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Symmetrical and Non-symmetrical *meso-meso* Directly-Linked Hydroporphyrin Dyads: Synthesis and Photochemical Properties

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Abstract

A series of a rigid *meso-meso* directly-linked chlorin-chlorin, chlorin-bacteriochlorin, and bacteriochlorin-bacteriochlorin dyads, including free bases as well as Zn(II), Pd(II) and Cu(II) complexes has been synthesized, and their absorption, emission, singlet oxygen ($^1\text{O}_2$) photosensitization, and electronic properties have been examined. Marked bathochromic shift of the long-wavelength Q_y absorption band and increase in fluorescence quantum yields in dyads, compared to the corresponding monomers, are observed. Non-symmetrical dyads (except bacteriochlorin-bacteriochlorin) show two distinctive Q_y bands, corresponding to the absorption of each dyad component. A nearly quantitative S_1 - S_1 energy transfer between hydroporphyrins in dyads, leading to an almost exclusive emission of hydroporphyrin with a lower S_1 energy, have been determined. Several symmetrical and all non-symmetrical dyads exhibit a significant reduction of fluorescence quantum yields in solvents of high dielectric constants; this is attributed to the photoinduced electron transfer. The complexation of one macrocycle by Cu(II) or Pd(II) enhances intersystem crossing in the adjacent, free base dyad component, which is manifested by a significant reduction in fluorescence and increase in quantum yield of $^1\text{O}_2$ photosensitization.

Graphical abstract

Supporting Information Available. Synthesis of compound **1**, additional discussion of the structure of dyads, additional absorption and emission spectra, computational data 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

Arrays of tetrapyrrolic macrocycles directly connected between their *meso* positions represent an interesting class of molecules, since due to orthogonal arrangement of macrocycles there is a little direct π -conjugation between dyad components, however due to their close proximity, there is a substantial through-space electronic interaction between chromophores, which significantly affects electronic, optical, and electrochemical properties of the resulting constructs.^{1–14} *Meso-meso* linked porphyrin,^{1–9} chlorin,^{10–12} bacteriochlorin,¹² and corrole^{13,14} dyads have been reported, and their spectral and electronic properties, as well as energy- and electron transfer processes between array components have been examined. Resulting dyads have been applied, for example, as biomimetic models for photosynthetic light harvesting^{2–4} and electron transfer arrays,⁵ fluorescence imaging agents,⁶ molecular wires,^{1,7} molecules for information storage,⁸ and triplet state photosensitizers.^{9,12}

The vast majority of such arrays reported so far are composed of porphyrins, while arrays of hydroporphyrins have been explored far less.^{10–12} Hydroporphyrins - chlorins and bacteriochlorins, are partially saturated tetrapyrrolic macrocycles that differ substantially from fully unsaturated porphyrins, in terms of electronic, optical, and electrochemical properties.^{15–18} In particular, hydroporphyrins exhibit enhanced absorption in the red (chlorins) or near-IR (bacteriochlorins) spectral window, and they exhibit intense fluorescence in the respective regions.^{16–18} Thus, they are more efficient in photon harvesting in visible and near-IR spectral windows, which is utilized by natural light harvesting antenna.¹⁵ Moreover, due to their near-IR absorption and emission, hydroporphyrins are used for a host of photomedical applications, such as photodynamic therapy and *in vivo* imaging.^{19–22} Hydroporphyrins are easier to oxidize than porphyrins,²³ and are therefore more prone to the oxidative photoinduced electron transfer (PET), which is utilized in natural photosynthetic reaction centers, where hydroporphyrins function as primary electron donors.¹⁵ Thus, it can be expected that hydroporphyrin dyads will exhibit set of properties, distinctive from those observed in analogous porphyrin arrays. For example, we recently reported a series of symmetrical *meso-meso* directly-linked¹² and strongly conjugated^{24,25} hydroporphyrin dyads. For the *meso-meso* directly linked bacteriochlorin dyad, fluorescence quantum yield Φ_f and lifetime τ_f , as well as singlet oxygen 1O_2 quantum yield Φ are all progressively reduced when solvent dielectric constant (ϵ) increases, resulting in nearly complete quenching of fluorescence and 1O_2 photosensitization in solvents of high ϵ .¹² These quenching of photochemical activity in bacteriochlorin dyad is much more extensive than in corresponding chlorin¹² and porphyrin dyads.²⁶ Although details of excited state dynamics for these dyads are still being investigated, these observations indicate that directly linked hydroporphyrin arrays have a complex and rich photochemical properties. This has prompted us to examine the broader set of directly-linked hydroporphyrin arrays, which includes various symmetrical metal complexes, and non-symmetrical arrays i.e. arrays composed of two hydroporphyrins with distinctive electronic, optical, and redox properties. To the best of our knowledge, the only non-symmetrical directly-linked hydroporphyrin dyads have been reported only recently by

Borbas *et al.*¹¹ (non-symmetrical *meso-β* directly linked porphyrin-chlorin dyad were also reported²⁷).

Here, we report the synthesis and characterization of a series of symmetrical and non-symmetrical chlorin-chlorin, chlorin-bacteriochlorin, and bacteriochlorin-bacteriochlorin dyads (Chart 1). Symmetrical dyads include free base chlorin-chlorin **2C**¹² as well as bacteriochlorin-bacteriochlorin **2BC**¹² and **2BC1**, and chlorin-chlorin metal chelates: **2ZnC**, ¹² **2PdC**, **2CuC**, (note, that **2C** and **2BC** have been previously reported, and they are included here for comparison). Non-symmetrical chlorin-chlorin dyads are composed of one free base and one metal [Zn(II), Pd(II), or Cu(II)] complex of the same chlorin (**ZnC-C**, **PdC-C**, and **Cu-C** respectively). Asymmetry here is achieved by metalation of one chlorin component. It is well known that metalation significantly alters spectral, electronic and redox properties of hydroporphyrins.^{28,29} Chlorin-bacteriochlorin dyads include one composed of two-free base macrocycles (**C-BC**) and that composed of a Pd(II) complex of the same chlorin (**PdC-BC**). Finally, bacteriochlorin-bacteriochlorin dyad **BC-BC1** is composed of two bacteriochlorin free-bases with different sets of substituents on the macrocycle perimeter. As benchmarks we included monomers **ZnC**,^{28,30} **PdC**, **H₂C**,^{28,30} **H₂C-Ph**,³¹ **BC**,¹⁸ **BC1**, **BC-Tol**,¹² and **BC1-Tol**.

This set of compounds has enabled us to determine several key aspects of photophysics of directly linked hydroporphyrin dyads. First, we sought to determine how metalation and electronic asymmetry between dyads components affects the basic absorption and emission properties of dyads, and how efficient energy transfer is between dyads' components. Second, we determined to what extent emission properties in dyads are influenced by the solvent dielectric constant, in view of the possible PET between redox non-equivalent hydroporphyrin components. Finally, we intended to determine how heavy element complexation [i.e. Pd(II) or Cu(II)] by one hydroporphyrin in dyad affects fluorescence and singlet oxygen (¹O₂) photosensitization of the adjacent, free base hydroporphyrin. Tetrapyrrolic macrocycles are capable of photosensitizing ¹O₂ (as well as other reactive oxygen species) due to the high quantum yield of intersystem crossing (ISC).³² Complexation of a heavy element, particularly Pd(II) or Pt(II), greatly increases ISC rate and quantum yield, and consequently quantum yield of ROS photosensitization.³² However, insertion of Pd(II) and Pt(II) into chlorins causes substantial hypsochromic shift of the Q_y band, placing it out of the "therapeutic window" and thus rendering them potentially less efficient for deep tissue PDT^{33–35} (note however, that complexation of bacteriochlorins with Pd(II) causes a bathochromic shift of the Q_y band²⁹). In addition, metal complexation alters redox properties of the tetrapyrrolic macrocycles, which affects the efficiency of ROS photosensitization.³⁶ Moreover, for Pd(II) and Pt(II) complexes of hydroporphyrins reduction of the T₁ lifetime (to < 10 μs) is observed,^{29,36} which makes these chelates less useful for applications where long T₁ lifetime (i.e. hundreds of microseconds) is desirable. Alternative strategies to enhance ISC in tetrapyrrolic macrocycles without complexation of heavy element by central nitrogen atoms include T₁-T₁ energy transfer,^{37–43} enhancement of ISC through interaction with an unpaired electron of a metal^{44,45} or stable organic radical,⁴⁶ and the "remote" heavy atom effect.^{47,48} In principle, these strategies allow ISC rate and T₁ lifetime in tetrapyrrolic macrocycles to be tuned without undesirable alteration of optical and

redox properties. We have therefore determined here whether heavy metal complexation of one hydroporphyrin improve $^1\text{O}_2$ photosensitization (as an indirect measure of T_1 formation) of the free base hydroporphyrin in dyads.

Experimental Section

Known compounds **ZnC**,³⁰ **H₂C**,³⁰ **2C**,¹² **2ZnC**,¹² **BC-B**,¹² **BC-Tol**,¹² **2BC**,¹² and **C-Br**,³¹ were synthesized following the reported procedures. Pyrrole **S3**⁴⁹ was previously synthesized, and here it was prepared essentially followed reported procedure. Pyrrole **S4**⁵⁰ was also reported, and here was prepared by a different procedure.

General procedure for palladium catalyzed reactions

Schlenk flask was charged with all reagents and solvent was added. The resulting mixture was degassed by freeze-thaw cycles (two times), and filled with nitrogen. A palladium catalyst was added to the reaction flask, and the mixture was degassed again by freeze-thaw cycles (two times), and filled with nitrogen. Reaction flask was warmed to the room temperature and placed in the pre-heated oil bath (85 °C). TLC, UV-Vis spectroscopy, and LD-MS were used to monitor the progress of the reaction. When consumption of the hydroporphyrin starting material was determined, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. The final purification was done by column chromatography, as specified below.

C-BC—Samples of **BC-B** (19.7 mg, 0.037 mmol), **C-Br** (20.1 mg, 0.037 mmol), Cs_2CO_3 (121.7 mg, 0.37 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (12.8 mg, 0.011 mmol) in toluene/DMF (12 mL, 2:1), were reacted overnight as described in *General procedure*. Column chromatography (silica, hexanes/DCM 1:1) afforded a green brown solid sample; 11.4 mg, 36% ^1H NMR (CDCl_3 , 400 MHz) δ -1.88 (s, 1H), -1.70 (s, 1H), -1.39 (s, 2H), 1.72 (s, 3H), 1.76 (s, 3H), 1.83 (s, 3H), 1.84 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 2.06 (s, 6H), 2.55 (s, 3H), 3.61 (d, J = 17.3 Hz, 1H), 3.64 (d, J = 17.3 Hz, 1H), 3.77 (d, J = 17.3 Hz, 1H), 3.85 (d, J = 17.3 Hz, 1H), 4.53 (s, 2H), 4.58 (s, 3H), 7.20 (s, 2H), 7.74 (dd, J = 1.8, 4.6 Hz, 1H), 7.80 (d, J = 4.8 Hz, 1H), 8.38 (d, J = 4.8 Hz, 1H), 8.55 (d, J = 4.3 Hz, 2H), 8.77–8.80 (m, 3H), 8.96 (s, 1H), 8.98 (d, J = 4.3 Hz, 1H), 9.01 (d, J = 4.6 Hz, 1H), 9.05 (dd, J = 1.9, 4.4 Hz, 1H), 9.29 (d, J = 4.6 Hz, 1H), 9.87 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.5, 21.6, 30.8, 31.3, 31.6, 31.8, 45.4, 46.0, 46.1, 47.8, 52.3, 52.6, 65.5, 94.8, 97.3, 97.9, 106.8, 111.1, 112.6, 118.0, 121.2, 121.3, 122.9, 123.4, 123.8, 127.1, 127.8, 128.2, 131.6, 131.9, 132.8, 134.6, 135.1, 135.4, 136.1, 136.4, 137.6, 138.3, 139.2, 139.3, 141.0, 142.1, 152.0, 152.6, 153.9, 161.9, 165.1, 169.0, 169.2, 175.2; MS ($[\text{M}]^+$, $\text{M} = \text{C}_{56}\text{H}_{56}\text{N}_8\text{O}$): Calcd: 856.4572, Obsd: (HRMS, ESI) 856.4539.

PdC-BC—A solution of **C-BC** (5.0 mg, 5.3 μmol) and $\text{Pd}(\text{OAc})_2$ (7.9 mg, 0.035 mmol) was stirred in chloroform/MeOH (6 ml of 5:1) was stirred at 50 °C, for 5h. The resulting mixture was concentrated. Column chromatography (silica, hexanes/ CH_2Cl_2 2:1) afforded a brown green solid; 2.2 mg, 40%; ^1H NMR (CDCl_3 , 400 MHz) δ -1.96 (s, 1H), -1.49 (s, 1H), 1.73 (s, 3H), 1.77 (s, 3H), 1.79 (s, 6H), 1.90 (s, 6H), 2.03 (s, 3H), 2.04 (s, 3H), 2.50 (s,

3H), 3.60 (d, $J = 17.2$ Hz, 1H), 3.70 (d, $J = 17.3$ Hz, 1H), 3.76 (d, $J = 16.9$ Hz, 1H), 3.86 (d, $J = 16.8$ Hz, 1H), 4.50 (s, 2H), 4.55 (s, 3H), 7.15 (s, 2H), 7.61 (d, $J = 4.8$ Hz, 1H), 7.75 (dd, $J = 1.7, 4.6$ Hz, 1H), 8.14 (d, $J = 4.8$ Hz, 1H), 8.43 (d, $J = 4.6$ Hz, 1H), 8.54 (dd, $J = 1.8, 4.6$ Hz, 1H), 8.71 (s, 1H), 8.75–8.78 (m, 4H), 8.86 (d, $J = 4.6$ Hz, 1H), 9.02 (dd, $J = 2.1, 4.5$ Hz, 1H), 9.73 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.3, 21.5, 22.8, 29.5, 29.9, 30.5, 30.8, 31.3, 31.5, 32.1, 45.1, 45.5, 46.0, 47.8, 50.6, 52.3, 65.5, 95.9, 97.3, 97.3, 97.9, 100.1, 100.9, 111.7, 112.0, 118.0, 121.3, 122.9, 123.3, 123.7, 126.9, 127.0, 127.1, 127.8, 127.9, 130.8, 131.9, 132.1, 135.4, 136.1, 136.3, 137.3, 137.6, 137.8, 137.9, 138.7, 138.9, 139.0, 145.9, 147.1, 151.2, 153.9, 161.6, 161.7, 169.0, 169.3; MS ($[\text{M}]^+$, $\text{M} = \text{C}_{56}\text{H}_{54}\text{N}_8\text{OPd}$): Calcd: 960.3469, Obsd: (HRMS, ESI) 960.3456.

PdC—A solution of **H₂C** (10.0 mg, 0.022 mmol) and $\text{Pd}(\text{OAc})_2$ (14.7 mg, 0.065 mmol) in chloroform/MeOH mixture (10 mL, 5:1) was stirred at room temperature, for 7h. The resulting solution was concentrated. Column chromatography (silica, hexanes/ CH_2Cl_2 2:1) afforded a red solid; 10.9 mg, 89% ^1H NMR (CDCl_3 , 400 MHz) δ 1.84 (s, 6H), 2.02 (s, 6H), 2.60 (s, 3H), 4.58 (s, 2H), 7.23 (s, 2H), 8.40 (d, $J = 4.5$ Hz, 1H), 8.45 (d, $J = 4.7$ Hz, 1H), 8.54 (d, $J = 4.7$ Hz, 1H), 8.68 (s, 1H), 8.71 (d, $J = 4.5$ Hz, 1H), 8.74 (s, 1H), 8.81 (d, $J = 4.5$ Hz, 1H), 8.96 (d, $J = 4.6$ Hz, 1H), 9.67 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.2, 21.6, 31.0, 45.6, 50.2, 95.5, 97.7, 110.0, 122.5, 126.8, 126.9, 127.0, 127.8, 127.9, 131.1, 131.9, 137.1, 137.5, 137.6, 137.7, 138.5, 138.5, 139.0, 144.6, 145.6, 149.9, 161.6; MS ($[\text{M}]^+$, $\text{M} = \text{C}_{31}\text{H}_{28}\text{N}_4\text{Pd}$): Calcd: 562.1355, Obsd: (HRMS, ESI) 562.1354.

PdC-C—A mixture of **2C** (21.9 mg, 0.024 mmol) and $\text{Pd}(\text{OAc})_2$ (5.4 mg, 0.024 mmol) in chloroform/MeOH (20 mL, 5:1) was stirred at 50 °C, for 5h. The resulting mixture was concentrated. Column chromatography (silica, hexanes/ CH_2Cl_2 2:1) afforded a green solid; 7.8 mg, 32% ^1H NMR (CDCl_3 , 400 MHz) δ -1.74 (s, 1H), -1.41 (s, 1H), 1.80 (s, 3H), 1.80 (s, 3H), 1.84 (s, 3H), 1.86 (s, 1H), 1.88 (s, 6H), 1.92 (s, 6H), 2.50 (s, 3H), 2.53 (s, 3H), 3.76–3.92 (m, 4H), 7.14 (s, 1H), 7.16 (s, 1H), 7.18 (s, 1H), 7.19 (s, 1H), 7.62 (d, $J = 4.8$ Hz, 1H), 7.78 (d, $J = 4.8$ Hz, 1H), 8.16 (d, $J = 4.8$ Hz, 1H), 8.38 (d, $J = 4.8$ Hz, 1H), 8.45 (d, $J = 4.6$ Hz, 1H), 8.52 (d, $J = 4.3$ Hz, 1H), 8.72 (s, 1H), 8.76 (d, $J = 4.6$ Hz, 1H), 8.87 (d, $J = 4.6$ Hz, 1H), 8.95 (s, 1H), 8.96 (d, $J = 4.4$ Hz, 1H), 9.00 (d, $J = 4.7$ Hz, 1H), 9.03 (d, $J = 4.6$ Hz, 1H), 9.28 (d, $J = 4.7$ Hz, 1H), 9.74 (s, 1H), 9.85 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.4, 21.5, 21.6, 29.9, 30.5, 31.0, 31.3, 31.7, 45.1, 46.2, 50.9, 52.8, 94.8, 96.0, 106.8, 110.0, 110.9, 112.0, 121.5, 123.8, 123.9, 126.9, 127.1, 127.2, 127.8, 128.0, 128.3, 130.9, 131.7, 132.2, 132.8, 134.5, 135.2, 137.2, 137.6, 137.7, 138.0, 138.2, 138.7, 138.9, 139.0, 139.2, 139.2, 141.1, 141.9, 146.0, 147.2, 151.4, 152.1, 152.6, 161.8, 165.0, 175.3; MS ($[\text{M}+\text{H}]^+$, $\text{M} = \text{C}_{62}\text{H}_{56}\text{N}_8\text{Pd}$): Calcd: 1019.3756, Obsd: (HRMS, ESI) 1019.3762

2PdC—A mixture of **2C** (12.9 mg, 0.014 mmol) and $\text{Pd}(\text{OAc})_2$ (19.0 mg, 0.084 mmol) in chloroform/MeOH (10 mL, 5:1) was stirred at 50 °C for 5h. The resulting mixture was concentrated. Column chromatography (silica, hexanes/ CH_2Cl_2 , 2:1) afforded a green solid; 14.2 mg, 90%; ^1H NMR (CDCl_3 , 500 MHz) δ 1.81 (s, 6H), 1.84 (s, 6H), 1.88 (s, 6H), 1.93 (s, 6H), 2.52 (s, 6H), 3.81 (d, $J = 16.8$ Hz, 2H), 3.92 (d, $J = 16.8$ Hz, 2H), 7.16 (s, 2H), 7.18 (s, 2H), 7.66 (d, $J = 4.8$ Hz, 2H), 8.19 (d, $J = 4.8$ Hz, 2H), 8.44 (d, $J = 4.6$ Hz, 2H), 8.72 (s, 2H), 8.76 (d, $J = 4.6$ Hz, 2H), 8.86 (d, $J = 4.6$ Hz, 2H), 9.01 (d, $J = 4.6$ Hz, 2H), 9.72 (s, 2H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 21.3, 21.4, 21.5, 30.6, 31.2, 45.2, 50.9, 96.0, 109.9, 111.5, 124.0, 126.9, 127.1, 127.2, 127.8, 128.0, 130.8, 132.2, 137.2, 137.6, 137.7, 138.0, 138.7, 138.9, 139.0, 146.0, 147.0, 151.2, 161.8; MS ($[\text{M}+\text{H}]^+$, $\text{M} = \text{C}_{62}\text{H}_{54}\text{N}_8\text{Pd}_2$): Calcd: 1125.2643, Obsd: (HRMS, ESI) 1125.2640.

ZnC-C—A mixture of **2C** (30.0 mg, 0.033 mmol) and $\text{Zn}(\text{OAc})_2$ (6.0 mg, 0.033 mmol) in chloroform/MeOH (30 mL, 5:1) was stirred at 50 °C, for 3h. The resulting solution was concentrated. Column chromatography (silica, hexanes/ CH_2Cl_2 3:2) afforded a green solid; 13.6 mg, 42% ^1H NMR (CDCl_3 , 500 MHz) δ -1.72 (s, 1H), -1.41 (s, 1H), 1.79 (s, 3H), 1.81 (s, 3H), 1.84 (s, 3H), 1.88 (s, 3H), 1.89 (s, 3H), 1.91 (s, 3H), 1.93 (s, 1H), 1.94 (s, 1H), 2.51 (s, 3H), 2.54 (s, 3H), 3.66–3.75 (m, 2H), 3.82–3.94 (m, 2H), 7.15 (s, 1H), 7.16 (s, 1H), 7.18 (s, 1H), 7.20 (s, 1H), 7.62 (d, $J = 4.6\text{ Hz}$, 1H), 7.81 (d, $J = 4.8\text{ Hz}$, 1H), 8.25 (d, $J = 4.6\text{ Hz}$, 1H), 8.38 (d, $J = 4.8\text{ Hz}$, 1H), 8.44 (d, $J = 4.2\text{ Hz}$, 1H), 8.53 (d, $J = 4.3\text{ Hz}$, 1H), 8.64 (s, 1H), 8.82 (d, $J = 4.4\text{ Hz}$, 1H), 8.89 (d, $J = 4.3\text{ Hz}$, 1H), 8.96–8.97 (m, 2H), 9.00 (d, $J = 4.6\text{ Hz}$, 1H), 9.16 (d, $J = 4.3\text{ Hz}$, 1H), 9.28 (d, $J = 4.6\text{ Hz}$, 1H), 9.67 (s, 1H), 9.85 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.4, 21.5, 21.6, 30.6, 31.0, 31.5, 31.8, 44.9, 46.2, 51.4, 53.2, 94.7, 94.8, 106.7, 109.4, 111.4, 112.0, 121.3, 123.6, 123.9, 127.0, 127.4, 127.5, 127.7, 127.8, 128.2, 128.3, 128.8, 131.6, 131.8, 132.8, 133.3, 134.5, 135.2, 137.3, 137.6, 138.3, 138.8, 138.9, 139.2, 139.3, 141.0, 142.2, 145.8, 146.5, 147.2, 147.3, 152.1, 152.6, 154.6, 156.0, 160.9, 165.3, 171.2, 175.1; MS ($[\text{M}+\text{H}]^+$, $\text{M} = \text{C}_{62}\text{H}_{56}\text{N}_8\text{Zn}$): Calcd: 977.3992, Obsd: (HRMS, ESI) 977.4012.

CuC-C—A mixture of **2C** (15.0 mg, 0.016 mmol) and $\text{Cu}(\text{OAc})_2$ (3.0 mg, 0.016 mmol) in chloroform/MeOH (15 mL, 5:1) was stirred at 50 °C, for 1h. The resulting solution was concentrated. Column chromatography (silica, hexanes/ CH_2Cl_2 2:1) afforded the titled compounds as a green solid (8.9 mg, 57%) as well as **2CuC** (green solid 4.0 mg, 24%). Data for **CuC-C**, ^1H NMR (CDCl_3 , 400 MHz) δ -1.89 (s, 1H), -1.66 (s, 1H), 1.85–1.88 (br, 12H) 2.31 (s, 3H), 2.58 (s, 3H), 6.91 (br, 2H), 7.21 (s, 2H), 8.48 (s, 2H), 8.88–8.95 (m, 3H), 9.25 (s, 1H), 9.82 (s, 1H); MS ($[\text{M}]^+$, $\text{M} = \text{C}_{62}\text{H}_{56}\text{N}_8\text{Cu}$): Calcd: 976.3997, Obsd: (HRMS, ESI) 976.4006. Data for **2CuC**; MS ($[\text{M}]^+$, $\text{M} = \text{C}_{62}\text{H}_{54}\text{N}_8\text{Cu}_2$): Calcd: 1036.3058, Obsd: (HRMS, ESI) 1036.3074.

5-Methoxy-8,8,18,18-tetramethyl-2,12-diphenylbacteriochlorin (BC1)

A solution of **1** (291 mg, 0.896 mmol) and 2,6-DTBP (4.0 mL, 17.92 mmol) in CH_2Cl_2 (180 mL) was stirred for 0.5 h and then treated with TMSOTf (0.81 mL, 4.48 mmol) at room temperature. The reaction mixture was stirred for 16 h at room temperature. The reaction mixture concentrated and column chromatography was performed [silica, CH_2Cl_2 /hexanes (1:1)] afforded a green solid (116 mg, 47%): ^1H NMR (CDCl_3 , 500 MHz) δ -1.77 (s, 1H), -1.66 (s, 1H), 1.95 (s, 6H), 1.99 (s, 6H), 4.40 (s, 2H), 4.47 (s, 2H), 4.56 (s, 3H), 7.64–7.68 (m, 2H), 7.80–7.85 (m, 4H), 8.26 (d, $J = 7.0\text{ Hz}$, 2H), 8.32 (d, $J = 7.0\text{ Hz}$, 2H), 8.69 (s, 1H), 8.74 (d, $J = 2.0\text{ Hz}$, 1H), 8.86 (s, 1H), 8.89 (s, 1H), 9.06 (d, $J = 2.2\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.3, 22.8, 30.3, 31.1, 31.8, 45.8, 46.2, 47.6, 51.9, 65.2, 95.8, 97.9, 116.5, 121.4, 127.3, 127.7, 129.2, 129.9, 131.2, 131.4, 133.0, 134.1, 134.9, 135.4, 135.7, 136.6, 137.3, 137.4, 153.0, 159.9, 169.7, 170.2; MS ($[\text{M}]^+$, $\text{M} = \text{C}_{37}\text{H}_{36}\text{N}_4\text{O}$): Calcd: 552.2884, Obsd: (HRMS, ESI) 552.2888.

BC1-Br—A solution of **BC1** (21.5 mg, 0.027 mmol) in THF (15 mL) was treated room temperature with NBS (4.8 mg, 0.027 mmol). The resulting mixture was stirred for 15 min. Saturated aqueous NaHCO₃ solution was added. The resulting mixture was extracted with ethyl acetate. The organic extract was washed with brine, dried (Na₂SO₄), and concentrated. Column chromatography [silica, hexanes/CH₂Cl₂ (1:1)] afforded a green solid; 16.0 mg, 94%; ¹H NMR (CDCl₃, 400 MHz) δ −1.95 (s, 1H), −1.74 (s, 1H), 1.93 (s, 12H), 4.42 (s, 2H), 4.51 (s, 3H), 4.52 (s, 2H), 7.61–7.67 (m, 2H), 7.76–7.82 (m, 4H), 8.21–8.25 (m, 4H), 8.79 (s, 1H), 8.84 (s, 1H), 9.03 (d, *J* = 2.1 Hz, 1H), 9.09 (d, *J* = 2.2 Hz, 1H); MS ([M+H]⁺, M = C₃₇H₃₅BrN₄O): Calcd: 632.604, Obsd: (MALDI-MS) 632.443.

BC1-B—A mixture of **BC1-Br** (20.2 mg, 32 μmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46 μL, 320 μmol), triethylamine (89 μL, 640 μmol), and (PPh₃)₂PdCl₂ (2.2 mg 3.2 μmol) in 1,2-dichloroethane (8 mL) was reacted as described in *General Procedure* at 85 °C for 16 hours. The reaction mixture was concentrated, and the residue was purified by column chromatography [silica, hexane/CH₂Cl₂, (1:1)] to provide a green solid (19.1 mg, 88%); ¹H NMR (CDCl₃, 500 MHz) δ −1.37 (s, 1H), −1.04 (s, 1H), 1.72 (s, 12H), 1.91 (s, 6H), 1.92 (s, 6H), 4.36 (s, 2H), 4.51 (s, 3H), 4.60 (s, 2H), 7.60–7.67 (m, 2H), 7.78–7.81 (m, 4H), 8.21 (d, *J* = 7.6 Hz, 2H), 8.27 (d, *J* = 7.6 Hz, 2H), 8.74 (s, 1H), 8.81 (s, 1H), 8.92 (s, 1H), 9.30 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 25.4, 29.9, 30.8, 31.5, 45.3, 46.6, 46.9, 53.3, 65.0, 84.4, 95.9, 96.8, 115.6, 123.3, 127.1, 127.6, 129.0, 129.1, 129.5, 131.4, 132.3, 133.3, 134.8, 136.2, 136.9, 137.4, 138.6, 141.4, 151.9, 166.4, 169.1, 169.7; MS ([M]⁺, M = C₄₃H₄₇BN₄O₃): Calcd: 678.3743, Obsd: (HRMS, ESI) 678.3739.

BC1-Tol—Samples of **BC1-Br** (15.5 mg, 0.024 mmol), 4-tolylboronic acid pinacol ester (5.2 mg, 0.024 mmol), (Pd(PPh₃)₄) (2.8 mg, 0.0024 mmol), K₂CO₃ (33.2 mg, 0.240 mmol), in toluene/DMF (6 mL, 2:1), was reacted as described in *General Procedure* at 85 °C under N₂ for 18 hours. Column chromatography (silica, hexanes/CH₂Cl₂, 2:1) afforded a reddish green solid: 14.3 mg, 91%; ¹H NMR (CDCl₃, 400 MHz) δ −1.79 (s, 1H), −1.56 (s, 1H), 1.84 (s, 6H), 1.93 (s, 6H), 2.64 (s, 3H), 4.04 (s, 2H), 4.42 (s, 2H), 4.53 (s, 3H), 7.47–7.51 (m, 2H), 7.54–7.64 (m, 2H), 7.69–7.72 (m, 2H), 7.75–7.81 (m, 4H), 8.10–8.12 (m, 2H), 8.22 (d, *J* = 2.1 Hz, 1H), 8.26–8.28 (m, 2H), 8.82 (s, 1H), 8.85 (s, 1H), 8.99 (d, *J* = 2.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 31.0, 31.2, 47.5, 52.0, 65.3, 96.0, 96.2, 116.4, 121.7, 127.3, 127.5, 128.7, 129.0, 129.1, 130.3, 131.3, 131.4, 132.2, 133.0, 134.5, 134.6, 135.2, 136.2, 136.6, 136.8, 137.0, 140.0, 153.7, 159.6, 169.6; MS ([M]⁺, M = C₄₄H₄₂N₄O): Calcd: 642.3353, Obsd: (HRMS, ESI) 642.3359.

2BC1—A solution of **BC1-Br** (10.0 mg, 16 μmol), **BC1-B** (11.0 mg, 16 μmol), Cs₂CO₃ (52.1 mg, 160 μmol), and Pd(PPh₃)₄ (5.5 mg, 4.8 μmol) in toluene/DMF (9 mL, 2:1) was reacted as described in *General Procedure* at 85 °C under for 18 hours. The mixture was diluted with ethyl acetate, washed (water and brine), dried (Na₂SO₄), and concentrated. The residue was purified by column chromatography (hexane/CH₂Cl₂, 1:1) to give a pink solid (7.2 mg, 41%); ¹H NMR (CDCl₃, 500 MHz) δ −1.52 (s, 2H), −1.09 (s, 2H), 1.70 (s, 6H), 1.73 (6H), 1.98 (s, 6H), 2.02 (s, 6H), 3.65 (d, *J* = 17.1 Hz, 2H), 3.76 (d, *J* = 17.1 Hz, 2H), 4.51 (s, 4H), 4.58 (s, 6H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.78–7.81 (m, 6H), 7.85 (d, *J* = 7.3 Hz, 4H), 8.30 (d, *J* = 7.3 Hz, 4H), 8.91 (s, 2H),

8.93 (s, 2H), 9.08 (d, $J = 2.0$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 29.9, 30.5, 31.1, 31.2, 31.6, 45.6, 46.2, 47.7, 52.2, 65.4, 96.1, 96.7, 112.3, 116.8, 121.8, 127.3, 127.4, 128.8, 129.2, 130.6, 131.1, 131.4, 133.5, 134.2, 134.8, 135.4, 136.4, 136.9, 137.1, 137.8, 154.0, 162.1, 169.8. HRMS ($[\text{M}+\text{H}]^+$, $\text{M} = \text{C}_{74}\text{H}_{70}\text{N}_8\text{O}_2$): Calcd: 1103.5695, Obsd: (HRMS, ESI) 1103.5676.

BC-BC1—A solution of **BC1-Br** (7.6 mg, 12 μmol), **BC-B** (6.3 mg, 12 μmol), Cs_2CO_3 (39.1 mg, 120 μmol), and $\text{Pd}(\text{PPh}_3)_4$ (4.2 mg, 3.6 μmol) in toluene/DMF (6 mL, 2:1) was reacted as described in **General Procedure** at 85 $^\circ\text{C}$ under N_2 for 18 hours. The mixture was diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (hexane/ CH_2Cl_2 , 1:1) to give a pink solid (5.5 mg, 48%); ^1H NMR (CDCl_3 , 400 MHz) δ -1.92 (s, 1H), -1.52 (s, 1H), -1.46 (s, 1H), -1.10 (s, 1H), 1.67 (s, 3H), 1.69 (s, 3H), 1.74 (s, 3H), 1.75 (s, 3H), 1.99 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 3.57–3.75 (m, 4H), 4.50 (s, 4H), 4.56 (s, 3H), 4.58 (s, 3H), 7.29–7.34 (m, 1H), 7.41–7.44 (m, 2H), 7.59–7.63 (m, 1H), 7.72 (d, $J = 2.1$ Hz, 1H), 7.77–7.83 (m, 5H), 8.29–8.31 (m, 2H), 8.53 (dd, $J = 1.9, 4.6$ Hz, 1H), 8.75–8.78 (m, 3H), 8.90 (s, 1H), 8.92 (s, 1H), 9.02 (dd, $J = 1.9, 4.4$ Hz, 1H), 9.07 (d, $J = 2.2$ Hz, 1H). Due to the low solubility, no satisfactory ^{13}C NMR spectra have been obtained. MS ($[\text{M}]^+$, $\text{M} = \text{C}_{62}\text{H}_{62}\text{N}_8\text{O}_2$): Calcd: 950.4990, Obsd: (HRMS, ESI) 950.4992.

Results and Discussion

Synthesis

Preparation of chlorin dyads relies on a PIFA-mediated dimerization of the **ZnC** monomer^{10,12} and subsequent demetalation of the resulting **2ZnC** leading to the free-base **2C**.¹² Non-symmetrical metal complexes were prepared by a statistical metalation of **2C** with corresponding metal acetates, in $\text{CHCl}_3/\text{MeOH}$ (Scheme 1) which affords mono-metalated **ZnC-C**, **PdC-C**, and **CuC-C** in moderate yield (42%, 32%, and 57% yield, respectively). Metalation, even when conducted with the 1 equiv of metal salt, leads to the formation of the mixture of mono- and di-metalated dyads, which can be separated by a column chromatography, however, formation of di-metalated product significantly diminished the yield of the target mono-metalated dyads. Synthesis of **2PdC** was accomplished by refluxing of the **2C** with an excess of $\text{Pd}(\text{OAc})_2$ in 90% yield, while **2CuC** was isolated as a side product in synthesis of **CuC-C** in 24% yield.

For synthesis of chlorin-bacteriochlorin and bacteriochlorin-bacteriochlorin dyads we applied a strategy employed previously for synthesis of analogous bacteriochlorin dyads, which entails Suzuki reaction as a key step.^{4,11,12,51} The required chlorins and bacteriochlorin building blocks, were either known compounds (i.e. **C-Br**³¹ and **BC-B**¹²), or were prepared analogously to those reported previously (Schemes 2–4). Thus, **BC1** was prepared through TMSOTf-mediated self-condensation⁵² of dihydrodipyrin **1**, (the latter was prepared following the route reported previously for analogous dihydrodipyrins, see Scheme S1). Bromination of **BC1** by NBS⁵² afforded **BC1-Br** in 94% yield (Scheme 2). Subsequent Suzuki reaction of **BC1-Br** with **BC-B**¹² afforded dyad **BC-BC1** in 48% yield. Similarly, Suzuki reaction of **C-Br**³¹ with **BC-B** afforded **C-BC** in 36% yield (Scheme 3).

Metalation of the **C-BC** with $\text{Pd}(\text{OAc})_2$ provides selectively **PdC-BC** in 40% (Scheme 3). No bacteriochlorin metallation was observed under this condition, which is consistent with the previous report that metallation of synthetic bacteriochlorins required harsher condition (i.e. strong base) than metallation of chlorins.²⁹

Symmetrical **2BC1** dyad was prepared in Suzuki reaction of **BC1-B** (prepared in Miyaura reaction of **BC1-Br** with **2**, in 88% yield) with **BC1-Br** in 41% yield (Scheme 4). Note, that attempted synthesis of symmetrical bacteriochlorin dyads by PIFA-mediated dimerization of corresponding monomers (either free base or Zn(II) complex) were unsuccessful.

Benchmark monomer **BC1-Tol** was prepared in Suzuki reaction of **BC1-Br** with corresponding boronic ester in 91% yield (Scheme 5), while **PdC** were prepared by the metallation of **H₂C³⁰** with $\text{Pd}(\text{OAc})_2$ in 89% yield (Scheme 6).

Characterization

Resulting dyads were characterized by ^1H , ^{13}C NMR and HRMS. The data are consistent with the proposed structures. In particular, each ^1H NMR spectra of non-symmetrical dyads consist of resonances of protons from two different hydroporphyrins. Resonances of protons at the 17-positions of each hydroporphyrin in each dyad are significantly shifted upfield (~ 1 ppm) compared to monomers (Figure S1). This effect is consistent with the orthogonal mutual arrangement of the macrocycles, which places the protons at 17 position within a shielding cone of neighboring macrocycle. Moreover, each dyad (symmetrical and non-symmetrical) is axially chiral, which is manifested by a differentiation of proton shifts of the respective diastereotopic protons, observed in ^1H NMR (specifically H^{17} and these of geminal CH_3 groups, see Figure S1). The DFT calculations confirm a nearly perpendicular arrangement of macrocycles in dyads (Figure S2), with the dihedral angles between macrocycles $180^\circ \pm 2^\circ$. The orthogonal geometry of these dyads is relatively stable, as the temperature-dependent ^1H NMR spectra for **2C** and **2BC** in CDCl_3 do not show noticeable changes in the chemical shift of protons up to 50°C . Moreover, DFT calculations suggest that the energy barrier for rotation around $\text{C}^{15}\text{-C}^{15}$ single bond is at least 150 kJ/mol (Table S1).

Absorption and emission properties

Absorption spectra of dyads are presented in Figures 1–2, and summarized in Table 1 (spectra of corresponding monomers are presented in Figures S3–S4, SI). The spectrum of each symmetrical dyad shows features characteristic of given hydroporphyrins,^{18,28} with the maximum of long-wavelength Q_y band shifted bathochromically, compared to both corresponding monomers and 15-aryl-substituted monomers (Table 1. Note, that formally, use of Q_y , B , etc. descriptions for absorption bands in dyads is incorrect, however, for simplicity, we use this notation to describe absorption spectra of both monomers and dyads). Metal complexation of the dyads causes a significant hypsochromic shift of the Q_y band [by 27 nm, 46 nm, and 30 nm, for Zn(II), Pd(II), and Cu(II), respectively], which is similar to those observed for monomers.^{28,33} Note that for **2PdC**, **2CuC**, **2ZnC**, and **2C**, the Q_y band shows a slight shoulder on the short wavelength side, whereas for **2BC** and **2BC1**, a new distinctive band appears at the shorter wavelength to the Q_y band. This splitting is probably due to the exciton coupling between macrocycles.⁵⁶ For non-symmetrical chlorin-chlorin

and chlorin-bacteriochlorin dyads, absorption spectra show two distinctive Q_y bands, for which the maxima are slightly shifted hypsochromically, compared to that of symmetrical dyads (e.g. compare **2ZnC** with **ZnC-C**, **2BC** with **C-BC**, and **2BC1** with **BC-BC1**). The metal complexation has a negligible effect on the absorption wavelength of the neighboring free-base hydroporphyrin component (e.g. compare absorption of the free base chlorin in **ZnC-C** with that of **PdC-C** and **C-BC** with that in **ZnC-BC**). Chlorin-bacteriochlorin dyads also exhibit distinctive, clearly resolved the B bands (i.e. shortest wavelength bands), whereas for chlorin-chlorin dyads B band of individual dyads components overlap.

The absorption spectrum of **BC-BC1** is different from those of other non-symmetrical hydroporphyrin dyads reported here, since it consists of a strong band at 746 nm, and a much weaker shoulder at 713 nm, and no distinguishable Q_y bands from individual bacteriochlorins. This pattern resembles those observed for symmetrical **2BC1** and **2BC**.

Emission spectra of symmetrical dyads **2C**, **2ZnC**, **2BC** and **2BC1**, as well as **BC-BC1** in toluene (Figure 3, Table 1; for spectra of corresponding monomers see Figures S5 and S6) show a strong 0–0 band with a small Stokes shift (0 – 5 nm), similar to the analogous monomers.⁵⁷ Emission spectra of non-symmetrical dyads **ZnC-C**, **PdC-C**, **C-BC**, and **PdC-BC** predominantly show one strong band, with the wavelength corresponding to emission of the longer-wavelength absorbing component, regardless of the excitation wavelength. There is a second, very weak emission band at the shorter wavelength, corresponding to the short-wavelength absorbing component. Excitation spectra of each dyad, monitored at the main emission peak, closely resemble the absorption spectra. These results indicate a very efficient energy transfer from the shorter to the longer-wavelength absorbing hydroporphyrin components. Comparison of excitation and absorption spectra allowed estimation of the energy transfer efficiency (ETE) as > 0.95 for most of the dyads, except for **PdC-BC**, for which ETE of 0.86 was determined. It is interesting to note, that high ETE is observed even from the Pd(II)-coordinated chlorin, despite very fast intersystem crossing (ISC) in the monomer **PdC**, as well as **2PdC** (which is manifested by a significant reduction of the fluorescence quantum yield Φ_f , see below). Apparently, S_1 - S_1 energy transfer from the Pd(II) chlorin to the directly linked hydroporphyrin is faster than ISC (S_1 - S_1 , rather than T_1 - T_1 as a dominant ET mechanism, is indicated by the similarity of Φ_f of the free base component regardless of the excitation wavelength). **2PdC** shows a very weak fluorescence, while both **2CuC** and **CuC-C** are essentially non-fluorescent, regardless of excitation wavelength.

Φ_f for symmetrical chlorin and bacteriochlorin dyads in toluene are markedly higher (1.2–1.9-fold) than for the corresponding monomers (Table 1). For non-symmetrical dyads **ZnC-C**, and **BC-BC1**, Φ_f in toluene is similar to that determined for the respective symmetrical dyads (**2C**, and **2BC1**), while Φ_f for **C-BC** is more similar to monomer **BC**. Note, that insertion of Zn(II) in chlorin does not affect Φ_f of non-symmetrical dyads. In contrast, Φ_f for **PdC-C** and **PdC-BC** is significantly reduced compared to the corresponding free base analogs (6.2-fold and 2.5-fold, respectively). This Φ_f reduction is most likely due to the “remote” heavy atom effect, i.e. enhancement of ISC of the free base hydroporphyrin component by Pd(II) complexation of the neighboring macrocycle. Similar reduction of Φ_f , attributed to enhanced ISC, has been reported previously for the chlorin-bispyridine-Ru(II)

dyad.⁴⁸ We cannot however rule out other processes, such as photoinduced electron transfer, being responsible for reduction of Φ_f in **PdC-C** and **PdC-BC**. More detailed spectroscopic studies are required to clarify this issue.

Effect of solvent dielectric constant on dyads fluorescence

Φ_f for non-symmetrical dyads **ZnC-C**, **C-BC**, **PdC-C**, and **BC-BC1** as well as for symmetrical bacteriochlorin dyads **2BC** and **2BC1**, exhibit a dramatic reduction (more than 40 times) in DMF compared to that observed in toluene (Table 1; for Φ_f of **ZnC-C** and **BC-BC1** in range of solvents of different ϵ , see Table 2). Reduction of Φ_f in DMF is also observed, albeit to a lesser degree for **2ZnC** (4.7 fold) and **PdC-C** (1.25 fold). Φ_f for **2C** and all examined monomers (chlorins and bacteriochlorins) are nearly the same in DMF and toluene. Observed reduction of Φ_f in polar solvents is consistent with the PET, which may occur in polar solvents (such as DMF). Solvents of high ϵ stabilizes charge-separated state, formed upon electron transfer and thus make PET energetically possible (in solvents of low ϵ energy of charge-separated state is higher than energy of S_1).²⁷ It is known that bacteriochlorins are easier to oxidize and harder to reduce than analogous chlorins,²³ and similarly Zn(II) chlorins are significantly easier to oxidize and slightly harder to reduce than chlorin free bases.²⁸ Therefore, it is reasonable to assume that in **ZnC-C**, the metalated chlorin is an electron donor, while the free base chlorin is an electron acceptor. Similarly, in **C-BC** the bacteriochlorin component is an electron donor. On the other hand, Pd(II) chelates of chlorins are only slightly easier to oxidize and slightly harder to reduce than corresponding free bases.^{10,58} Thus, the observed reduction of Φ_f in DMF for **PdC-C** is much less pronounced (1.25 fold, compared to toluene) than that for **ZnC-C**. For **BC1-BC** the direction of electron transfer is less obvious, however a inspection of available redox data for monomers, analogous to that composing **BC-BC1**, lead to conclusion that photoexcited 2,12-diphenylbacteriochlorin component is an electron donor.^{29,59} Further detailed studies are required to fully understand PET processes occurring in all dyads reported here.

Effect of metalation on the singlet oxygen (1O_2) photosensitization

The relative quantum yield of 1O_2 photosensitization was determined by comparing 1O_2 luminescence intensity at 1270 nm generated by dyads, to that observed for tetraphenylporphyrin ($\Phi = 0.67^{54}$). Φ determined for **ZnC-C** and **C-BC** (0.56 and 0.65, respectively) correspond well with those reported previously for analogous chlorins⁶⁰ and bacteriochlorins.¹² Insertion of Pd(II) into the macrocycle enhances Φ significantly for **2PdC** (up to 1.00), and **PdC-C** (1.7-fold compared to **2C**), but only slightly for **PdC-BC** (1.1-fold compared to **C-BC**). Direct excitation at the longest absorption band indicates that 1O_2 photosensitization efficiency of the free base component in **PdC-C** increases 1.5-fold (compared to **2C**), and 1.2-fold for the BC component in **PdC-BC** (compared to **C-BC**). Combining both fluorescence data and 1O_2 photosensitization experiments together, it is reasonable to assume, that excitation of the **PdC** component in **PdC-C** and **PdC-BC** leads to the (predominantly) S_1 - S_1 energy transfer to the free base chlorin or bacteriochlorin 1O_2 photosensitization mainly occurs through ISC in the dyads free base component, where ISC is enhanced due to the “remote” heavy atom effect of Pd in the neighboring macrocycle

(enhanced ISC in dyad free base hydroporphyrin components is inferred by both substantial reduction of Φ_f and enhanced Φ). Note that the extent of Φ_f reduction (5-fold for **PdC-C** vs. **ZnC-C** and 2.2-fold for **PdC-BC** vs. **C-BC**) is much larger than the respective increase in Φ (1.7-fold for **PdC-C** and 1.1 for **PdC-BC**). However, increase in ISC quantum yield does not always result in the same increase in Φ , as the latter depends on both yield and lifetime of T_1 ,⁶¹ and enhanced ISC is usually accompanied by a decrease in T_1 lifetime.^{29,36} In polar solvent (DMF) Φ is reduced to ~0 for **ZnC-C** and **C-BC**, while for **PdC-C** and **PdC-BC** 1O_2 emission could still be seen in DMF, though we did not attempt to quantify Φ in DMF.

For **2CuC** excitation in toluene leads to a negligible 1O_2 production, while for **CuC-C**, efficient 1O_2 photosensitization is observed ($\Phi = 0.86$; direct excitation of free base component shows 1.4-fold increase in 1O_2 photosensitization, compared to **2C**). It has been previously reported that excitation of the Cu(II) complexes of porphyrins and bacteriochlorins leads to the ultrafast formation of tripdoublet 2T or tripquartet 4T states, which decay to the ground state within nanosecond time range.^{29,62} Due to this short-lived triplet state, Cu(II) complexes of tetrapyrrolic macrocycles usually show very low Φ .⁵⁴ On the other hand, in non-symmetrical porphyrin dyads containing Cu(II) and free-base porphyrins, enhanced ISC in the free base component has been observed due to the through-bond exchange electron interaction.^{42,43} This latter mechanism most likely operates for **CuC-C**.

Electronic properties

The absorption and emission properties indicate substantial electronic interactions between macrocycles in both symmetrical and non-symmetrical directly-linked dyads. This interaction is manifested by the bathochromic shift of the absorption Q_y and emission bands of dyad components, and increase in dyad Φ_f , compared to monomers (both unsubstituted and 15-arylsubstituted). In the non-symmetrical chlorin-chlorin and chlorin-bacteriochlorin, each dyad component maintains its individual identity, as indicated by the presence of clearly distinctive Q_y bands for each hydroporphyrin. In case of **BC-BC1**, interactions between macrocycles leads to significant alteration of the absorption spectrum, which no longer preserves the features of individual chromophores. Based on the above consideration we concluded, that the strength of interchromophoric interactions decreases in the following order: symmetrical bacteriochlorin-bacteriochlorin ~ symmetrical chlorin-chlorin > non-symmetrical bacteriochlorin-bacteriochlorin > non-symmetrical chlorin-chlorin > chlorin-bacteriochlorin. This trend is additionally supported by the degree to which Pd(II) coordination reduces Φ_f and increases Φ in the adjacent macrocycle (i.e. **PdC-C** > **PdC-BC**).

Further insight into electronic structure and the interchromophoric interaction in dyads has been obtained from DFT calculations. Here, only a basic discussion is presented; detailed computational characterization and comprehensive discussion of results will be presented in due publication. Four MOs are considered (HOMO-1, HOMO, LUMO, and LUMO+1), since according to the Gouterman theory the configuration interactions of electronic transitions between these MOs (i.e. HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1, etc.), give

rise to the absorption features of tetrapyrrolic macrocycles.⁶³ The energies and shapes of the relevant MOs (HOMO-1, HOMO, LUMO, and LUMO+1) for representative symmetrical and non-symmetrical dyads and monomers are given in Table 3. For symmetrical **2ZnC** and **2BC1**, linear combination of MOs of monomers results in a new set of MO, fully delocalized on the entire dyad. Thus, for **2ZnC** combination of HOMO of both monomers results in new MOs (now formally HOMO and HOMO-1 of dyad) with an energy difference

$E = 0.07$ eV. Similarly, combinations of LUMO of both **ZnC** components leads to LUMO and LUMO+1 of **2ZnC** ($E = 0.15$ eV), combination of HOMO-1 of **ZnC** gives HOMO-2 and HOMO-3 of **2ZnC** ($E = 0.06$ eV), and combination of LUMO+1 of both monomers gives LUMO+2 and LUMO+3 of dyad ($E = 0.04$ eV). The identical pattern of splitting is observed for **2BC1**, where $E(\text{HOMO}) = 0.06$ eV, $E(\text{LUMO}) = 0.11$ eV, $E(\text{HOMO-1}) = 0.03$, and $E(\text{LUMO+1}) = 0.01$ eV. Similar combination of MOs of monomer has been observed in strongly conjugated hydroporphyrin dyads.²²

For **ZnC-C** and **C-BC**, MOs are localized nearly entirely on the single macrocycle; thus HOMO is localized on Zn chelate and bacteriochlorin components of the **ZnC-C** and **C-BC**, respectively. Shapes and energies of these MOs resemble that of corresponding HOMO of **ZnC** and **BC** benchmarks, respectively (both MOs are stabilized by 0.04 eV for **C-BC** and 0.06 eV for **ZnC-BC**, compared to the benchmark monomers). Similarly, formal HOMO-1 for **ZnC-C** and **C-BC** are localized at the chlorin moiety, and their distribution and energies are similar to HOMO in **H₂C**. Conversely, LUMOs for **ZnC-C** and **C-BC** maintain LUMO character of **H₂C** and **BC**, respectively (energies of LUMO in dyads are lower by 0.09 eV for **C-BC** and 0.11 eV for **C-BC**, compared to their counterparts in monomers). Similarly, HOMO-1 and HOMO-2 as well as LUMO+1 and LUMO+2 in **ZnC-C** and **C-BC** essentially possess a characteristic of the relevant orbitals in monomers. This situation is different in **BC-BC1**, where both HOMO and HOMO-1 resulted from the linear combination of HOMOs of the monomers. Both MOs are delocalized over the entire molecule, and the difference of energy difference between them $E = 0.07$ eV. The same is true for HOMO-2 and HOMO-3 of **BC-BC1**, which resulted from a linear combination of HOMO-1 of monomers ($E = 0.04$ eV). In this regard, **BC-BC1** resemble more symmetrical dyads. However, LUMO and LUMO+1 (as well LUMO+2 and LUMO+3) are mostly localized on the one macrocycle, and maintain characteristics of relevant MOs in monomers (i.e. LUMO of **BC-BC1** resembles LOMO of **BC1**, LUMO+1 resembles LUMO of **BC**, etc.).

The DFT calculations thus support our conclusion regarding the strength of the electronic interactions between hydroporphyrins, drawn from the spectroscopic data. For **C-BC** and **ZnC-C** individual macrocycles preserve to a large extent, their electronic structures characteristic for monomers, while for **BC-BC1**, new delocalized MOs resulted from a linear combination of HOMOs (as well as HOMO-1) are present. This difference in electronic structure (as well as optical properties) of **BC-BC1**, compared to other non-symmetrical dyads, is most likely a result of (coincidentally) the same energies of HOMOs (and nearly the same of HOMO-1) of the macrocycles constituting **BC-BC1**, whereas there is substantial difference in MOs energies in hydroporphyrins of which other dyads are composed (as well as between LUMO and LUMO+1 of **BC** and **BC1**). Therefore, **BC-BC1**

behaves more closely to analogous symmetrical dyads, despite the distinctive optical properties of its constituents. This conclusion emphasizes the importance of the monomers electronic structure to the properties of the resulting dyads. MOs energies in bacteriochlorins (as well as chlorins) can be broadly tuned by the peripheral substituents, and as such, the proper choice of monomers should allow for construction of directly-linked bacteriochlorin-bacteriochlorin dyads, where each macrocycle retain its individual characteristics, as in case of **ZnC-C** and **(Pd)C-BC**.

Conclusion

A range of directly-linked hydroporphyrin-hydroporphyrin dyads can be synthesized using either PIFA-mediated oxidative coupling (for chlorin-chlorin) or the Suzuki reaction (for chlorin-bacteriochlorin and bacteriochlorin-bacteriochlorin dyads), and subsequent symmetrical or non-symmetrical metalation of the resulting dyads. Hydroporphyrin dyads feature a range of interesting properties, depending on the electronic structure of constituent monomers. Symmetrical (or nearly symmetrical) arrays exhibit a marked bathochromic shift of the long-wavelength absorption bands, and enhanced Φ_f . In non-symmetrical dyads, each macrocycle maintains its individual properties, and a very efficient S_1 - S_1 energy transfer is observed, even for dyads in which energy donor contains a heavy element (Pd). The influence of heavy elements (Pd(II) or Cu(II)) on the properties of the adjacent macrocycle, manifested by reduction of Φ_f and increase in Φ , has been clearly observed. Moreover, the photochemical properties of most of the dyads exhibit a strong dependence of their photochemical properties on the solvent dielectric constant, which is attributed to the PET. Overall, directly linked hydroporphyrin arrays constitute a useful platform for development of photonic agents for a variety of biomedical and energy-related applications. The dyads reported here are also useful tools for fundamental studies on energy and electron transfers in electronically coupled systems, the “remote” heavy atom effect, metal-metal interactions, etc.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Synopsis

Symmetrical and non-symmetrical *meso-meso* linked chlorin-chlorin, chlorin bacteriochlorin and bacteriochlorin-bacteriochlorin dyads, (free base and Zn(II), Pd(II) or Cu(II) complexes) are reported. For non-symmetrical dyads an efficient singlet-singlet energy transfer is observed. Insertion of heavy element [Pd(II) or Cu(II)] significantly enhances $^1\text{O}_2$ photosensitization. Most of the dyads exhibit a significant reduction of the fluorescence in highly polar solvents, suggesting a charge transfer character of the excited state.

Figure 1.

Absorption spectra of symmetrical dyads in toluene: **2PdC** (black), **2ZnC** (blue), **2CuC** (orange), **2C** (red), **2BC** (green), and **2BC1** (purple). All spectra were taken at the room temperature and normalized at the maximum of their *B* bands.

Figure 2.

Absorption spectra of non-symmetrical dyads in toluene: **PdC-C** (black), **ZnC-C** (blue), **CuC-C** (orange), **C-BC** (red), **PdC-BC** (green), and **BC-BC1** (purple). All spectra were taken at the room temperature and normalized at the maxima of their *B* bands.

Figure 3.

Emission spectra of symmetrical dyads in toluene: **2ZnC** (blue), **2C** (red), **BC** (purple), **2BC** (green), and **2BC1** (purple). All spectra were taken at room temperature and normalized at the maxima of their emission bands.

Figure 4. Emission spectra of non-symmetrical dyads in toluene: **PdC-C** (black), **ZnC-C** (blue), **C-BC** (red), **PdC-BC** (green), and **BC-BC1** (purple). All spectra were taken at room temperature and normalized at the maxima of their emission bands.

Scheme 1.
Metallation of **2C**.

Scheme 2.
Synthesis of **BC-BC1**.

Scheme 3. Synthesis of chlorin-bacteriochlorin dyads **C-BC** and **PdC-BC**.

Scheme 4.
Synthesis of symmetrical **2BC1** dyad.

Scheme 5.
Synthesis of benchmark monomer **BC1-Tol**.

Scheme 6.
Synthesis of **PdC**

Chart 1.

Structures of dyads and monomers discussed in this paper (Ms = 2,4,6-trimethylphenyl).

Table 1

Absorption and photochemical properties of hydroporphyrin dyads and benchmark monomers.

Compound	λ_{abs}^a	λ_{em}^a	$\Phi_{\text{f}}(\text{toluene})^b$	$\Phi_{\text{f}}(\text{DMF})$	ETE ^c	Φ^d
2C^e	421, 508, 650	654	0.31	0.29	-	0.53
2ZnC	408, 419, 623	628	0.15	0.032	-	0.48
2PdC	408, 604	-	< 0.005	< 0.005	-	1.00
2CuC	415, 620	-	< 0.005	< 0.005	-	< 0.03
2BC^e	372, 510, 706, 731	738	0.28	0.003	-	0.65
2BC1	386, 524, 729, 754	760	0.27	0.013	-	-
ZnC-C	408, 419, 506, 613, 646	646	0.31	< 0.005 ^f	> 0.95 ^g	0.54
PdC-C	417, 596, 646	645	0.05	0.04	> 0.95 ^g	0.90
CuC-C	419, 506, 610, 646	-	< 0.005	< 0.005	-	0.86
C-BC	366, 399, 512, 642, 719	719	0.24	< 0.005	0.99	0.65
PdC-BC	366, 398, 510, 595, 718	718	0.11	< 0.005	0.86	0.74
BC-BC1	381, 520, 713, 746	754	0.29	0.007	-	0.62
H₂C^h	393, 399, 498, 636	636	0.22	0.22	-	0.44
ZnC^h	403, 604	605	0.08	0.08	-	-
PdC	396, 588	589	< 0.005	< 0.005	-	-
BC1	372, 510, 731	737	0.21	0.20	-	-
BC-Tol	369, 508, 712	715	0.22	0.20	-	-
BC1-Tol	375, 518, 734	736	0.24	0.21	-	-
H₂C-Phⁱ	411, 640	-	-	-	-	-

^a All data taken in toluene at the room temperature.^b Fluorescence quantum yield Φ_{f} was determined in air-equilibrated solvents upon excitation at the maximum of the *B* band of corresponding chlorin. Φ_{f} was determined using tetraphenylporphyrin in air-equilibrated toluene ($\Phi_{\text{f}} = 0.070^{53}$) as a reference. Estimated error $\pm 5\%$. A long bandpass filter (with cut off 600 nm) was used for each Φ_{f} determination to eliminate subharmonic band from excitation.^c Energy transfer efficiency ETE (all data in toluene) was determined as a ratio of Φ_{f} of the component with longer emission wavelength (energy acceptor) upon excitation at the chlorin *B* band to the same Φ_{f} obtained upon excitation at the maximum of the bacteriochlorin *B* band (unless noted otherwise).

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Φ Quantum yield of $^1\text{O}_2$ photosensitization Φ was determined by comparing the $^1\text{O}_2$ luminescence intensity ($\lambda_{\text{em}} = 1270 \text{ nm}$) to that generated by tetraphenylporphyrin in air-equilibrated toluene ($\Phi = 0.67^{54}$). Samples were excited at the maximum of the B band. Estimated error $\pm 10\%$.

Φ Data taken from ref. 12).

Φ Φ is approximate, due to the very weak emission and presence of an additional weak peak at 660 nm of unknown origin (most likely a trace amount of **2C** impurity).

Φ ETE was determined by comparing absorption and fluorescence excitation spectra, monitored at the wavelength where energy acceptor emits exclusively.

Φ All data (except Φ) for **H₂C_{28,55}** and **ZnC_{28,55}** were reported previously. For consistency, all data for these compounds reported here were re-determined in our laboratory, and are consistent with those reported previously.

Φ Data taken from ref. 31.

Table 2

Φ_f for **ZnC-C** and **BC-BC1** in solvents of different dielectric constants.

Dyad	Solvent	Φ_f
ZnC-C	Toluene	0.31
	THF	0.061
	CH ₂ Cl ₂	0.17
	PhCN	~ 0.006
	DMF	< 0.005
BC-BC1	Toluene	0.29
	THF	0.14
	CH ₂ Cl ₂	0.028
	DMF	~ 0.007

Note, that for **ZnC-C** Φ_f in THF ($\epsilon = 7.58$) is much lower than in CH₂Cl₂ ($\epsilon = 8.93$). We speculate, that coordination of THF to Zn(II) alters significantly redox properties of **ZnC** component of dyad and facilitates PET.

Table 3DFT calculated **FMOs** for representative dyads and benchmark monomers.^a

Compound	HOMO-1 [eV]	HOMO [eV]	LUMO [eV]	LUMO+1 [eV]
2ZnC	-5.11	-4.78	-2.25	-1.61
	-5.17	-4.85	-2.10	-1.58
2BC1	-4.90	-4.45	-2.35	-1.03
	-4.93	-4.51	-2.24	-1.02
ZnC-C

-5.03	-4.81	-2.27	-1.71
	-5.15	-4.91	-2.14	-1.60
C-BC	-4.95	-4.54	-2.31	-1.68
	-5.00	-4.87	-2.16	-1.00
BC-BC1	-4.89	-4.52	-2.33	-1.02
	-4.93	-4.45	-2.19	-0.96
H₂C^b	-5.02	-4.87	-2.18	-1.68
ZnC^b	-5.11	-4.78	-2.12	-1.56
BC^b	-4.91	-4.48	-2.20	-0.93

^a All calculations were conducted employing the DFT B3LYP 6-31G* method. For symmetrical dyads as “HOMO”, “HOMO-1”, etc., two orbitals, formed from linear combination of respective MOs of corresponding monomers are listed. For non-symmetrical dyads, pairs of MOs, corresponding to respective MOs localized on each individual macrocycle, are listed (e.g. as a “HOMO” for **ZnC-C**, a MOs with the highest energy localized on free base and Zn complex, are listed, etc.).

^b Energies for **H₂C**,²⁶ **ZnC**,²⁶ and **BC**¹⁶ were reported previously. Here, for consistency, we repeated this computation, obtaining identical results as reported.