Supporting Information for

Controlling Energy and Charge Transfer in Linear Chlorophyll Dimers

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Proton nuclear magnetic resonance spectra were recorded on a Varian 400 spectrometer with TMS as an internal standard, and the chemical shifts are given in ppm downfield from TMS. Laser desorption mass spectra were obtained with a PE Voyager DE-Pro MALDI-TOF mass spectrometer using dithranol as a matrix. High resolution fast atom bombardment mass spectra were obtained with the 70-SE-4F mass spectrometer at the University of Illinois at Champaign-Urbana. Commercially available reagents were purchased from Sigma-Aldrich Co. and used without further purification. All solvents were spectrophotometric grade unless otherwise noted. Flash chromatography was performed using Sorbent Technologies (Atlanta, GA) silica gel.

Synthesis

Methyl 3-ethyl-20-(4'-iodophenyl)-pyropheophorbide *a* (1.1)

Methyl 20-(4'-aminophenyl)-3-ethylpyropheophorbide *a* [1] (0.200 g, 0.312 mmol), isoamylnitrite (0.730 g, 6.23 mmol), and diiodomethane (0.830 g, 3.10 mmol) were dissolved in 1,2-dichloroethane (25 mL). Dry nitrogen was bubbled through the stirring solution for 30 min before the reaction mixture was then refluxed under nitrogen for 5 hrs in the dark. After cooling to room temperature, the solution was diluted with chloroform and washed with saturated sodium bicarbonate solution, water and finally with brine. The combined aqueous washings were extracted with chloroform. The organic fractions were combined and the solvent removed on a rotary evaporator. The resulting purple solid was chromatographed on a silica gel column using chloroform / acetone (95:5) as the mobile phase yielding **1.1** (0.090 g, 38 %). ^{1}H NMR (δ in $CDCl_3$) 9.50, 9.36 (s, 1 H, 5- and 10- meso H), 8.10 (dd, 1 H, J = 1.4, 8.0 Hz, phenyl H's), 7.95 (dd, 1 H, J = 1.3, 7.9 Hz, phenyl H's), 7.84 (dd, 1 H, J = 1.4, 7.9 Hz, phenyl H's), 7.38 (dd, 1 H, J = 1.4, 7.9 Hz, phenyl H's), 5.19 (dd, 2 H, J = 1.0, 20.6 Hz, 13^2-CH_2), 4.22 (q, 1 H, J = 7.1, 17-H), 4.08 (dd, 1 H, J = 3.3, 8.3, 18-H), 3.79 (q, 2 H, J = 7.5 Hz, 3a- CH_2-), 3.71 (obscured q, 2 H, J = 7.7, 8a- CH_2), 3.68 (s, 3 H, 17d-OCH_3), 3.56, 3.28, 2.33 (s, 3 H, 2-, 7- and 12-Me), 2.52 (m, 2 H, 17a-CH_2-), 2.20 (m, 2 H, 17b-CH_2-), 1.71, 1.64 (t, 3 H, J = 7.6, 3b- and 8b- CH_3), 1.06 (d, 3 H, J = 7.0 Hz, 18-CH_3), 1.25, -1.49 (broad s, 1 H, NH) MS-MALDI (m/z): $[M]^+$ calcd for $C_{40}H_{41}IN_4O_3$, 752.2; found, 752.6.

Zinc methyl 3-ethyl-20-(4'-triisopropylsilylethynylphenyl)-pyrochlorophyllide *a* (1.2)

Methyl 3-ethyl-20-(4'-triisopropylsilylethynylphenyl)-pyropheophorbide *a*[2] (0.120 g, 0.149 mmol) was dissolved in 65 mL of dichloromethane / methanol (4:1) with zinc acetate dehydrate (0.690 g, 3.14 mmol). The reaction mixture was refluxed under nitrogen with stirring in the dark for 2 hrs in the dark. After cooling to room temperature, the blue-green solution is diluted with chloroform and washed with water, pH 4.8 buffer solution and again with water. After the organics are combined and dried over anhydrous sodium sulfate, the solvent is removed on a rotary evaporator. The conversion from pheophorbide to chlorophyllide is quantitative. ^{1}H NMR (δ in $CDCl_3$ w/ pyridine-d5) 9.55, 9.20 (s, 1 H, 5- and 10- meso H), 8.05 (dd, 1 H, J = 1.8, 7.8 Hz, phenyl H's), 7.84 (dd, 1 H, J = 1.8, 7.8 Hz, phenyl H's), 7.65 (dd, 1 H, J = 1.8, 7.7 Hz, phenyl H's), 7.41 (dd, 1 H, J = 1.8, 7.8 Hz, phenyl H's), 5.09 (dd, 2 H, J = 8.1, 19.6 Hz, 13^2-

CH$_2$), 4.16 (q, 1 H, J = 7.0, 17-H), 3.90 (q, 1 H, J = 4.0, 18-H), 3.76 (q, 2 H, J = 7.4 Hz, 3a- CH$_2$-), 3.66 (obscured q, 2 H, J = 7.6, 8a- CH$_2$), 3.69 (s, 3 H, 17d-OCH$_3$), 3.53, 3.26, 2.21 (s, 3 H, 2-, 7- and 12-Me), 2.42 (m, 2 H, 17a-CH$_2$-), 2.17 (m, 2 H, 17b-CH$_2$-), 1.72, 1.59 (t, 3 H, J = 7.6, 3b- and 8b- CH$_3$), 1.12 (s, 3 H, TIPS -C$\underline{\text{H}}$(CH$_3$)$_2$), 1.24 (br s, 18 H, TIPS -CH(C$\underline{\text{H}}_3$)$_2$), 0.80 (d, 3 H, J = 7.0 Hz, 18-CH$_3$). HRMS-FAB (m/z): [M+H]$^+$ calcd for $C_{51}H_{60}N_4O_3SiZn$, 869.3805; found, 869.3808.

Zinc methyl 3-ethyl-20-(4'-ethynylphenyl)-pyrochlorophyllide *a* (1.3)

Compound **1.2** (0.063 g, 0.072 mmol) was dissolved in 25 mL of THF and cooled to 0°C. To the blue/green solution, TBAF (95 μL, 1M in THF) was then added dropwise. After stirring for 1 hr under N$_2$, the reaction mixture was warmed to RT, diluted with dichloromethane and washed with water (5x) and brine. The combined aqueous washings were extracted with dichloromethane. The organic fractions were combined and dried over sodium sulfate. Following solvent removal by rotary evaporation, the resulting blue/green residue was chromatographed on a silica gel column using THF / hexanes / dichloromethane (1:3:6) as the mobile phase yielding **1.3** (0.046 g, 90 %). ^{1}H NMR (δ in CDCl$_3$ w/ pyridine-d5) 9.54, 9.20 (s, 1 H, 5- and 10- meso H), 8.08 (br d, 1 H, J = 8.0 Hz, phenyl H's), 7.85 (br d, 1 H, J = 8.0 Hz, phenyl H's), 7.66 (br d, 1 H, J = 8.0 Hz, phenyl H's), 7.45 (br d, 1 H, J = 8.0 Hz, phenyl H's), 5.08 (br d, 2 H, J = 6.5 Hz, 13^2-CH$_2$), 4.68 (t, 1 H, J = 7.2, 17-H), 4.14 (dd, 1 H, J = 5.7, 13.6, 18-H), 3.64 (q, 2 H, J = 7.6 Hz, 3a- CH$_2$-), 3.74 (obscured q, 2 H, J = 7.1, 8a- CH$_2$), 3.68 (s, 3 H, 17d-OCH$_3$), 3.52, 3.25, 2.26 (s, 3 H, 2-, 7- and 12-Me), 2.57 (m, 2 H, 17a-CH$_2$-), 2.38 (m, 2 H, 17b-CH$_2$-), 1.70, 1.57 (t, 3 H, J = 7.4, 3b- and 8b- CH$_3$), 1.10 (d, 3 H, J = 7.1 Hz, 18-CH$_3$). HRMS-FAB (m/z): [M]$^+$ calcd for $C_{42}H_{40}N_4O_3Zn$, 712.2392; found, 712.2390.

(Methyl 3-ethyl-20-phenyl-pyrochlorophyllide *a*)acetylene(zinc methyl 3-ethyl-20-phenyl-pyrochlorophyllide *a*) (1b)

Compound **1.3** (0.043 g, 0.060 mmol), Compound **1.1,** (0.045 g, 0.055 mmol), tri(o-tolyl)phosphine (0.023, 0.077 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.012 g, 11 μmol) were combined in 20 mL dry, deoxygenated Toluene:TEA (5:1). The reaction mixture was heated to 35°C and stirred under N_2 for 3 hrs. Following solvent removal by rotary evaporation, the resulting blue/green residue was chromatographed on a silica gel column using Chloroform / THF (9:1) as the mobile phase yielding **1b** (0.050 g, 62 %). ^{1}H NMR (δ in $CDCl_3$ w/ pyridine-d5) %). ^{1}H NMR (δ in $CDCl_3$) 9.51, 9.37 (s, 1 H, Zn 5- and 10- meso H), 9.48, 9.28 (s, 1 H, FB 5- and 10- meso H), 8.20 (dd, H, J = 1.7, 12.7 Hz, Zn phenyl H's), 8.18 (dd, 1 H, J = 1.7, 12.7 Hz, FB phenyl H's), 8.08 (overlapping dd, 1 H, J = 2.3, 7.6 Hz, FB phenyl H's), 8.07 (overlapping dd, 1 H, J = 2.4, 7.7 Hz, Zn phenyl H's), 7.92 (dd, 1 H, J = 1.8, 7.6 Hz, FB phenyl H's), 7.89 (br d, 1 H, J = 7.6 Hz, Zn phenyl H's), 7.70 (dd, 1 H, J = 1.8, 7.6 Hz, FB phenyl H's), 7.63 (br d, 1 H, J = 7.5 Hz, Zn phenyl H's), 5.09 (br d, 2 H, J = 5.4 Hz, FB 13^2-CH_2), 4.97 (br d, 2 H, J = 6.6 Hz, Zn 13^2-CH_2), 4.31 (m, 2 H, J = 7.1 Hz, 17-H), 4.12 (dd, 2 H, J = 3.5, 8.5 Hz, FB 18-H), 4.02 (dd, 2 H, J = 4.7, 7.9 Hz, Zn 18-H), 3.83 (q, 2 H, J = 7.6 Hz, FB 3a- CH_2-), 3.71 (m, 8 H, Zn 3a- CH_2-, Zn 17d-OCH_2-, 8a-CH_2-), 3.60 (obscured d, 2 H, J = 7.2 Hz, FB 17d-OCH_2-), 3.60, 3.29, 2.43 (s, 4 H, FB 2-, 7- and 12-CH_3), 3.54, 3.27, 2.30 (s, 3 H, Zn 2-, 7- and 12-CH_3), 3.64 (s, 3 H, Zn 17d-OCH_3), 3.60 (s, 3 H, FB 17d-OCH_3), 2.56 (m, 2 H, FB 17a-CH_2-), 2.38 (m, 2 H, Zn 17a-CH_2-), 2.23 (m, 4 H, 17b-CH_2-), 1.72, 1.68 (overlapping t, 3 H, J = 7.6 Hz, Zn 3b- and 8b-CH_3), 1.71, 1.64 (overlapping t, 6 H, J = 7.6 Hz, FB 3b- and 8b-CH_3), 1.14 (d, 3 H, J = 7.1 Hz, Zn 18-CH_3), 1.10 (d, 3 H, J = 6.4 Hz, FB 18-CH_3), -1.42 (broad s, 1 H, FB NH). MS-MALDI (m/z): $[M]^+$ calcd for $C_{82}H_{80}N_8O_6Zn$, 1336.5; found, 1337.1.

Di(zinc methyl 3-ethyl-20-phenyl-pyrochlorophyllide *a*)acetylene (1a)

Compound **1b** (0.045 g, 0.034 mmol) was dissolved in 15 mL of dichloromethane / methanol (4:1) with zinc acetate dehydrate (0.100 g, 0.456 mmol). The reaction mixture was refluxed under nitrogen with stirring in the dark for 2 hrs in the dark. After cooling to room temperature, the blue-green solution is diluted with chloroform and washed with water, pH 4.8 buffer solution and again with water. After the organics are combined and dried over anhydrous sodium sulfate, the solvent is removed on a rotary evaporator. The conversion from pheophorbide to chlorophyllide is quantitative. ^{1}H NMR (δ in $CDCl_3$ w/ pyridine-d5) 9.49, 9.16 (s, 1 H, 5- and 10- meso H), 8.12 (dd, 1 H, J = 1.2, 7.7 Hz, phenyl H's), 7.96 (dd, 1 H, J = 1.2, 7.9 Hz, phenyl H's), 7.77 (dd, 1 H, J = 1.1, 7.7 Hz, phenyl H's), 7.46 (dd, 1 H, J = 1.0, 7.8 Hz, phenyl H's), 5.04 (dd, 2 H, J = 6.7, 19.4 Hz, 13^2-CH_2), 4.18 (q, 1 H, J = 7.2, 17-H), 3.88 (dd, 1 H, J = 4.3, 7.9, 18-H), 3.69, 3.66 (obscured q, 2 H, J = 7.5 Hz, 3a-, 8a-CH_2-), 8a- CH_2), 3.63 (s, 3 H, 17d-OCH_3), 3.49, 3.21, 2.21 (s, 3 H, 2-, 7- and 12-Me), 2.38 (m, 2 H, 17a-CH_2-), 2.24 (m, 2 H, 17b-CH_2-), 1.65, 1.55 (t, 3 H, J = 7.5, 3b- and 8b- CH_3), 0.80 (d, 3 H, J = 6.9 Hz, 18-CH_3) HRMS-FAB (m/z): $[M]^+$ calcd for $C_{82}H_{78}N_8O_6Zn_2$, 1398.4627; found, 1398.4630.

Zinc methyl 3-ethyl-20-(Zinc 2-octyl-1-dodecyl 3-ethyl-20-(4'-ethynylphenyl)-pyrochlorophyllide *a*)-pyrochlorophyllide *a* (2)

Methyl 20-bromo-3-ethylpyropheophorbide *a*[3] (0.025 g, 0.040 mmol), Zinc 2-octyl-1-dodecyl 3-ethyl-20-(4'-ethynylphenyl)-pyrochlorophyllide *a* [2](0.047 g, 0.048 mmol), tri(o-tolyl)phosphine (0.010, 0.033 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.005 g, 5 μmol) were combined in 1.1 mL dry, deoxygenated DMF:TEA (10:1). The reaction mixture was stirred at room temperature under N_2 for 56 hrs. The solvent was then removal by rotary evaporation and the resulting purple residue was chromatographed on a silica gel column using THF / EtOAc /

hexanes (1:1:4) as the mobile phase. The green fraction was dissolved in 15 mL of dichloromethane / methanol (4:1) with zinc acetate dihydrate (0.100 g, 0.456 mmol). The reaction mixture was refluxed under nitrogen with stirring in the dark for 2 hrs in the dark. After cooling to room temperature, the blue-green solution is diluted with chloroform and washed with water, pH 4.8 buffer solution and again with water. The organics were combined and dried over anhydrous sodium sulfate and the solvent was removed on a rotary evaporator. The blue / green residue was then chromatographed on a SEC column using THF as the mobile phase. The chromatographed product was finally precipitated from hexanes to yield **2** (0.010 g, 16 %). ^{1}H NMR (δ in $CDCl_3$ w/ pyridine-d5) 9.50, 9.37, 9.17, 9.04 (s, 1 H, 5- and 10- meso H), 8.21 (dd, 1 H, J = 0.7, 7.8 Hz, phenyl H's), 8.09 (dd, 1 H, J = 1.0, 7.6 Hz, phenyl H's), 7.89 (dd, 1 H, J = 0.8, 7.8 Hz, phenyl H's), 7.50 (dd, 1 H, J = 1.1, 7.7 Hz, phenyl H's), 5.06 (dd, 2 H, J = 2.8, 19.7, Hz, 13^2-CH_2), 4.98 (br s, 2 H, 13^2-CH_2), 4.89, 4.31 (q, 1 H, J = 7.0, 17-H), 4.02, 3.91 (dd, 1 H, J = 4.5, 7.7, 18-H), 3.80 (t, 2 H, J = 5.0 Hz, 3a- CH_2-), 3.70 (q, 2 H, J = 7.3 Hz, 3a- CH_2-), 3.63, 3.55 (obscured q, 2 H, J = 7.8, 8a- CH_2), 3.65 (s, 3 H, 17d-OCH_3), 3.64, 3.56, 3.51, 3.22, 3.15, 2.30 (s, 3 H, 2-, 7- and 12-Me), 2.38 (m, 2 H, 17a-CH_2-), 2.23 (m, 2 H, 17b-CH_2-), 1.66, 1.64, 162, 156 (overlapping t, 3 H, J = 7.7, 3b- and 8b- CH_3), 1.71, 0.83 (d, 3 H, J = 6.9 Hz, 18-CH_3), 1.35 (m, 1 H, branched alkyl -$C\underline{H}(CH_2\text{-})_2$), 1.09 (br s, 32 H, branched alkyl -CH_2-), 0.73 (q, 6 H, J = 6.2 Hz, branched alkyl -CH_3) HRMS-FAB (m/z): $[M]^+$ calcd for $C_{95}H_{112}N_8O_6Zn_2$, 1588.7288; found, 1588.7291.

Zinc methyl 3-ethyl-20-(triisopropylsilylethynyl)-pyrochlorophyllide *a* (3.1)

Methyl 3-ethyl-20-(triisopropylsilylethynyl)-pyropheophorbide *a* [2] (0.100 g, 0.157 mmol) was dissolved in 150 mL of dichloromethane / methanol (4:1) with zinc acetate dehydrate (1.000 g, 4.556 mmol). The reaction mixture was refluxed under nitrogen with stirring in the dark for 2 hrs in the dark. After cooling to room temperature, the blue-green solution is diluted with chloroform and washed with water, pH 4.8 buffer solution and again with water. After the organics are combined and dried over anhydrous sodium sulfate, the solvent is removed on a rotary evaporator. The conversion from pheophorbide to chlorophyllide is quantitative. ^{1}H NMR (δ in $CDCl_3$ w/ pyridine-d5) 9.40, 9.04 (s, 1 H, 5- and 10- meso H), 5.01 (br s, 2 H, 13^2-CH_2), 4.81 (q, 1 H, J = 7.0, 17-H), 4.29 (m, 1 H, 18-H), 3.92 (dd, 2 H, J = 3.6, 8.2 Hz, 3a- CH_2-), 3.69, 3.68 (overlapping q, 2 H, J = 7.5 Hz, 17d -OCH_2- and 8a- CH_2-), 3.60 (s, 3 H, 17d-OCH_3), 3.58, 3.48, 3.19 (s, 3 H, 2-, 7- and 12-CH_3), 2.46 (m, 2 H, 17a-CH_2-), 2.04 (m, 2 H, 17b-CH_2-), 1.67, 1.64 (t, 3 H, J = 7.8, 3b- and 8b- CH_3), 1.50 (d, 3 H, J = 7.0 Hz, 18-CH_3), 1.35 (m, 18 H, TIPS -$CH(C\underline{H}_3)_2$), 1.25 (q, 3 H, J = 6.3 Hz, TIPS -$C\underline{H}(CH_3)_2$). HRMS-FAB (m/z): $[M]^+$ calcd for $C_{45}H_{56}N_4O_3SiZn$, 792.3413; found, 792.3412.

Zinc methyl 3-ethyl-20-ethynyl-pyrochlorophyllide *a* (3.2)

Compound **3.1** (0.050 g, 0.063 mmol) was dissolved in 25 mL of THF and cooled to 0°C. To the blue/green solution, TBAF (85 μL, 1M in THF) was then added dropwise. After stirring for 1 hr under N_2, the reaction mixture was warmed to RT, diluted with dichloromethane and washed with water (5x) and brine. The combined aqueous washings were extracted with dichloromethane. The organic fractions were combined and dried over sodium sulfate. Following solvent removal by rotary evaporation, the resulting blue/green residue was chromatographed on a silica gel column using THF / hexanes / dichloromethane (1:3:6) as the mobile phase yielding **3.2** (0.038 g, 94 %). ^{1}H NMR (δ in $CDCl_3$ w/ pyridine-d5) 9.42, 9.05 (s, 1 H, 5- and 10- meso H), 5.00 (br s, 2 H, 13^2-CH_2), 4.71 (q, 1 H, J = 7.0 Hz, 17-H), 3.96 (dd, 1 H, J = 3.3, 8.1 Hz, 18-H), 3.92 (s, 1 H, ethynyl H), 3.74 (t, 2 H, J = 6.3 Hz, 3a-CH_2-), 3.68 (overlapping d and q, 4 H, J = 7.5 Hz, 17d-OCH_2-, 8a-CH_2-), 3.61 (s, 3 H, 17d-OCH_3), 3.55, 3.41, 3.19 (s, 3 H, 2-, 7- and 12-CH_3), 2.37 (m, 2 H, 17a-CH_2-), 2.09 (m, 2 H, 17b-CH_2-), 1.67, 1.64 (t, 3 H, J = 7.6 Hz, 3b- and 8b-CH_3), 1.52 (d, 3 H, J = 7.1 Hz, 18-CH_3). MALDI-MS (m/z): $[M]^+$ calcd for $C_{36}H_{36}N_4O_3Zn$, 638.1; found, 638.2.

1,4-bis(zinc methyl 3-ethyl-20-ethynyl-pyrochlorophyllide *a*) benzene (3)

Compound **3.2** (0.034 g, 0.053 mmol), 1,4-tribromobenzene (0.005 g, 0.021 mmol), tri(o-tolyl)phosphine (0.010, 0.033 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.005 g, 5 μmol) were combined in 6 mL dry, deoxygenated Toluene:TEA (5:1). The reaction mixture was heated to 50°C and stirred under N_2 for 2 hrs. Following a second addition of tri(o-tolyl)phosphine (0.010, 0.033 mmol) and tris(dibenzylideneacetone)dipalladium(0) (0.005 g, 5 μmol), the reaction mixture was stirred for another hour at 50°C under N_2. The solvent was then removal by rotary evaporation and the resulting blue/green residue chromatographed on a SEC column using THF as the mobile phase. The chromatographed product was finally precipitated from hexanes to yield **3** (0.013 g, 46 %). ^1H NMR (δ in $CDCl_3$ w/ pyridine-d5) 9.42, 9.08 (s, 2 H, 5- and 10- meso H), 7.92 (s, 4 H, central phenyl H's), 5.04 (br s, 4 H, 13^2-CH_2), 4.85 (q, 2 H, J = 7.0, 17-H), 4.06 (dd, 2 H, J = 2.7, 8.3, 18-H), 3.73 (m, 8 H, 3a-CH_2-, 17d-OCH_2-), 3.69 (obscured q, 4 H, J = 7.4, 8a-CH_2-), 3.62, 3.57, 3.20 (s, 6 H, 2-, 7- and 12-CH_3), 3.60 (s, 6 H, 17d-OCH_3), 2.42 (m, 4 H, 17a-CH_2-), 1.96 (m, 4 H, 17b-CH_2-), 1.84 (m, 6 H, 18-CH_3), 1.70 (overlapping t, 6 H, J = 4.7 Hz, 3b-CH_3), 1.68 (overlapping t, 6 H, J = 7.8 Hz, 8b-CH_3). HRMS-FAB (m/z): [M]+ calcd for $C_{78}H_{74}N_8O_6Zn_2$, 1346.4314; found,1346.4309.

Optical Spectroscopy

Femtosecond transient absorption measurements were performed with the following apparatus: A Spectra-Physics Millenium V frequency-doubled CW Nd:YVO_4 laser was used to pump a Coherent MIRA Ti:sapphire oscillator. The 110 fs, 828-nm pulses from the oscillator were stretched to ~200 ps using a four-pass, reflective, single-grating pulse stretcher and were used to seed a homemade regenerative amplifier, which includes a Medox two-step Pockels cell and driver. The amplifier was pumped at a 2 kHz repetition rate by a Quantronix 527DP frequency-doubled Nd:YLF laser (4.1 mJ/pulse). The amplified Ti:sapphire pulse (0.5 mJ/pulse) was recompressed to approximately 120 fs by a four-pass, reflective, single grating compressor. The pulse energy after compression was 320 μJ/pulse. Two 5% reflective beam splitters were placed in the output path to generate two 828-nm beams for white light generation. The remaining 828-nm light was frequency doubled by using a 1-mm-type I LBO crystal to give 414-nm 120-fs, 75-μJ pulses.[4] The 828-nm light from the first 5% beam splitter was passed through a waveplate-polarizer pair to control its intensity, and a few microjoules were focused into a 1-mm sapphire disk to generate white light continuum pulses. All reflective optics were used both to focus the 828-nm pulse into the sapphire and recollimate the white light output, thus limiting the chirp on the white light pulse to <200 fs from 450 to 750 nm. The 828-nm light from the second 5% beam splitter was used to create a second white light continuum by focusing the 828-nm pulse into a 2-mm sapphire disk, using a 100 mm focal length (f.l.) lens. This white light was used to seed the first stage of a two-stage optical parametric amplifier, which has been described previously.[5] The first stage contains a Type II BBO crystal, which was pumped with about 20 μJ of 414-nm light focused into the crystal with a 300 mm f.l. lens. After removal the IR idler beam and residual 414-nm pump light, the first stage produced transform-limited pulses having ~1.0 μJ/pulse from 460 to 750 nm. This light was then focused into the Type I BBO of the second stage of the OPA with a 75 mm f.l. lens. The second stage amplifies the first stage light upon overlap with the remaining 55 μJ/pulse of 414 nm pump light. The final amplified pulse energy was ~7.5 μJ/pulse after filtering out the residual 414-nm and IR idler light. The optical path for the probe beams and the chopping scheme used in the pump-probe experiments were described by Lukas et al.[4] The instrument was outfitted with a CCD array detector (Ocean Optics PC2000) for simultaneous collection of spectral and kinetic data.[6]

Fluorescence lifetime measurements were made using a Hamamatsu C4780 picosecond fluorescence lifetime measurement system, consisting of a C4334 Streakcope™ and a C4792-01 synchronous delay generator. The excitation light source was supplied by a home-built cavity-dumped Ti:Sapphire laser[7] with a NEOS N13389 3 mm fused-silica acousto-optic modulator (AOM). The AOM was driven by a NEOS Technologies N64389-SYN 10 W driver to deliver 38 nJ, sub-50 fs pulses at an 820 kHz repetition rate. The laser pulses were frequency doubled to 400 nm by focusing the 800 nm fundamental into a 1 mm Type I BBO crystal.

Acknowledgment

High resolution fast atom bombardment mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. The 70-SE-4F mass spectrometer was purchased in part with funds from the National Institute of General Medical Sciences (GM 27029).

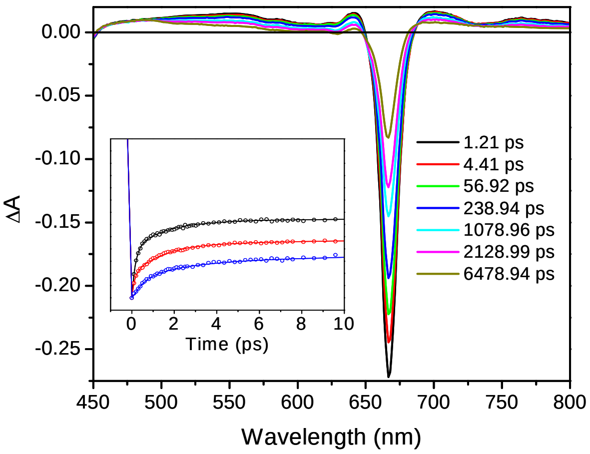

Figure S1. Transient absorption spectra of **2** in THF following excitation with 665 nm, 120 fs laser pulses. Inset: power dependent transient absorption kinetics of **2** monitored at 668 nm using 1.00 (—), 0.66 (—), and 0.33 (—) μJ per 665 nm excitation pulse.

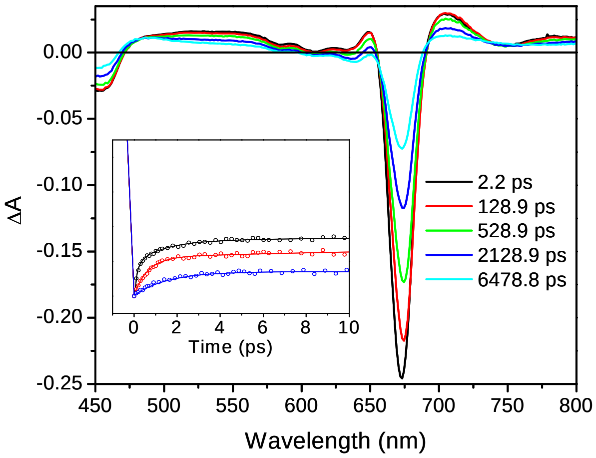

Figure S2. Transient absorption spectra of **3** in THF following excitation with 665 nm, 120 fs laser pulses. Inset: power dependent transient absorption kinetics of **3** monitored at 671 nm using 1.00 (—), 0.66 (—) and 0.33 (—) μJ per 665 nm excitation pulse.

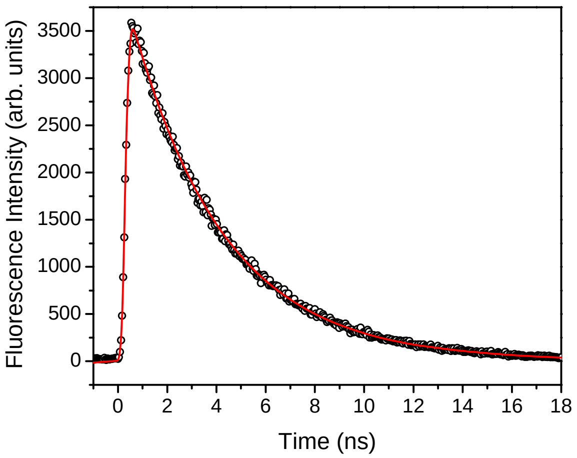

Figure S3. Time resolved fluorescence data for **1** in THF following excitation with 400 nm, 120 fs laser pulses (◦◦◦◦). The fit to the data is also shown (—).

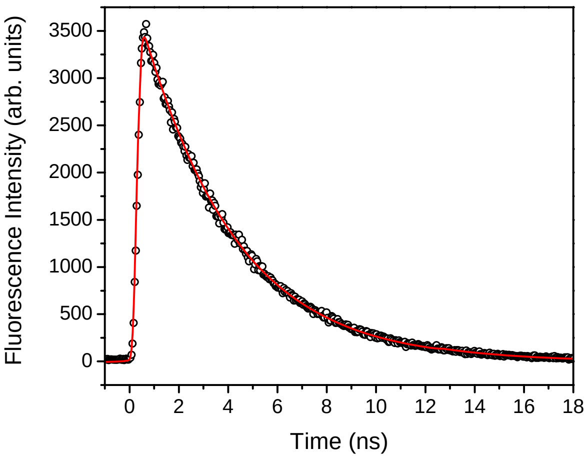

Figure S4. Time resolved fluorescence data for **2** in THF following excitation with 400 nm, 120 fs laser pulses (◦◦◦◦). The fit to the data is also shown (—).

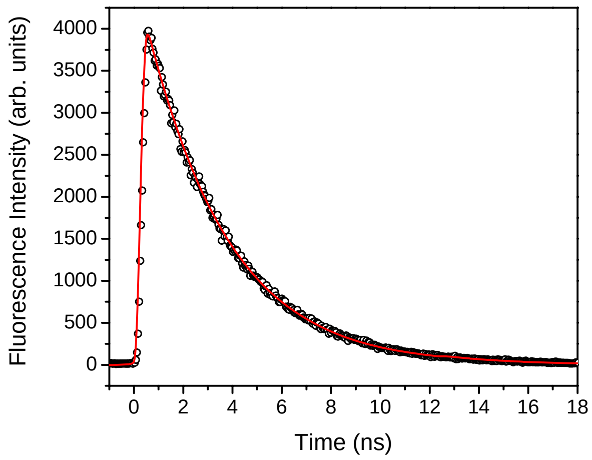

Figure S5. Time resolved fluorescence data for **3** in THF following excitation with 400 nm, 120 fs laser pulses (◦◦◦◦). The fit to the data is also shown (—).

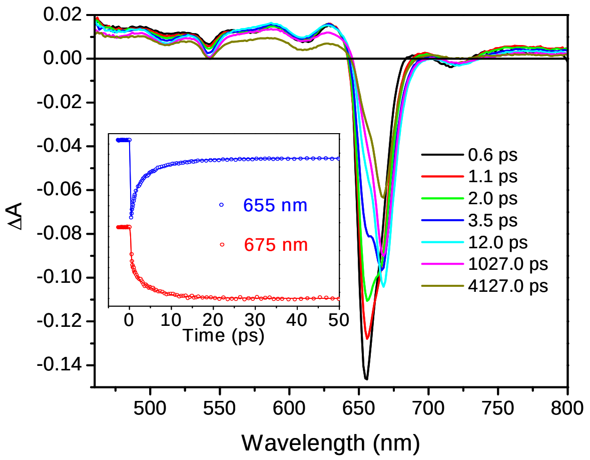

Figure S6. Transient absorption spectra of **1b** in THF following excitation with 655 nm, 120 fs laser pulses. Inset: transient absorption kinetics for **1b** at (◦◦◦◦) 655 nm and at (◦◦◦◦) 675 nm. Nonlinear least-squares fits to the data are also shown.

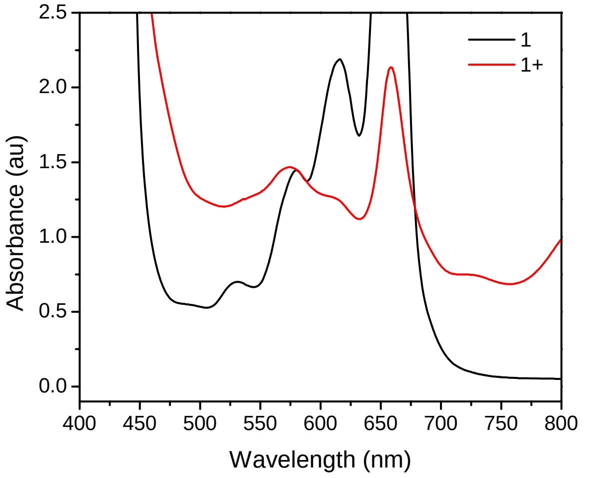

Figure S7. Ground-state absorption spectra of **1** in DCM:THF (9:1) following the addition of I_2 / $AgClO_4$ dissolved in acetonitrile.

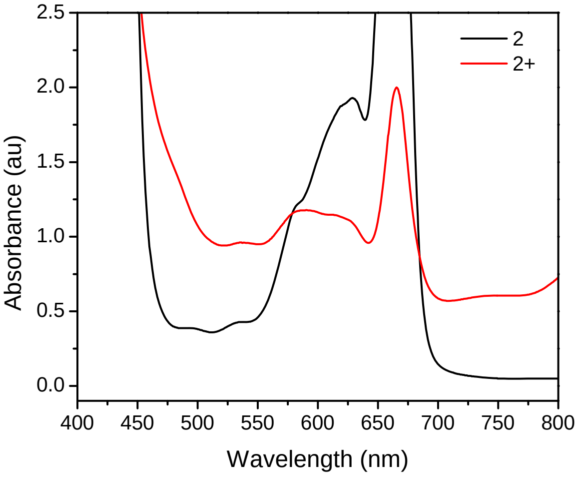

Figure S8. Ground-state absorption spectra of **2** in DCM:THF (9:1) following the addition of I_2 / $AgClO_4$ dissolved in acetonitrile.

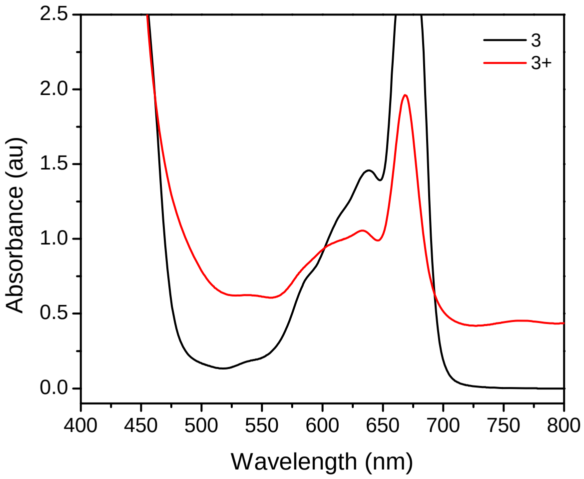

Figure S9. Ground-state absorption spectra of **3** in DCM:THF (9:1) following the addition of I_2 / $AgClO_4$ dissolved in acetonitrile.

Numbering key for chlorins:

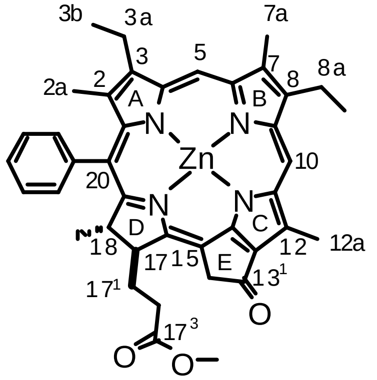

Table S1. Proton hyperfine splittings [a] for known Chl resonances in $\mathbf{1a}^{+\bullet}$-$\mathbf{3}^{+\bullet}$ obtained by ENDOR Spectroscopy in DCM:THF (9:1) at 250 K

	Proton Assignment				
Compound	Var. β, γ	2a, 7a, 8a, 5, 10	12a	17	18
ZCPh	0.4	3.4	6.9	7.7	6.9
ZCEPh	0.3	3.6	7.4	7.4	6.3
$\mathbf{1a}^{+.}$	0.6	3.3	6.8	7.8	6.8
$\mathbf{2}^{+.}$	0.5	3.3	6.3	8.1	6.8
$\mathbf{3}^{+.}$	0.7	1.6	3.5	3.5	3.0

[a] Values in MHz

Table S2. Atomic Coordinates for $ZCPh^{+\bullet}$ obtained using Gaussian 03[8] with the Perdew-Wang 1991 nonlocal functional and the 6-31G* basis set.

Atom	X	Y	Z
N	0.842115	1.369633	-0.17729
C	0.652949	2.70875	-0.38098
C	-0.57746	3.389567	-0.38595
C	-1.8513	2.851541	-0.2603
N	-2.1015	1.516504	-0.08844
C	-3.45746	1.378076	-0.08757
C	-4.13018	0.140814	-0.03033
C	-3.51068	-1.09955	-0.01816
N	-2.13098	-1.26099	0.009742
C	-1.93082	-2.58112	-0.08231
C	-0.78503	-3.38806	-0.16313
C	0.501213	-2.88493	-0.16996
N	0.77832	-1.53458	-0.0837
C	2.113273	-1.36199	0.008144
C	2.809125	-0.11857	-0.0628
C	2.205826	1.140097	-0.23986
C	2.899341	2.419736	-0.5366
C	1.927771	3.377036	-0.61684
C	-3.10766	3.60486	-0.34341
C	-4.11247	2.685184	-0.23368
C	-3.15498	-3.32304	-0.14651
C	-4.18273	-2.41671	-0.10282
C	2.821463	-2.70122	0.212734
C	1.765302	-3.69884	-0.30731
C	-1.25921	-4.83643	-0.26347
C	-2.82139	-4.75919	-0.25171
O	-3.56902	-5.71138	-0.31582
C	2.084311	4.849239	-0.88028
C	2.138617	5.694289	0.408454
C	4.358352	2.663837	-0.78701
C	-3.20106	5.087346	-0.53057
C	-5.59774	2.910995	-0.24252
C	-6.22525	2.918896	1.165961
C	-5.65418	-2.66223	-0.15659
C	4.305135	-0.19981	0.068472
C	4.925837	0.170017	1.270953
C	6.312305	0.085547	1.414277
C	7.099108	-0.36859	0.354632
C	6.493074	-0.74233	-0.847
C	5.107038	-0.66217	-0.98699
Zn	-0.64111	0.074481	0.264516
C	3.147675	-2.93491	1.704822
C	2.013173	-4.12569	-1.77013
O	-0.50451	0.061556	2.448418
H	-0.52283	4.461386	-0.53728
H	-5.2142	0.160563	-0.05526
H	3.748242	-2.75977	-0.36036
H	1.715961	-4.59731	0.318404
H	-0.92586	-5.46418	0.572773
H	-0.93765	-5.34215	-1.18194
H	2.996183	5.024521	-1.45968
H	1.262063	5.201869	-1.51459
H	2.242397	6.756907	0.166047
H	1.229686	5.570197	1.007757
H	2.990467	5.402847	1.031762
H	4.774654	1.951035	-1.50318
H	4.507747	3.668792	-1.18934
H	4.958216	2.579217	0.124196
H	-2.70045	5.407612	-1.45277
H	-4.24065	5.419037	-0.58717
H	-2.72796	5.62804	0.298918
H	-5.81619	3.863311	-0.73754
H	-6.08515	2.140519	-0.85367
H	-7.30584	3.082549	1.101847
H	-6.05783	1.96961	1.687212
H	-5.7965	3.71679	1.781326
H	-6.10544	-2.18426	-1.03536
H	-5.85669	-3.73427	-0.2077
H	-6.16111	-2.25523	0.727437
H	4.316893	0.527753	2.097607
H	6.776082	0.373929	2.353399
H	8.177714	-0.4325	0.464238
H	7.099285	-1.09358	-1.67716
H	4.642379	-0.94376	-1.92901
H	2.240669	-2.88122	2.318033
H	3.587062	-3.92982	1.83254
H	3.862538	-2.19855	2.078679
H	2.072851	-3.2528	-2.42984
H	2.956012	-4.67729	-1.84479
H	1.213293	-4.77393	-2.14022
H	-0.22529	0.894425	2.862297
H	-1.31263	-0.21287	2.911905

Table S3. Atomic Coordinates for ZCEPh$^{+\bullet}$ obtained using Gaussian 03[8] with the Perdew-Wang 1991 nonlocal functional and the 6-31G* basis set.

Atom	X	Y	Z	Atom	X	Y	Z
C	6.371856	-0.03852	0.149606	H	-5.69018	-0.23207	0.063622
C	7.177545	1.131782	0.151826	H	3.484181	-2.37714	-0.60361
C	8.562567	1.025653	0.264922	H	1.663617	-4.42969	0.161996
C	9.168441	-0.23624	0.379187	H	-0.91962	-5.49588	0.552266
C	8.382439	-1.40001	0.379469	H	-1.00598	-5.38292	-1.20963
C	6.996431	-1.30969	0.265288	H	2.128431	5.318648	-1.41807
C	4.967256	0.05427	0.035842	H	0.376411	5.386376	-1.48248
C	3.739459	0.156956	-0.06262	H	1.253211	6.963501	0.250513
N	0.244038	1.477827	-0.23523	H	0.297565	5.688966	1.051362
C	-0.05065	2.814686	-0.42111	H	2.074213	5.625985	1.096611
C	-1.34006	3.386255	-0.42227	H	4.158352	2.415684	-1.44105
C	-2.56995	2.748936	-0.27102	H	3.773401	4.094243	-0.98736
N	-2.69573	1.387223	-0.09662	H	4.221474	2.90662	0.258036
C	-4.04039	1.139809	-0.04063	H	-3.60669	5.244909	-1.39136
C	-4.59989	-0.15937	0.049225	H	-5.18713	5.082273	-0.59829
C	-3.88354	-1.34871	0.052946	H	-3.7415	5.438691	0.367793
N	-2.47961	-1.39311	0.028484	H	-6.62534	3.41128	-0.60829
C	-2.18243	-2.69619	-0.0662	H	-6.75391	1.660755	-0.71033
C	-0.9647	-3.42079	-0.19609	H	-7.96874	2.513083	1.30235
C	0.271672	-2.82616	-0.25948	H	-6.59857	1.503956	1.832665
N	0.434747	-1.43669	-0.17711	H	-6.47912	3.27631	1.916688
C	1.741801	-1.17111	-0.10442	H	-6.41329	-2.66176	-0.88316
C	2.333597	0.15266	-0.1442	H	-5.9987	-4.17276	-0.03098
C	1.620962	1.380199	-0.28597	H	-6.41158	-2.69835	0.889891
C	2.21522	2.694915	-0.52625	H	2.132345	-2.72306	2.157648
C	1.160888	3.585237	-0.61931	H	3.582142	-3.59117	1.587651
C	-3.87967	3.390248	-0.31342	H	3.64948	-1.82939	1.86102
C	-4.80711	2.376886	-0.16636	H	1.769808	-3.01471	-2.58688
C	-3.33903	-3.53657	-0.08516	H	2.816726	-4.36335	-2.0646
C	-4.44603	-2.70525	-0.00279	H	1.067862	-4.62344	-2.28231
C	2.586409	-2.43285	0.03207	H	-0.5599	0.951003	2.704122
C	1.601316	-3.51958	-0.4584	H	-1.62528	-0.17463	2.87683
C	-1.33622	-4.89563	-0.27593				
C	-2.90404	-4.94027	-0.20413				
O	-3.57962	-5.9587	-0.24149				
C	1.220005	5.069656	-0.84498				
C	1.209934	5.884405	0.464769				
C	3.662848	3.042872	-0.68307				
C	-4.11597	4.857264	-0.49279				
C	-6.30458	2.477484	-0.1175				
C	-6.87032	2.439515	1.317133				
C	-5.89075	-3.07979	-0.00518				
Zn	-1.13101	0.076082	0.219242				
C	3.014287	-2.65119	1.500199				
C	1.824457	-3.90274	-1.93665				
O	-0.82953	0.07382	2.363783				
H	6.700007	2.109843	0.063431				
H	9.176826	1.92899	0.265238				
H	10.25462	-0.3128	0.468462				
H	8.856525	-2.38013	0.468646				

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