Synthesis and Excited-state Photodynamics of a Chlorin–Bacteriochlorin Dyad—Through-space *Versus* Through-bond Energy Transfer in Tetrapyrrole Arrays

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Received 10 October 2007, accepted 1 November 2007, DOI: 10.1111/j.1751-1097.2007.00258.x

ABSTRACT

Understanding energy transfer among hydroporphyrins is of fundamental interest and essential for a wide variety of photochemical applications. Toward this goal, a synthetic free base ethynylphenylchlorin has been coupled with a synthetic free base bromobacteriochlorin to give a phenylethyne-linked chlorin-bacteriochlorin dvad (FbC-pe-FbB). The chlorin and bacteriochlorin are each stable toward adventitious oxidation because of the presence of a geminal dimethyl group in each reduced pyrrole ring. A combination of static and transient optical spectroscopic studies indicate that excitation into the Q_{ν} band of the chlorin constituent (675 nm) of FbC-pe-FbB in toluene results in rapid energy transfer to the bacteriochlorin constituent with a rate of $\sim (5 \text{ ps})^{-1}$ and efficiency of >99%. The excited bacteriochlorin resulting from the energy-transfer process in FbC-pe-FbB has essentially the same fluorescence characteristics as an isolated monomeric reference compound, namely a narrow (12 nm fwhm) fluorescence emission band at 760 nm and a long-lived (5.4 ns) Q_v excited state that exhibits a significant fluorescence quantum yield ($\Phi_f = 0.19$). Förster calculations are consistent with energy transfer in FbC-pe-FbB occurring predominantly by a through-space mechanism. The energy-transfer characteristics of FbC-pe-FbB are compared with those previously obtained for analogous phenylethynelinked dyads consisting of two porphyrins or two oxochlorins. The comparisons among the sets of dyads are facilitated by density functional theory calculations that elucidate the molecular-orbital characteristics of the energy donor and acceptor constituents. The electron-density distributions in the frontier molecular orbitals provide insights into the through-bond electronic interactions that can also contribute to the energytransfer process in the different types of dyads.

INTRODUCTION

Molecules with intense absorption in the red and near-infrared (NIR) regions are attractive for applications encompassing solar cells (1), medical imaging (2) and photodynamic therapy

(3–7). Chlorophylls and bacteriochlorophylls are important naturally occurring pigments that exhibit strong absorption features in the red and NIR regions of the spectrum, respectively (Chart 1). Over the past several years, we have been working to develop *de novo* synthetic methods for preparing chlorins (dihydroporphyrins) and bacteriochlorins (tetrahydroporphyrins) that retain the fundamental spectral and photophysical characteristics of the naturally occurring macrocycles, yet are synthetically malleable, as required for basic scientific studies or diverse applications (8–18). The one or two reduced pyrrole rings in the synthetic chlorins or bacteriochlorins, respectively, each incorporate a geminal dimethyl group to block adventitious dehydrogenation, rendering the synthetic hydroporphyrins far more stable than naturally occurring pigments.

We have recently exploited the new synthetic methods to gain access to chlorins bearing substituents that afford significantly enhanced red absorption spectral features. Such auxochromes include acetyl (13), triisopropylsilylethynyl (13), formyl (19), phenyl (20) and vinyl (13) groups located at the 3,13-positions. The substituents were introduced at the 3.13-positions because the electronic transition that gives rise to the Q_{ν} band is polarized along this axis. The chlorin acetvlation methodology has also been extended to gain facile access to 13¹-oxophorbines, the core molecular framework of chlorophylls (14). Studies of the photophysical, vibrational and redox properties of a large family of these synthetic chlorins along with molecular-orbital and four-orbital analysis have given insights into the factors that control the effects of peripheral substituents on the electronic characteristics of these hydroporphyrin complexes (20,21).

A very large number of dyads and larger constructs that contain porphyrins have been prepared for studies in artificial photosynthesis (22). A sizable number of covalently linked architectures that contain chlorins also have been prepared (for a review of the early literature, see Ref. 23; for representative chlorin dyads and multads prepared more recently, see Refs. 24–45). Extensive work has also been devoted to the preparation and study of self-assembling chlorins (46). However, relatively few bacteriochlorin-containing dyads have been prepared (47–54). Moreover, to our knowledge, no chlorinbacteriochlorin dyads have been prepared that incorporate

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a relatively rigid intervening linker. The approach of self-assembly ultimately may prove to be the simplest and most versatile strategy for constructing multi-pigment architectures for light-harvesting applications. At present, however, studies of energy-transfer dynamics are greatly facilitated by the use of a covalent strategy wherein the constituents of interest are joined at a defined distance of separation in a welldefined architecture.

In the present study, we have taken advantage of the new synthetic routes to hydroporphyrins to prepare a dyad consisting of a free base (Fb) chlorin (C) and bacteriochlorin (B) joined by a phenylethyne (pe) linker (FbC-pe-FbB, Chart 2). The properties of each chlorin or bacteriochlorin constituent are established by comparison with two benchmark monomers (Chart 2). One benchmark lacks the linker moiety (FbC1, FbB1) and the other benchmark contains the linker moiety (FbC2, FbB2). We then investigate the energytransfer characteristics of the FbC-pe-FbB dyad using a combination of static and transient optical spectroscopy.

A key objective of the present study was to understand how the mechanism of energy transfer in covalently linked hydroporphyrin arrays compares with that in analogous porphyrin arrays (55), given the profound differences in spectral characteristics of the respective arrays. To address this issue, the



FbC-pe-FbB

Benchmark monomers:



Chart 2.

energy-transfer characteristics of the chlorin-bacteriochlorin dyad FbC-pe-FbB are compared with those of a porphyrinporphyrin dyad and an oxochlorin-oxochlorin dyad, each of which contains a phenylethyne linker (39). The chlorinbacteriochlorin, oxochlorin-oxochlorin and porphyrin-porphyrin dyads exhibit strong red/NIR, modest red and weak red absorption, respectively. Insights into the mechanism of energy transfer are obtained by Förster energy-transfer calculations and by density functional theory (DFT) calculations. The former concern the through-space (TS) interactions between the donor and acceptor constituents, while the latter elucidate the molecular-orbital (MO) characteristics of the energy donor and acceptor constituents. The electron-density distributions in the frontier MOs provide insights into through-bond (TB) electronic interactions that can also contribute to the energy-transfer process. Collectively, the results and comparisons of the energy-transfer characteristics of this set of dyads provide added insight into the design principles that produce ultrafast and essentially quantitative excited-state energy flow among tetrapyrrole constituents in covalently linked arrays.

MATERIALS AND METHODS

Synthesis. General. ¹H NMR (400 MHz) and ¹³C NMR (75 MHz) spectra were collected at room temperature in CDCl₃ unless noted otherwise. Absorption spectra were obtained at room temperature in toluene or CH2Cl2. Chlorins and the chlorin-bacteriochlorin dyad were analyzed by laser desorption mass spectrometry (LD-MS) in the absence of a matrix (56). Fast-atom bombardment mass spectrometry (FAB-MS) or electrospray ionization mass spectrometry (ESI-MS) data are reported for the molecule ion or protonated molecule ion. Melting points are uncorrected. Preparative size-exclusion chromatography (SEC) was performed using Bio-Rad Bio-Beads SX-1 (200-400 mesh). Analytical SEC was performed on a HPLC using two columns (500, 500 Å in series, 30 cm each) with absorption spectral detection (752 nm) and elution with tetrahydrofuran (THF, 0.8 mL min^{-1}). All commercially available materials were used as received. All palladiumcoupling reactions were carried out using standard Schlenk-line techniques. The Sonogashira coupling reactions were carried out using tris(dibenzylideneacetone)dipalladium(0) [Pd2(dba)3] and the ligand tri-o-tolylphosphine [P(o-tol)3] in the absence of copper reagents (57,58). Palladium insertion and transmetalation of hydroporphyrins have not been observed under these conditions. Toluene and triethylamine (TEA) were degassed with argon for 5 min prior to use.

Noncommercial compounds. The following compounds were prepared *via* literature procedures: Zn(II)-5-(2-phenylethynyl)-10,15, 20-triphenylporphyrin (59), 1-formyl-5-(4-(2-(triisopropylsilyl)ethynyl) phenyl)dipyrromethane (1) (60), 8-bromo-2,3,4,5-tetrahydro-1,3,3-trimethyldipyrrin (3) (13), Zn(II)-3,13-dibromo-17,18-dihydro-10-mesityl-18,18-dimethylporphyrin (**ZnC3**) (13), **FbB1** (12), **FbB2** (17) and 15-bromo-5-methoxy-8,8,18,18-tetramethyl-2,12-di-*p*-tolylbacter-iochlorin (**FbB3**) (17).

8,9-Dibromo-1-formyl-5-[4-(2-(triisopropylsilyl)ethynyl)phenyl]dipyrromethane (2). Following a procedure for 8,9-dibromination of 1-formyldipyrromethanes (13), a solution of 1 (410 mg, 0.952 mmol) in dry THF (9.5 mL) at -78°C under argon was treated portionwise with N-bromosuccinimide (NBS, 339 mg, 1.90 mmol). The reaction mixture was stirred for 1 h at -78°C. The mixture was allowed to warm to -20°C, whereupon a mixture of hexanes was added. The reaction mixture was then allowed to warm to 0°C. The organic layer was washed with ice-cold water, dried (K2CO3) and concentrated at ambient temperature. The resulting brown solid was purified by column chromatography (silica, hexanes/CH₂Cl₂/ethyl acetate [7:2:1]) to afford a yellow solid (0.406 g, 73%): mp 78-80°C (dec); ¹H NMR (300 MHz, THF-d₈) δ 1.02-1.14 (m, 21H), 5.42 (s, 1H), 5.68-5.71 (m, 1H), 5.88–5.92 (m, 1H), 6.80–6.83 (m, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 9.41 (s, 1H), 10.84 (brs, 1H), 11.24 (brs, 1H);¹³C NMR (THF-*d*₈) δ 12.4, 19.2, 45.1, 90.9, 98.4, 100.3, 108.4, 111.2,

112.3, 121.1, 123.3, 129.5, 133.0, 134.8, 135.1, 141.6, 142.4, 178.8. Anal. Calcd. for $C_{27}H_{32}Br_2N_2OSi:$ C, 55.11; H, 5.48; N, 4.76. Found: C, 55.92; H, 5.71; 4.52; FAB-MS obsd 586.0676, calcd 586.0650 ($C_{27}H_{32}Br_2N_2OSi$).

Notes: (1) All of the workup operations should be performed without heating, and preferably under chilled conditions. (2) The chromatography solvent mixture (hexanes/CH₂Cl₂/ethyl acetate) was stored over anhydrous K_2CO_3 prior to use.

5-(2-Phenylethynyl)-10,15,20-triphenylporphyrin. A solution of Zn(II)-5-(phenylethynyl)-10,15,20-triphenylporphyrin (4.2 mg, 0.0060 mmol) in CH₂Cl₂ (1.0 mL) was treated dropwise with trifluoroacetic acid (TFA, 25 μL, 0.18 mmol) for 1 min. The solution was stirred at room temperature for 3 h. CH₂Cl₂ was added, and the reaction mixture was washed (saturated aqueous NaHCO₃, water, brine) and dried (Na₂SO₄). The organic layer was concentrated and chromatographed (silica, hexanes then hexanes/CH₂Cl₂ [1:2]) to give a purple solid (2.8 mg, 73%): ¹H NMR δ –2.32 (brs, 2H), 7.49–7.50 (m, 1H), 7.56–7.60 (m, 2H), 7.72–7.81 (m, 9H), 8.04 (d, J = 7.2 Hz, 2H), 8.17–8.22 (m, 6H), 8.76 (s, 4H), 8.92 (d, J = 4.4 Hz, 2H), 9.75 (d, J = 4.4 Hz, 2H); LD-MS obs6 639.6; ESI-MS obs6 639.2526, caled 639.2543 [(M + H)⁺, M = C₄₆H₃₀N₄]; λ_{abs} (toluene) 434, 533, 574, 609, 668 nm; λ_{em} (toluene) 671 nm; Φ_f (Ar-purged toluene) 0.11; τ (Ar-purged toluene) 11.5 ns.

 $\hat{Zn}(\tilde{H})$ -3,13-Bis(2-phenylethynyl)-17,18-dihvdro-18,18-dimethyl-10mesitylporphyrin (ZnC1). Following a standard procedure (13,57,58), samples of ZnC3 (19.3 mg, 0.0284 mmol) and phenylacetylene (18.7 μ L, 0.175 mmol) were coupled using Pd₂(dba)₃ (5.20 mg, 0.00568 mmol) and P(o-tol)₃ (10.4 mg, 0.0341 mmol) in toluene/TEA (5:1, 12 mL) at 60°C under argon. After 6 h, phenylacetylene (18.7 µL, 0.175 mmol), Pd₂(dba)₃ (5.20 mg, 0.00568 mmol), and P(o-tol)₃ (10.4 mg, 0.0341 mmol) were added to the reaction mixture. After 12 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was chromatographed (silica, hexanes then hexanes/CH₂Cl₂ [1:1]) to afford a green solid (14.8 mg, 72%): ¹H NMR (300 MHz) & 1.88 (s, 6H), 2.04 (s, 6H), 2.60 (s, 3H), 4.55 (s, 2H), 7.23 (s, 2H), 7.41–7.54 (m, 6H), 7.78–7.92 (m, 4H), 8.38 (d, J = 4.5 Hz, 1H), 8.53 (s, 1H), 8.66 (s, 1H), 8.84 (s, 1H), 8.86 (d, J = 4.5 Hz, 1H), 8.99 (s, 1H), 9.82 (s, 1H), LD-MS obsd 721.3;FAB-MS obsd 720.2261, calcd 720.2231 ($C_{47}H_{36}N_4Zn$); λ_{abs} (toluene) 426, 652 nm.

3,13-Bis(2-phenylethynyl)-17,18-dihydro-18,18-dimethyl-10-mesitylporphyrin (**FbC1**). A solution of **ZnC1** (9.0 mg, 0.012 mmol) in CH₂Cl₂ (0.4 mL) was treated dropwise with TFA (29 μ L, 0.37 mmol) for 2 min. The solution was stirred at room temperature for 3 h. CH₂Cl₂ was added, and the reaction mixture was washed (saturated aqueous NaHCO₃, water, brine) and then dried (Na₂SO₄). The organic layer was concentrated and chromatographed (silica, hexanes the hexanes/CH₂Cl₂ [6:4]) to afford a green solid (7.1 mg, 87%): ¹H NMR (300 MHz) δ -1.74 (brs, 1H), -1.45 (brs, 1H), 1.88 (s, 6H), 2.06 (s, 6H), 2.61 (s, 3H), 4.65 (s, 2H), 7.25 (s, 2H), 7.44-7.58 (m, 6H), 7.85-7.99 (m, 4H), 8.43 (d, J = 4.5 Hz, 1H), 8.72 (s, 1H), 8.79 (s, 1H), 8.91 (d, J = 4.5 Hz, 1H), 9.00 (s, 1H), 9.25 (s, 1H), 9.98 (s, 1H), LD-MS obsd 660.3; FAB-MS obsd 659.3189, calcd 659.3175 [(M + H)⁺, M = C₄₇H₃₈N₄]; λ_{abs} (toluene) 429, 676 nm.

3,13-Bis(2-phenylethynyl)-17,18-dihydro-18,18-dimethyl-10-(4-ethynylphenyl)porphyrin (**FbC2**). A solution of 3,13-bis(2-phenylethynyl)-17, 18-dihydro-18,18-dimethyl-10-(4-(2-(triisopropylsilyl)ethynyl)phenyl)porphyrin (**FbC5**) (22.1 mg, 0.0227 mmol) in 3.0 mL of THF was treated with tetrabutylammonium fluoride (TBAF, 0.138 mL, 5 equiv, 1 M in THF) and stirred for 1 h at room temperature. The mixture was poured into CH₂Cl₂. The organic layer was extracted (5% NaHCO₃, H₂O), dried (Na₂SO₄) and concentrated. The resulting solid was chromatographed (silica, hexanes then hexanes/CH₂Cl₂ [4:1]) to give a green solid (7.2 mg, 41%): ¹H NMR δ –1.91 (brs, 1H), –1.50 (brs, 1H), 2.06 (s, 6H), 3.31 (s, 1H), 4.67 (s, 2H), 7.44–7.60 (m, 6H), 7.85–7.90 (m, 4H), 7.96–8.00 (m, 2H), 8.10–8.12 (m, 2H), 8.58 (d, *J* = 4.5 Hz, 1H), 9.03 (s, 1H), 8.98 (d, *J* = 4.5 Hz, 1H), 9.02 (s, 1H), 9.31 (s, 1H), 10.03 (s, 1H); LD-MS obsd 640.7; FAB-MS obsd 640.2607, calcd 640.2627 (C₄₆H₃₂N₄); λ_{abs} (toluene) 429, 676 nm.

Alternative streamlined procedure for **FbC2**. A solution of Zn(II)-3, 13-bis(2-phenylethynyl)-17,18-dihydro-18,18-dimethyl-10-(4-(2-(triiso-propylsilyl)ethynyl)phenyl)-porphyrin (**ZnC5**) (20.8 mg, 0.0242 mmol) in 2.6 mL of THF was treated with TBAF (72.5 μ L, 3 equiv, 1 M in THF) and stirred for 0.5 h at room temperature. The mixture was

poured into CH₂Cl₂. The organic layer was extracted (5% NaHCO₃, H₂O), dried (Na₂SO₄) and concentrated. The resulting crude product was dissolved in CH₂Cl₂ (1.0 mL) and then treated dropwise with TFA (101 μ L, 1.30 mmOl) for 2 min. The solution was stirred at room temperature for 4 h. CH₂Cl₂ was added, and the reaction mixture was washed (saturated aqueous NaHCO₃, water, brine) and then dried (Na₂SO₄). The organic layer was concentrated and chromatographed (silica, hexanes then hexanes/CH₂Cl₂ [7:3]) to afford a green solid (13.2 mg, 85%): ¹H NMR δ –1.91 (brs, 1H), –1.50 (brs, 1H), 2.06 (s, 6H), 3.31 (s, 1H), 4.67 (s, 2H), 7.44–7.60 (m, 6H), 7.85–7.90 (m, 4H), 7.96–8.00 (m, 2H), 8.10–8.12 (m, 2H), 8.58 (d, *J* = 4.5 Hz, 1H), 9.02 (s, 1H), 9.31 (s, 1H), 10.03 (s, 1H); LD-MS obsd 640.7; FAB-MS obsd 640.2607, calcd 640.2627 (C₄₆H₃₂N₄); λ_{abs} (toluene) 429, 676 nm.

Zn(II)-3,13-Dibromo-17,18-dihydro-18,18-dimethyl-10-[4-(2-(triisopropylsilyl)ethynyl)-phenyl]porphyrin (ZnC4). Following a streamlined procedure (15), a solution of 2 (301 mg, 0.511 mmol) and 3 (138 mg, 0.511 mmol) in anhydrous CH₂Cl₂ (16 mL) was treated with solution of p-toluenesulfonic acid (p-TsOH·H₂O, 486 mg, 2.55 mmol) in anhydrous methanol (4 mL) under argon. The red reaction mixture was stirred at room temperature for 50 min. A sample of 2,2,6,6-tetramethylpiperidine (0.866 mL, 5.00 mmol) was added. The reaction mixture was concentrated. The resulting solid was dissolved in CH₃CN (51 mL) and subsequently treated with 2,2,6,6tetramethylpiperidine (2.17 mL, 12.7 mmol), Zn(OAc)₂ (1.41 g, 7.66 mmol) and silver triflate (AgOTf, 394 mg, 1.53 mmol). The resulting suspension was refluxed for 20 h exposed to air. The crude mixture was filtered through a pad of silica (CH₂Cl₂) followed by column chromatography of the resulting solid (silica, hexanes/CH2Cl2 [1:2]) to afford a green solid (112.8 mg, 27%): ¹H NMR (THF- d_8) δ 1.28 (brs, 21H), 2.04 (s, 6H), 4.60 (s, 2H), 7.82 (d, J = 7.8 Hz, 2H), 8.02 (d, J = 7.8 Hz, 2H), 8.43 (d, J = 4.0 Hz, 1H), 8.58-8.61 (m, 2H),8.84 (s, 2H), 8.90 (d, J = 4.0 Hz, 1H), 9.68 (s, 1H); LD-MS obsd 814.3; FAB-MS obsd 814.0671, calcd 8.0680 ($C_{39}H_{40}Br_2N_4SiZn$); λ_{abs} (toluene) 412, 622 nm.

 $Zn(\hat{II})$ -3, $\hat{I}3$ -Bis(2-phenylethynyl)-17,18-dihydro-18,18-dimethyl-10-[4-(2-(triisopropylsilyl)ethynyl)phenyl]porphyrin (**ZnC5**). Following a standard procedure (13,57,58), samples of **ZnC4** (54.6 mg, 0.0667 mmol) and phenylacetylene (59.5 μ L, 0.533 mmol) were coupled using Pd₂(dba)₃ (12.2 mg, 0.0133 mmol) and P(o-tol)₃ (24.4 mg, 0.0800 mmol) in toluene/TEA (51.1, 30 mL) at 60°C under argon. After 12 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was chromatographed (silica, hexanes then hexanes/CH₂Cl₂ [1:1]) to afford a green solid (41.6 mg, 72%): ¹H NMR (300 MHz) δ 1.26–1.28 (brs, 21H), 2.03 (s, 6H), 4.54 (s, 2H), 7.44–7.54 (m, 6H), 7.78–7.85 (m, 4H), 7.90–7.93 (m, 2H), 8.00– 8.03 (m, 2H), 8.45 (d, J = 4.5 Hz, 1H), 8.50 (s, 1H), 8.76 (s, 1H), 8.80 (s, 1H), 8.81 (d, J = 4.5 Hz, 1H), 9.00 (s, 1H), 9.70 (s, 1H); LD-MS obsd 855.3; FAB-MS obsd 858.3119, calcd 858.3096 (C₅₅H₅₀N₄SiZn); λ_{abs} (toluene) 427, 652 nm.

3,13-Bis(2-phenylethynyl)-17,18-dihydro-18,18-dimethyl-10-[4-(2-(triisopropylsilyl)ethynyl)phenyl]porphyrin (FbC5). A solution of **ZnC5** (37.4 mg, 0.0434 mmol) in CH₂Cl₂ (1.4 mL) was treated dropwise with TFA (101 μ L, 1.30 mmol) for 2 min. The solution was stirred at room temperature for 3 h. CH₂Cl₂ was added, and the reaction mixture was washed (saturated aqueous NaHCO₃, water, brine) and then dried (Na₂SO₄). The organic layer was concentrated and chromatographed (silica, hexanes then hexanes/CH₂Cl₂ [8:2]) to afford a green solid (26.8 mg, 77%): ¹H NMR δ –1.92 (brs, 1H), -1.50 (brs, 1H), 1.25–1.28 (brs, 21H), 2.07 (s, 6H), 4.66 (s, 2H), 7.44–7.60 (m, 6H), 7.86–7.90 (m, 4H), 7.97–8.00 (m, 2H), 8.10–8.12 (m, 2H), 8.60 (d, J = 4.5 Hz, 1H), 8.82 (s, 1H), 8.90 (s, 1H), 8.98 (d, J = 4.5 Hz, 1H), 9.02 (s, 1H), 10.02 (s, 1H); LD-MS obsd 796.9; FAB-MS obsd 797.4073, calcd 797.4040 [(M + H)⁺, M = C₅₅H₅₂N₄Si]; λ_{abs} (toluene) 429, 676 nm.

Chlorin-bacteriochlorin dyad **FbC-pe-FbB**. Following a reported procedure (17,57-59), samples of **FbC2** (11.2 mg, 0.0175 mmol) and **FbB3** (11.5 mg, 0.0175 mmol) were coupled using Pd₂(dba)₃ (3.20 mg, 0.00350 mmol) and P(o-tol)₃ (6.92 mg, 0.0227 mmol) in toluene/TEA (5:1, 8.0 mL) at 60° C under argon. After 6 h, Pd₂(dba)₃ (3.20 mg, 0.00350 mmol) and P(o-tol)₃ (6.92 mg, 0.0227 mmol) were added to the reaction mixture. After 13 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was filtered through a pad of silica (hexanes/CH₂Cl₂, [1:2]). The eluate was

concentrated and then further purified by preparative SEC (THF) and column chromatography (silica, hexanes/CH₂Cl₂ [4:6]). (The final silica column chromatography procedure removes any residual impurities including polystyrene-derived fragments from the SEC column.) The desired fraction was concentrated to give a purple solid (9.3 mg, 44%): ¹H NMR (300 MHz) δ –1.98 (brs, 1H), –1.62 (brs, 1H), –1.45 (brs, 1H), -1.17 (brs, 1H), 1.94, 2.01 (2s, 12H), 2.04 (s, 6H), 2.62 (s, 6H), 4.38 (s, 2H), 4.50-4.54 (m, 3H), 4.67 (s, 2H), 4.79 (s, 2H), 7.20-7.64 (m, 12H), 7.85-8.30 (m, 10H), 8.6 (s, 1H), 8.67-8.77 (m, 3H), 8.83 (brs, 1H), 8.92-8.94(m, 2H), 9.04 (brs, 1H), 9.32 (brs, 1H), 9.87 (s, 1H), 9.88 (s, 1H); LD-MS obsd 1218.2; FAB-MS obsd 1219.5783, calcd 1219.5751 [(M + H)⁺, M = C₈₅H₇₀N₈O]; λ_{abs} (toluene) 387, 430, 554, 675, 756 nm. Note: The column chromatography (silica) of FbC-pe-FbB should be performed in an expeditious manner, as the compound decomposed during lengthy (~3 h) purification on silica. Following isolation, the dyad was quite stable upon routine handling in toluene and upon prolonged storage (>1 year at 0°C).

Photophysical measurements. Static absorption (Varian Cary 100) and fluorescence (Spex Fluorolog Tau 2) measurements were performed as described previously for other compounds, typically for very dilute (μ M) solutions of the compounds in toluene (61,62). Fluorescence lifetimes were obtained using a phase-modulation technique (61). Argon-purged solutions with an absorbance of ≤ 0.10 at λ_{exc} were used for the fluorescence spectral and lifetime measurements. For fluorescence spectra, the excitation or detection monochromator typically had a band pass of 1.8 or 3.7 nm, respectively, and spectra were obtained using 0.2 nm data intervals. The emission spectra were corrected for detection-system spectral response. Fluorescence quantum yields were determined for argon-purged solutions of the compound relative to chlorophyll *a* in benzene ($\Phi_f = 0.325$ [63]) and were corrected for solvent refractive index. Transient absorption measurements utilized 5–10 μ M solutions excited with 130 fs, 8 μ J, 431 nm flashes and probed with white-light pulses of comparable durations (64). All measurements were carried out at room temper-

The fits of the transient-absorption time profiles for **FbC-pe-FbB** in Fig. 3 utilized a function consisting of the instrument profile plus two exponentials plus a constant. The shorter and longer components reflect the lifetimes of the excited chlorin and bacteriochlorin components, respectively. The same time constant for the shorter component is derived within the reported error limits for any of the following conditions: (1) the time constant for the longer component is fixed to have the 5.4 ns lifetime of the excited bacteriochlorin measured by fluorescence detection, or (3) the time profiles are truncated at ~ 100 ps and fit to a function containing a single exponential decay. Local and global data fitting were carried out using routines written with IgorPro software (Wavemetrics, Inc.).

Calculations. Förster calculations. Calculations of the rate of excited-state energy transfer assuming a Förster TS mechanism were carried out using PhotochemCad (65). The calculations were performed for three phenylethyne-linked dyads in toluene: chlorinbacteriochlorin FbC-pe-FbB, oxochlorin-oxochlorin ZnO-pe-FbO and porphyrin-porphyrin ZnP-pe-FbP. The following parameters were utilized in the calculations for all three dyads: dielectric constant, 1.496; orientation factor $\kappa^2 = 1.125$ on the basis of similar calculations on other tetrapyrrole dyads (38,66); center-to-center distance, R = 15.6 Å. For all three dyads, these calculations assumed that (1) the dipole-dipole approximation is valid, (2) the same center-to-center separation of the macrocycles is the relevant distance even though the three dyads may differ in the extent to which electron density is delocalized onto the linker and other peripheral groups, (3) the same orientation factor applies even though there may be differences in the alignment of the relevant transition dipoles. These assumptions are reasonable considering the uncertainties involved. Moreover, the range of uncertainties is not sufficient to account for the significant differences in the Förster rates that are calculated among the different classes of dyads (vide infra).

The Förster calculations on the three dyads also employed the following dyad-specific parameters. Dyad **FbC-pe-FbB**: FbC fluore-scence yield $\Phi_f = 0.42$ and excited-state lifetime $\tau = 8.0$ ns (for reference compound **FbC2**); FbB molar absorption coefficient $\epsilon = 120\ 000\ M^{-1}cm^{-1}$ at the $Q_y(0,0)$ maximum of 755 nm on the basis of a literature value for the parent compound **FbB1** (12); also see

Ref. 67 for estimates for the 15-arylethynyl analog thereof. Dvad ZnO**pe-FbO**: ZnO fluorescence yield $\Phi_f = 0.04$ and excited-state lifetime $\hat{\tau} = 0.7$ ns; FbO molar absorption coefficient $\epsilon = 54\ 000\ \text{M}^{-1}\text{cm}^{-1}$ at the $Q_{1}(0,0)$ maximum of 658 nm on the basis of values for reference compounds (39). Dyad ZnP-pe-FbP: ZnP fluorescence yield $\Phi_{\rm f} = 0.035$ and excited-state lifetime $\tau = 2.4$ ns on the basis of values for related reference compounds (38,39); FbP molar absorption coefficient $\epsilon = 45\ 000\ \text{M}^{-1}\text{cm}^{-1}$ at the $Q_y(0,0)$ maximum of 574 nm, which was obtained using the spectrum for 5-(2-phenylethynyl)-10,15,20-triphenylporphyrin obtained herein and assuming that the latter compound has the same ε value at the $Q_{\nu}(1,0)$ maximum as that for an analog in which the phenyl rather than the ethynyl moiety of the phenylethynyl group is attached to the macrocycle, namely Zn(II)-5-(4ethvnvlphenvl)-10,15,20-trimesitylporphyrin (38). Finally, an additional calculation was performed on FbC-pe-FbB using $\Phi_f \sim 0.3$ and $\epsilon \sim 80\ 000\ {\rm M}^{-1}{\rm cm}^{-1}$ to examine how reasonable extremes in these parameters (based on data from related chlorins and bacteriochlorins) would affect the calculated Förster rate.

Density functional theory calculations. Density functional theory calculations were performed with Spartan '06 for Windows (Wavefunction, Inc.) (67) on a PC (Dell Optiplex GX270) equipped with a 3.2 GHz CPU and 3 GB RAM. The hybrid B3LYP functional and a $6-31G^*$ basis set were employed. For the calculations on each complex, the complete structure was used in the geometry optimization. The equilibrium geometries were fully optimized using the default parameters of the Spartan '06 program.

RESULTS

Synthesis

General. The synthetic approach to the free base chlorin– bacteriochlorin dyad relies on the following pathways: (1) a rational synthesis of chlorin building blocks (13), which affords a chlorin containing 3,13-bis(phenylethynyl) and 10ethynylphenyl groups, and (2) a copper-free Pd-catalyzed Sonogashira coupling (57–59) of the ethynylphenylchlorin and a bromobacteriochlorin (17) to give the phenylethyne-linked chlorin–bacteriochlorin construct.

Benchmark compounds. Four compounds were employed for comparison in the photophysical studies (Chart 2). Free base bacteriochlorins FbB1 (12) and FbB2 (17) were prepared using literature procedures, whereas the chlorins FbC1 and FbC2 were prepared herein. The synthesis of free base chlorin FbC1, which bears 3.13-phenylethynyl groups and a 10-mesityl substituent, is shown in Scheme 1. The conversion of 3,13dibromochlorin ZnC3 to the corresponding 3,13-bis(phenylethynyl)chlorin was performed by the copper-free Pd-mediated Sonogashira coupling using phenylacetylene. This method avoids possible transmetalation during the reaction with the zinc chelate. Thus, reaction of 3,13-dibromochlorin ZnC3 (13) with phenylacetylene in the presence of $Pd_2(dba)_3$ and $P(o-tol)_3$ gave 3,13-bis(phenylethynyl)chlorin ZnC1 in 72% yield. Demetalation of zinc chlorin ZnC1 with TFA in CH₂Cl₂ at room temperature gave the free base 3,13-bis(phenylethynyl)chlorin FbC1 in 87% yield. Compound FbC1 was characterized by absorption spectroscopy, ¹H NMR spectroscopy, LD-MS and FAB-MS analyses. The synthesis of free base chlorin FbC2, a benchmark and precursor to the dyad, is described below.

Chlorin precursors. The synthesis of chlorins relies on the condensation of an Eastern half and a Western half. The synthesis of the Eastern half employed herein begins with known 1-formyldipyrromethane 1 (60). Treatment of 1 with



2.0 molar equiv of NBS at -78° C gave the 8,9-dibromo-1formyldipyrromethane **2** in 72% yield (Scheme 2). The bromination occurs chemoselectively at the pyrrole unit in the presence of the ethyne and the formylpyrrole moieties, and regioselectively at the vicinal α -and β - (*i.e.* 8- and 9-) positions of the pyrrole. The stability of dibromo compound **2** is similar to that of analogous dibromo compounds (13). The 8,9dibromo-substitution pattern in **2** was established by NMR spectroscopy (HH-COSY and NOESY experiments). Compound **2** serves as the Eastern half for the chlorin-forming reaction. The bromo-substituted Western half **3** was prepared following literature procedures (13).

Chlorin formation. The synthesis of the 3,13-dibromochlorin **ZnC4** is shown in Scheme 2. The condensation of Eastern half **2** and Western half **3** in anhydrous CH_2Cl_2 was performed using a solution of *p*-TsOH·H₂O in anhydrous methanol under argon, affording a clear reddish-brown solution for 40–50 min. Neutralization with 2,2,6,6-tetra-methylpiperidine followed by concentration of the reaction mixture afforded a yellow solid. This crude tetrahydrobila-diene-*ab* was subjected to metal-mediated oxidative cyclization (2,2,6,6-tetramethylpiperidine, Zn(OAc)₂ and AgOTf) in refluxing acetonitrile in the presence of air for 20 h, affording the zinc chelate of the 3,13-dibromochlorin (**ZnC4**) in 27% yield starting from **2**. Compound **ZnC4**



was characterized by ¹H NMR spectroscopy, LD-MS and FAB-MS analyses.

The synthesis of the chlorin benchmark and building block FbC2 is shown in Scheme 3. The Sonogashira coupling of dibromochlorin ZnC4 and phenylacetylene was carried out in the presence of Pd₂(dba)₃ (20 mol%) and P(o-tol)₃ in toluene/TEA (5:1) at 60°C. After 18 h, workup including column chromatography gave 3,13-bis(phenylethynyl)chlorin ZnC5 in 72% yield. Demetalation of ZnC5 with TFA afforded the free base 3,13-bis(phenylethynyl)chlorin FbC5 in 77% yield. The free base chlorin FbC5 serves as the benchmark compound for the chlorin-bacteriochlorin dyad in photophysical studies. The cleavage of the triisopropylsilyl group in free base chlorin FbC5 using TBAF afforded the desired chlorin FbC2 in only 40% yield (along with the formation of several unknown chlorins), whereas use of the zinc chelate ZnC5 gave quantitative cleavage. Demetalation of the crude product with TFA afforded the free base chlorin FbC2 in 85% yield starting from ZnC5. The chlorins were characterized by absorption spectroscopy, ¹H NMR spectroscopy, LD-MS and FAB-MS analyses.

Phenylethyne-linked chlorin–bacteriochlorin dyad. The synthesis of **FbC-pe-FbB** was achieved through use of the copper-free Sonogashira coupling reaction (57,58), which has been applied for the synthesis of analogous phenylethyne-linked porphyrin



dyads (59). Thus, treatment of ethynylphenylchlorin **FbC2** and bromobacteriochlorin **FbB3** under the standard reaction conditions (20 mol% $Pd_2(dba)_3$ and $P(o-tol)_3$ in toluene/TEA [5:1] at 60°C with 1 equiv of each hydroporphyrin) afforded **FbC-pe-FbB** in 62% yield as judged by analytical SEC. The purification of the **FbC-pe-FbB** proceeds as follows: (1) removal of palladium reagents by silica-pad filtration, (2) separation of the target dyad by gravity-flow SEC and (3) final silica column chromatography to remove residual impurities. This three-column sequence has been used extensively to good effect in the synthesis of other dyads and larger arrays (57,58). In this manner, **FbC-pe-FbB** was isolated in 44% yield (Scheme 4). **FbC-pe-FbB** was characterized by absorption and fluorescence spectroscopy, ¹H NMR spectroscopy, LD-MS and FAB-MS analyses.

Photophysical characterization

Absorption spectra. The absorption spectra for the FbCpe-FbB dyad and the benchmark monomers chlorin FbC1 and bacteriochlorin FbB2 in toluene are shown in Fig. 1 (solid



spectra). The wavelengths of the main absorption bands for these compounds and additional reference monomers are listed in Table 1. The spectrum of **FbC-pe-FbB** is essentially the sum of the spectra of the benchmark monomers. This result is a manifestation of relatively weak (but not insignificant) electronic coupling between the two constituents of the dyad. The phenylethyne-linked arrays are thus quite distinct from the arrays wherein an ethynyl moiety directly joins two tetrapyrrole macrocycles; the latter exhibit profound spectral changes because of strong electronic coupling between the macrocycles.

	Table 1.	Summary	of photo	physical	data.*
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Several points regarding the absorption spectra are noteworthy. (1) The prominent low-energy feature (755 nm) in the spectrum of FbC-pe-FbB is exclusively the bacteriochlorin $Q_{\nu}(0,0)$ band, which is expected to have a molar absorption coefficient of $\sim 120\ 000\ M^{-1}\ cm^{-1}$ by analogy with the results for a related bacteriochlorin (12,68). (2) The spectra of chlorin reference compounds FbC1, FbC2 and FbC5 (Chart 2, Scheme 3) are basically indistinguishable. This result indicates the minimal effect of attachment of the ethyne group on the meso-aryl ring of the chlorin, similar to previous findings on porphyrin analogs (66). (3) The main absorption bands for the ethynylbacteriochlorin in FbC-pe-FbB and benchmark compound FbB2 (387, 548, 754 nm) are significantly redshifted compared to an analog FbB1, which lacks the ethynyl substituent (373, 511, 731 nm). Similarly, the bacteriochlorin $Q_{\nu}(0,0)/B(0,0)$ peak-intensity ratios for FbC-pe-FbB and FbB2 are larger than in FbB1. These spectral characteristics parallel those observed when an ethynyl group is directly appended to synthetic chlorins (20,21).

Fluorescence spectra, quantum yields and lifetimes. Fluorescence spectra of FbC-pe-FbB, chlorin FbC1 and bacteriochlorin FbB2 in toluene are shown in Fig. 1 (dashed spectra). The wavelengths of the prominent fluorescence features are listed in Table 1. Several points are particularly noteworthy regarding these spectra. The chlorin fluorescence (681 nm) observed for FbC-pe-FbB using several different excitation wavelengths (387, 430, 515, 550 nm) is reduced in intensity at least 50-fold compared to the level in monomers FbC1, FbC2 and FbC5. In contrast, the intensity of the bacteriochlorin fluorescence (760 nm) in FbC-pe-FbB is similar to that found for reference compound FbB2 regardless of whether the chlorin or bacteriochlorin component of the dyad is primarily excited; the corresponding fluorescence yield is $\Phi_f = 0.19$ (Table 1). Similarly, the lifetime of the lowest-energy (Q_v) singlet excited state of the bacteriochlorin constituent of FbC**pe-FbB** in toluene ($\tau = 5.4 \pm 0.5$ ns) is the same within experimental error as that measured for reference monomer FbB2 (5.7 \pm 0.6 ns) or for an analogous 5-methoxy-15-(arylethynyl)bacteriochlorin ($\Phi_f = 0.16$, $\tau = 5.3$ ns) examined previously (68). Thus, upon excitation of the chlorin, energy flows in very high yield to the bacteriochlorin. The resulting excited bacteriochlorin then behaves as though it were an isolated ethynylbacteriochlorin, with no (chargetransfer) quenching due to the presence of the chlorin constituent.

Compound	$\lambda_{\rm B}~({\rm nm})$	λ_{Q_y} (nm)	$\lambda_{\rm em}$ (nm)	Chlorin		Bacteriochlorin	
				$\Phi_{ m f}$	τ (ns)	$\Phi_{ m f}$	τ (ns)
FbC-pe-FbB	387, 430	755	760	< 0.01	0.0048 ± 0.0002	0.19	5.4 ± 0.5
FbC5	429	676	677	0.39	8.0 ± 0.5		
FbC2	430	675	677	0.42	$8.0~\pm~0.5$		
FbC1	429	676	678	0.37	8.1 ± 0.5		
FbB2	387	754	759			0.19	5.7 ± 0.6
FbB1	373	731	736			0.18	$4.8~\pm~0.5$
FbC5 FbC2 FbC1 FbB2 FbB1	429 430 429 387 373	676 675 676 754 731	677 677 678 759 736	0.39 0.42 0.37	$\begin{array}{r} 8.0 \ \pm \ 0.5 \\ 8.0 \ \pm \ 0.5 \\ 8.1 \ \pm \ 0.5 \end{array}$	0.19 0.18	

*For compounds in toluene at room temperature.



Figure 1. Normalized absorption spectra (solid) and fluorescence spectra (dashed) for (A) FbC-pe-FbB, (B) benchmark bacteriochlorin monomer FbB2 and (C) benchmark chlorin monomer FbC1 in toluene at room temperature. The excitation wavelengths used to elicit the fluorescence are 554 nm (FbC-pe-FbB), 548 nm (FbB2) and 550 nm (FbC1).

Transient absorption studies. Figure 2 shows representative time-resolved absorption difference spectra $(\Delta A =$ $A_{\text{transient state}} - A_{\text{ground state}}$ for **FbC-pe-FbB** in toluene. Typical kinetic profiles are shown in Fig. 3. The data were acquired using a 130 fs excitation flash at 431 nm, which is absorbed primarily (~85%) by the chlorin constituent of the dyad (see Fig. 1). As a consequence, the chlorin $Q_{\nu}(0,0)$ ground-state absorption band at 675 nm bleaches with the instrument response. The feature at this wavelength in the spectrum at 0.5 ps (Fig. 2) also contains a contribution from chlorin $Q_{\nu}(0,0)$ excited-state stimulated emission. This emission is stimulated by the white-light probe pulse and is expected to have a shape similar to the static fluorescence profile of the chlorin, which is only slightly redshifted from the $Q_{\nu}(0,0)$ ground-state absorption band (see Fig. 1C). The combined $Q_{\nu}(0,0)$ bleaching and stimulated-emission feature of the chlorin at 675 nm disappears by 30 ps (Fig. 2). This decay occurs with a time constant of 4.7 \pm 0.2 ps, determined from global analysis of the decay profiles at 2 nm wavelength increments across this feature (Fig. 3A).



Figure 2. Time-resolved absorption difference spectra for **FbC-pe-FbB** in toluene at room temperature at two time delays following excitation with a 130 fs, 431 nm flash.



Figure 3. Representative kinetic profiles and fits for (A) the decay of the chlorin feature at 675 nm consisting of ground-state absorption bleaching plus excited-state stimulated emission and (B) growth of the analogous bacteriochlorin feature at 760 nm.

The decay of the chlorin feature at 675 nm is paralleled by a growth in the analogous combined $Q_y(0,0)$ bleaching plus stimulated emission due to the bacteriochlorin at 760 nm. This feature grows with a time constant of 4.9 ± 0.2 ps (Fig. 3B). As can be seen from the spectrum at 0.5 ps (Fig. 2), a small fraction of the bacteriochlorin feature develops more rapidly (with the instrument response). This latter contribution reflects the fact that the bacteriochlorin component of the dyad absorbs ~15% of the excitation photons. The bacteriochlorin $Q_y(0,0)$ feature at 760 nm is fully developed by ~30 ps, in concert with the decay of the chlorin $Q_y(0,0)$ feature. Subsequently, the difference spectrum does not change shape over the 2 ns time course of the measurements; however, the spectrum decays slightly in amplitude consistent with the 5.4 ns lifetime of the Q_y excited state of the bacteriochlorin determined above using fluorescence detection (Table 1).

Rate and yield of excited-state energy transfer. The characteristics of the energy-transfer process are readily derived using standard analysis embodied in Eq. (1)

$$k_{\rm ENT} = (\tau_{\rm C}^{\rm dyad})^{-1} - (\tau_{\rm C}^{\rm mon})^{-1}$$
 (1*a*)

$$\phi_{\rm ENT} = k_{\rm ENT} \, \times \, \tau_{\rm C}^{\rm dyad} \tag{1b}$$

Here, $\tau_{\rm C}^{\rm mon}$ is the lifetime of the excited chlorin benchmark monomer, which is governed by the rates of fluorescence, internal conversion and intersystem crossing. The lifetime of the excited chlorin in dyad **FbC-pe-FbB** is taken to be the average of the time constants for decay/growth of the chlorin/bacteriochlorin features in the transient absorption spectra described above, namely $\tau_{\rm C}^{\rm dyad} = 4.8$ ps. Thus, the lifetime for the excited chlorin in **FbC-pe-FbB** is considerably shorter than that for benchmark **FbC1** ($\tau_{\rm C}^{\rm mon} = 8.1$ ns) because of energy transfer to the bacteriochlorin. Substitution of the measured lifetimes into Eq. (1) gives a rate constant of $k_{\rm ENT} = (4.8 \text{ ps})^{-1}$ and a yield of $\Phi_{\rm ENT} > 0.99$ for the energytransfer process. Thus, excitation energy transfer from chlorin to bacteriochlorin is rapid and essentially quantitative.

DISCUSSION

Understanding the mechanism(s) of energy transfer in multicomponent architectures is essential for the rational design of systems wherein energy flow to a designated site occurs in an efficient manner. In covalently linked architectures, energy transfer can occur by two parallel mechanisms (55). One mechanism is the well-known Förster process, which entails the resonant coupling of the transition-dipole moments of the excited donor and the ground-state acceptor. The expected rate and efficiency of this process can be calculated for the energy donor and acceptor interacting TS in the geometry fixed by the covalent linker that joins the constituents in the dyad, even though the presence of the linker is not a factor in the calculation. The Förster process falls off as $1/R^6$, where R is typically taken as the center-to-center distance of the donor and acceptor chromophores. The other mechanism is the Dexter process, which entails the overlap of the wavefunctions of the excited donor and ground-state acceptor. The Dexter process typically falls off exponentially with distance. For dyads wherein the components are held more than a few bond lengths apart, a significant TS component to this electron-exchange interaction is precluded, and the process is driven by TB coupling mediated by the covalent linker that joins the donor and acceptor constituents of the dyad.

In practice, calculation of the Förster TS process is straightforward whereas that of the Dexter TB process is beyond the scope of the present paper. Hence, the presence of a TB process is typically inferred by the observation of an energy-transfer rate that is substantially faster than the rate calculated on the basis of TS (*i.e.* Förster) considerations. Thus, the observed energy-transfer rate is the sum of the TS and TB mechanisms, as shown in Eq. 2:

$$k_{\rm ENT} = k_{\rm TS} + k_{\rm TB} \tag{2}$$

Evidence for the TB mechanism can be obtained in several ways: (1) by alteration of the energy levels of the linker, (2) by structural constraints on the linkerdonor/acceptor attachment site such that conjugation between the linker and the donor or acceptor is altered, and (3) by attaching the linker to sites on the donor or acceptor where the frontier MOs have significant electron density versus nodes. None of these alterations is expected to change the TS contribution to energy transfer as long as the spectral features, distance of separation and transition-dipole orientation factor remain unchanged. We previously investigated a wide variety of porphyrin-porphyrin dyads and found that the dominant mechanism of energy transfer was a TB process mediated by the linker, with only a minor contribution via the Förster TS process (55). As part of this earlier work, sets of porphyrin-porphyrin arrays were designed to probe the TB process by each of the three aforementioned structural/electronic alterations.

In the following sections, we first assess the TS versus TB contributions to energy transfer in the chlorin-bacteriochlorin dyad FbC-pe-FbB. In this regard, we expected that energy transfer in this dyad would have a substantial, if not dominant, contribution from a TS mechanism, given the strong oscillator strength of the donor and acceptor transitions that give rise to the lowest energy emission/absorption bands (i.e. in the red/NIR). We then address the related question as to what extent TB electronic interactions might be present, as evidenced by the electron-density distributions in the frontier MOs of the energy donor and acceptor constituents of the dyad. To provide additional perspective on the interplay of TS and TB contributions to energy transfer in tetrapyrrole dyads in general, we then compare the energy-transfer characteristics of the chlorin-bacteriochlorin dyad FbC-pe-FbB with those previously obtained for analogous phenylethyne-linked dyads consisting of two porphyrins or two oxochlorins (39). These comparisons are facilitated by Förster TS energy-transfer calculations on the latter classes of dyads, as well as DFT calculations on their energy-donor and acceptor constituents that are aimed at assessing potential TB interactions (as dictated by the electron-density distributions in the frontier MOs).

Mechanism of energy transfer in chlorin-bacteriochlorin dyad FbC-pe-FbB

The Förster calculations on the yield and rate of the TS excitation energy-transfer from the chlorin to bacteriochlorin in **FbC-pe-FbB** result in values of $\Phi_{TS} = 0.99$ and $k_{TS} = (5.6 \text{ ps})^{-1}$. This very fast TS rate is driven by the strong transition dipole strengths of the hydroporphyrin

energy donor and acceptor constituents of the dyad. The finding that the calculated Förster rate is only marginally smaller than the measured value of $k_{\rm ENT} = (4.8 \text{ ps})^{-1}$ implies that the TS mechanism dominates energy transfer in the dyad. However, before drawing a firm conclusion, it is useful to explore how the uncertainties in the parameters used in the Förster calculations (e.g. the fluorescence yield of the energy donor and the molar absorption coefficient of the energy acceptor) affect the calculated TS energy-transfer rate. Accordingly, an additional calculation was performed in which the above parameters were altered to encompass reasonable lower limits based on data from related chlorins and bacteriochlorins (see Materials and Methods). This calculation resulted in a slightly slower Förster rate of $k_{\rm TS} = (12 \text{ ps})^{-1}$. The latter value when compared with the measured value of $k_{\rm ENT} = (4.8 \text{ ps})^{-1}$ would imply that the TS and TB mechanisms actually make comparable contributions to the energy-transfer dynamics in FbC-pe-FbB (see Eq. 2). Regardless, energy transfer is nearly quantitative because the measured rate, as well as the Förster rate calculated with a range of reasonable parameters, is at least 500-fold faster than the rate of the competitive intrinsic (monomer-like) decay processes in the excited chlorin.

Further insight into the extent to which TB electronic interactions might complement the clearly substantial TS contribution to energy transfer in FbC-pe-FbB can be gained via examination of the electron-density distributions in the frontier MO constituents of the dyad. The calculated electrondensity distributions are shown for the associated reference compounds in Fig. 4. The characteristics of all four orbitals are relevant because the Q_v excited states of both the chlorin and bacteriochlorin are composed of admixtures of promotions from the highest-occupied molecular orbital (HOMO) to the lowest-unoccupied molecular orbital (LUMO) and the secondhighest occupied molecular orbital (HOMO-1) to the secondlowest unoccupied molecular orbital (LUMO + 1) (69). In this regard, recent DFT calculations indicate that the contributions of the (HOMO \rightarrow LUMO)/(HOMO-1 \rightarrow LUMO+1) promotions to the Q_{y} excited state of chlorins and bacteriochlorins are approximately 60/40 and 70/30, respectively (70). This ratio of contributions is 50/50 for porphyrins.

Inspection of Fig. 4 reveals the following characteristics of the frontier MOs for chlorin–bacteriochlorin dyad **FbC-pe-FbB**.

(1) For the ethynylphenyl-substituted chlorin (Fig. 4A), there is relatively little electron density delocalized onto the ethynylphenyl group in any of the frontier MOs. (Note that "ethynylphenyl" implies the phenyl group is attached to the chlorin macrocycle and the ethyne moiety is a substituent on the phenyl ring. Conversely, "phenylethynyl" implies attachment of the ethynyl group to the macrocycle. See Chart 2.)

(2) For the phenylethynyl-substituted bacteriochlorin (Fig. 4B), there is little electron-density delocalized onto the phenylethynyl group in either the HOMO or LUMO; however, the extent of electron-density delocalization in the HOMO–1 and LUMO+1 is significant. In this regard, it should be noted that the phenyl of the phenylethynyl group can rotate with respect to the ethyne, and that the rotational barrier (governed by steric interactions, *etc.*) is only a fraction of kT. Furthermore, the rotation angle impacts the extent to which electron density delocalized from the macrocycle onto the ethyne



Figure 4. Electron-density distributions and energies of the frontier molecular-orbitals of the reference monomeric components of FbC-pe-FbB.

moiety is further delocalized onto the phenyl ring. For the minimized structure shown in Fig. 4B, the phenyl group is effectively coplanar with the bacteriochlorin macrocycle, so

that electron density in the HOMO-1 and LUMO+1 is delocalized both onto the ethyne and the phenyl. For other rotational angles, the electron density on the ethyne would remain substantial but that on the phenyl will diminish.

(3) For both the chlorin and bacteriochlorin, the HOMO has essentially no electron density at the *meso* position, which is the site of linker attachment for both constituents of the dyad. The latter result is expected because the HOMO of hydroporphyrins is an $a_2(\pi)$ orbital, which is derived from the porphyrin $a_{1u}(\pi)$ orbital that is the HOMO–1 for most *meso*-substituted porphyrins (see below).

Collectively, the electron-density distributions predicted for the constituents of FbC-pe-FbB imply relatively weak TB electronic interactions. The relevant electron-density distributions include the near-absence of electron density on the linker in any of the frontier MOs of the energy-donor chlorin, and the minimal electron-density on the linker of the HOMO and LUMO of the energy-acceptor bacteriochlorin (which make the major contribution to the wavefunction of the Q_y excited state [70]). Thus, the most consistent picture of energy transfer in FbC-pe-FbB is one wherein the TS contribution dominates. This is the result predicted by the Förster calculations performed using spectral parameters derived from benchmark monomers versus the calculation performed using spectral parameters that give a lower bound for TS interactions. Below, the energy-transfer characteristics of the chlorin-bacteriochlorin dyad are compared with those of different classes of tetrapyrrole dyads.

Comparison with results on other tetrapyrrole dyads

The energy-transfer mechanism in the chlorin-bacteriochlorin dyad can be compared with those that are operative in dyads that we have previously examined. These latter dyads are composed of either porphyrin (P) or oxochlorin (O) constituents linked by the same phenylethyne linker present in FbC-pe-FbB. In each case, the linker is attached to the *meso* (as opposed to β -pyrrole) positions of the tetrapyrrole constituents. The arrays studied earlier include the dyads denoted ZnP-pe-FbP and ZnO-pe-FbO in Chart 3. In all cases, the energy acceptor (i.e. bacteriochlorin in FbC-pe-FbB, free base porphyrin in ZnP-pe-FbP and free base oxochlorin in ZnO-pe-FbO) is the macrocycle that is directly appended to the ethynyl group of the linker. This follows because the singlet excited-state energy of the bacteriochlorin is intrinsically lower than that of the chlorin, likewise for the free base oxochlorin and porphyrin versus the metalated analogs. The ethynyl group appended to the energy acceptor serves to further lower the singlet excited-state energy, as evidenced by the substantial (up to 30 nm) absorption band shifts resulting from direct attachment of an ethynyl (or phenylethynyl) group to tetrapyrroles (20,21,39,71-73). For example, reference compound 5-(2-phenylethynyl)-10,15,20triphenylporphyrin (prepared here as a benchmark for the energy acceptor in the Förster calculations for ZnP-pe-FbP) has its $Q_{x}(0,0)$ absorption band at 668 nm (1.85 eV) compared with 649 nm (1.91 eV) for an analog in which the phenyl, rather than ethynyl, moiety of the phenylethynyl group is attached to a meso position of the porphyrin macrocycle.



Porphyrin–porphyrin dyad. In the case of porphyrin–porphyrin dyad **ZnP-pe-FbP**, we found previously that energy transfer from the zinc to free base subunit has a rate constant of $k_{\rm ENT} > (1 \text{ ps})^{-1}$ and an efficiency of $\Phi_{\rm ENT} > 99\%$. In contrast, the calculated Förster rate is $k_{\rm TS} = (57 \text{ ps})^{-1}$. The fact that the TS rate is at least 50-fold smaller than the measured value suggests that energy transfer in **ZnP-pe-FbP** is dominated by an electron-exchange-mediated TB mechanism (39). We previously found that the latter mechanism also dominates in related porphyrin dyads employing a diphenyl-ethyne linker or *p*-phenylene linker (55).

The significant TB contribution to energy transfer in the porphyrin–porphyrin dyad can be rationalized in terms of the characteristics of the frontier molecular orbitals (Fig. 5) as follows.

(2) Significant electron density is delocalized onto the ethyne moiety of the phenylethynyl group for the HOMO and LUMO of the phenylethynylporphyrin (Fig. 5B). However, there is little delocalization further onto the phenyl for the minimized, static structure shown. Nonetheless, even small rotations that move the phenyl and macrocycle away from perpendicularity will shift electron density from the intervening ethyne onto the phenyl ring, as is seen in the minimized structure for the analogous bacteriochlorin (Fig. 4B).

Collectively, the results and analysis support the dominance of the TB mechanism for excited-state energy transfer between *meso*-phenylethyne-linked porphyrins such as **ZnP-pe-FbP**. It should be noted, however, that the dominance of the TB mechanism for **ZnP-pe-FbP** does not imply that this mechanism completely dominates energy transfer in all classes of porphyrin dyads. In particular, we have shown that for porphyrin arrays wherein the HOMOs of the constituents are switched from $a_{2u}(\pi)$ to $a_{1u}(\pi)$, the overall energy-transfer rate is decreased by an order of magnitude and that the TS process becomes important (55). The decreased energy-transfer rate is a result of diminished TB electronic coupling that arises because the $a_{1u}(\pi)$ orbital has a node at the *meso*-site of linker attachment.

Oxochlorin-oxochlorin dyad. In the case of oxochlorin-oxochlorin dyad ZnO-pe-FbO, we previously found that energy transfer from the zinc to free base subunit has a measured rate constant $k_{\rm ENT} = (10 \text{ ps})^{-1}$ and an efficiency $\Phi_{\rm ENT} >$ 99%. The calculated Förster rate is $k_{\text{TS}} = (9.5 \text{ ps})^{-1}$. The finding that the measured and calculated Förster rates are comparable to one another suggests that the TS mechanism makes a substantial, perhaps the dominant, contribution to energy transfer in the oxochlorin-oxochlorin dyad. Nonetheless, the perturbations to the optical spectra observed previously upon the successive addition to the energyacceptor free-base oxochlorin of the ethyne, phenyl and then the energy-donor zinc oxochlorin to construct the dyad indicate that the inter-subunit TB interactions are significant, albeit weaker than in porphyrin-porphyrin dyad ZnP-pe-FbP (39). The potential TB contribution to excitation energy transfer between the two meso-linked oxochlorins in ZnO-pe-FbO versus the two meso-linked porphyrins in ZnP-pe-FbP can be further assessed by extending the arguments given above for ZnP-pe-FbP and FbC-pe-FbB.

(1) The HOMO of the phenylethynyl-substituted free base oxochlorin remains the $a_{2u}(\pi)$ -derived orbital (Fig. 6B) that is also the HOMO in the free base porphyrin (Fig. 5B). This result is unexpected, given that (to our knowledge) all other chlorin-type molecules examined to date exhibit $a_{1u}(\pi)$ -derived HOMOs, including the ethynylphenyl-substituted zinc oxochlorin constituent of **ZnO-pe-FbO** (Fig. 6A). The retention of the $a_{2u}(\pi)$ -derived HOMO for the free base oxochlorin derives from an interplay of factors that include a net electron-withdrawing effect of the keto group of the oxochlorin to stabilize all orbitals to some extent, a preferential destabilizing effect of macrocycle saturation in the oxochlorin on the a_{1u} -versus the a_{2u} -derived filled orbitals, and a destabilizing effect of meso-ethyne substitution on the $a_{2u}(\pi)$ - versus a_{1u} -derived orbitals. In addition to the orbital ordering, another net effect

ZnP-pe-FbP constituents

-UMO+ e_{gy}(π) 2.15 eV e_{gy}(π) -2.14 eV LUMO e_{gx}(π) -2.17 eV e_{gx}(π) -2.28 eV OMOH $a_{2u}(\pi)$ $a_{2u}(\pi)$ -5.04 eV 4.89 eV -OMOH $a_{1u}(\pi)$ $a_{1u}(\pi)$ -5.19 eV -5.18 eV B Α

Figure 5. Electron-density distributions and energies of the frontier molecular-orbitals of the reference monomeric components of ZnP-pe-FbP.

of these factors is that the spacing between the HOMO and HOMO–1 of the free base oxochlorin (Fig. 6B) is the smallest among the complexes. Thus, for an equality of all other factors, the contribution of the HOMO \rightarrow LUMO configuration of

Figure 6. Electron-density distributions and energies of the frontier molecular-orbitals of the reference monomeric components of ZnO-pe-FbO.

the free base energy-acceptor chromophore to the inter-subunit TB coupling will carry roughly the same weight for **ZnOpe-FbO** and **ZnP-pe-FbP**. (2) On the other hand, the HOMO of the ethynylphenylsubstituted zinc oxochlorin is an $a_{1u}(\pi)$ -derived orbital that has much less electron density at the site of linker attachment when compared with the $a_{2u}(\pi)$ HOMO of the zinc porphyrin (Fig. 6A versus 5B). The resulting ordering of HOMO and HOMO-1 is more typical of oxochlorins, chlorins and bacteriochlorins (Figs. 4 and 6A), and emphasizes the impact of the directly bonded ethyne group in the free base oxochlorin described above (Fig. 6B). Thus, for an equality of all other factors, the contribution of the HOMO \rightarrow LUMO configuration of the zinc-chelate energy-donor chromophore to the inter-subunit TB coupling will carry less weight for **ZnO-pe-FbO** compared to **ZnP-pe-FbP**.

Collectively, the above characteristics indicate that the TB contribution to energy transfer between the oxochlorin constituents of **ZnO-pe-FbO**, while substantial, should be less than half that between the porphyrin constituents of **ZnP-pe-FbP**. On the other hand, the TS interaction in the oxochlorin dyad is larger than that for the porphyrin dyad (due to the larger transition dipole strengths of the hydroporphyrin energy donor and acceptor subunits in the former dyad). This in turn increases the TS contribution to the energy-transfer rate for the oxochlorin dyad. Accordingly, the most consistent picture of the energy-transfer process in the oxochlorin dyad is one wherein both TS and TB processes contribute.

CONCLUSIONS

The results obtained here on a chlorin-bacteriochlorin dyad and comparison with the findings from previous work on dyads containing other tetrapyrrole macrocycles indicate that through proper design, both TS and TB mechanisms can be utilized to achieve ultrafast and essentially quantitative excitedstate energy transfer in tetrapyrrole-based arrays. In the case of meso-phenylethyne-linked dyads, the TS rate decreases along the series FbC-pe-FbB, $\sim (5 \text{ ps})^{-1} > \text{ZnO-pe-FbO}$, $\sim (10 \text{ ps})^{-1}$ > **ZnP-pe-FbP**, \sim (60 ps)⁻¹. The magnitude of the TS contribution to the overall energy-transfer rate (chlorin-bacteriochlorin > oxochlorin-oxochlorin > porphyrin-porphyrin) parallels the intensification (and redshift) in the associated fluorescence and absorption transitions in the constituent macrocycles. In contrast, the TB contribution follows the reverse trend for the same dyads (porphyrin-porphyrin > oxochlorin-oxochlorin > chlorin-bacteriochlorin). This trend parallels the extent of electron-density delocalization onto the linker in the MOs that are the key contributors to the wavefunction of the lowest energy singlet excited state.

Collectively, our results show that a favorable balance of TS and TB contributions can be achieved to give ultrafast and essentially quantitative excited-state energy transfer with different combinations of constituents. One question that arises from the present study is whether TB contributions to energy transfer in arrays of hydroporphyrins could be appreciably increased *via* tuning of the characteristics of the frontier MOs (*via* substituent effects) and the use of linker attachment sites where these orbitals have high electron density. (Indeed, the oxochlorin–oxochlorin dyad discussed here appears to exhibit some of these attributes.) If so, TB interactions could act in concert with the already substantial TS interaction to enhance the efficiency of excited-state energy transfer in arrays having diverse architectures.

concepts could be implemented in hydroporphyrin-based synthetic light-harvesting systems for solar-energy conversion. Finally, we note that the chlorin-bacteriochlorin dyad motif, with suitable tailoring, might also find use in biomedical applications, such as flow cytometry and optical molecular imaging, owing to its narrow bandwidths and substantial effective (>80 nm) Stokes shift between the red absorption and NIR fluorescence transitions.

Acknowledgements—This research was supported by grants from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy to D.H. (DE-FG02-05ER15661), D.F.B. (DE-FG02-05ER15660) and J.S.L. (DE-FG02-96ER14632). Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the Facility was obtained from the North Carolina Biotechnology Center and the National Science Foundation.

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