.8 mg, 80%. ^1H NMR δ 1.46 (s, 6H), 2.56 (s, 6H), 5.99 (s, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.56-7.50 (m, 2H), 7.62-7.57 (m, 1H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.94-7.89 (m, 3H); ^{13}C NMR δ 14.6, 14.7, 120.2, 121.2, 127.0, 128.9, 128.9, 130.9, 131.6, 132.2, 134.6, 138.7, 141.1, 143.1, 155.5, 165.8; ^{19}F NMR δ -146.2 (q, $J = 33.7$ Hz); HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{24}\text{BF}_2\text{N}_3\text{O}$ 444.2058; Found 444.2052.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Absorption spectra of BODIPY-chlorin arrays: **1-BDP** (blue), **2-(BDP)₂** (red), **Zn₂-(BDP)₂** (red, dashed), **3-BDP** (black), **4-BDP** (green), and **Zn₄-BDP** (green, dashed). All spectra were taken in toluene at room temperature and normalized at the maximum of the *B* band of chlorin.

Figure 2.
Normalized emission spectra of BODIPY-chlorin arrays: **1-BDP** (blue), **2-(BDP)₂** (red), **Zn₂-(BDP)₂** (red, dashed), **3-BDP** (black), **4-BDP** (green) and **Zn₄-BDP** (green, dashed). All spectra were taken in toluene at room temperature, with excitation at 475 nm.

Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Compound	R ³	R ¹³	R ¹⁰	M
1-BDP	-H		-OMe	H,H
2-(BDP)₂			-OMe	H,H
Zn2-(BDP)₂			-OMe	Zn

Chart 1.
Structures of BODIPY-chlorin arrays and benchmark monomers discussed in this paper.

Table 1

Absorption and emission properties of BODIPY-chlorin arrays and benchmark monomers.^{a)}

Compound	<i>B</i> [nm]	BODIPY/ <i>Q_x</i> [nm]	<i>Q_y</i> [nm]	λ_{em} [nm]	Φ_{f} (toluene) ^{b)}	Φ_{f} (DMF) ^{b)}	ETE (toluene) ^{c)}	ETE (DMF) ^{c)}
1-BDP	404, 418	504	657	661	0.35	0.25	0.97	0.96
2-(BDP) ₂	431	504, 548	678	683	0.41	0.38	0.96	0.97
3-BDP	406	503	636	641	0.21	0.20	0.90	0.92
4-BDP	428	503, 546	675	681	0.37	0.36	0.92	0.88
Zn2-(BDP) ₂	427	504	658	661	0.37	0.011	0.88	c)
Zn4-BDP	426	503	651	655	0.31	0.32	0.87	0.80
1	402, 417	506	656	659	0.33	0.34	-	-
2	431	514, 546	675	681	0.37	0.36	-	-
3	405	499	636	641	0.21	0.20	-	-
Zn2	425	519	651	656	0.33	0.38	-	-
BDP-TMS	-	504	-	517	-	-	-	-
BDP-NHBz	-	503	-	516	-	-	-	-

^{a)} Fluorescence quantum yields of the chlorin component upon excitation at the maximum of the *B* band. Φ_{f} was determined in air-equilibrated solvents, using tetraphenylporphyrin (TPP) in non-degassed toluene, as a standard ($\Phi_{\text{f}} = 0.070$). ²⁾ The estimated error in Φ_{f} is $\pm 5\%$.

^{b)} Efficiency of energy transfer, defined as a fluorescence quantum yield of chlorin component upon excitation at the maximum of BODIPY absorbance over fluorescence quantum yield of chlorin component upon direct excitation at the maximum of the *B* band.

^{c)} ETE could not be determined accurately due to a low intensity of fluorescence in DMF.