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Supplementary Information

Supramolecular ultrafast energy and electron transfer in a directly linked BODIPY-oxoporphyrinogen dyad upon fluoride ion binding

Mandeep K. Chahal, Anuradha Liyanage, Habtom B. Gobeze, Daniel T. Payne, Katsuhiko Ariga, Jonathan P. Hill and Francis D'Souza

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1.0 General Experimental

Reagents and dehydrated solvents (in septum-sealed bottles) used for syntheses and spectroscopic measurements were obtained from Tokyo Kasei Chemical Co., Wako Chemical Co. or Aldrich Chemical Co. and were used without further purification. Electronic absorption spectra were measured using JASCO V-570 UV/Vis/NIR spectrophotometer or Princeton Applied Research (PAR) diode array rapid scanning spectrometer. Fluorescence spectra were measured using a JASCO FP-670 spectrofluorimeter. ATR-FTIR spectra were obtained using a Thermo-Nicolet 760X FTIR spectrophotometer equipped with a SMART-iTX ATR accessory. ¹H-NMR spectra were obtained using JEOL AL300BX or JEOL AL400SSS spectrometers operating respectively at 300 and 400 MHz and using tetramethylsilane as an internal standard. Proton decoupled ¹³C-NMR spectra were obtained using JEOL AL300BX or JEOL AL400SSS spectrometers operating respectively at 76 and 101 MHz and using tetramethylsilane as an internal standard. Data was processed on Delta version 5.0.5.1, Always JNM-AL version 6.2 and MestReNova 6.0.2. ¹H NMR chemical shifts (δ) are reported in ppm relative to TMS for CDCl₃ (δ 0.00) or the residual solvent peak for other solvents. ¹³C NMR chemical shifts (δ) are reported in ppm relative to the solvent reported. Coupling constants (J) are expressed in Hertz (Hz), shift multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), double doublet (dd), multiplet (m) and broad singlet (bs). MALDI-TOF mass spectra were measured using a Shimadzu Axima AFR+ mass spectrometer with dithranol as matrix. High resolution ESI-MS mass spectra were measured using a Thermo Scientific Q-Exactive Plus instrument. (4-BrBn)₂OxP-CHO was prepared according to a literature method.^{S1} The connectivity and conformation of these compounds has been established using X-ray crystallography and NMR spectroscopy.^{S2}

Electrochemistry. Differential pulse voltammograms were recorded on an EG&G PARSTAT electrochemical analyzer using a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using nitrogen gas.

Femtosecond Transient Absorption Spectroscopy.

Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is $\pm 10\%$.

2.0 Synthesis



N₂₁,N₂₃-Bis([1,1'-biphenyl]-4-ylmethyl)-2-formyl-5,10,15,20-tetrakis(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dienylidene)porphyrinogen, (4-PhBn)2OxP-CHO. (4-BrBn)2OxP-CHO (300 mg, 0.20 mmol), phenylboronic acid (294 mg, 2.41 mmol, 12.0 [1,1'-bis(diphenylphosphino) equiv.), ferrocene]dichloropalladium(II) dichloromethane adduct, Pd(dppf)₂Cl₂.CH₂Cl₂ (294 mg, 0.40 mmol, 2.0 equiv.) and K_2CO_3 (1.11 g, 8.03 mmol, 40.0 equiv.) were placed in a dry flask under an atmosphere of dry nitrogen. A degassed mixture of toluene (16 mL), H₂O (2 mL) and ethanol (3 mL) was then added. The resulting mixture was stirred at 60 °C for 24 h under N₂ atmosphere. The mixture was cooled to room temperature and poured into water, extracted with dichloromethane and the combined organic fractions were dried over anhydrous Na_2SO_4 . Solvents were then evaporated under reduced pressure. The product was purified by column chromatography (SiO₂) eluting with dichloromethane to give (4-PhBn)₂OxP-CHO (Yield: 250 mg, 86%). UV/Vis (CH₂Cl₂): λ (ϵ , M⁻¹ cm⁻¹) = 254 (81000), 502 (99800) nm. ¹H NMR (300 MHz, CDCl₃): δ = 10.46 (s, 2H), 8.80 (s, 1H), 7.84 (s, 1H), 7.68 (s, 1H), 7.58-7.63 (m, 1H), 7.42-7.51 (m, 2H), 7.29-7.37 (m, 13H), 7.05-7.16 (m, 2H), 6.74-6.97 (m, 10H), 6.57 (s, 1H), 6.31-6.48 (m, 2H), 4.35-4.69 (m, 4H), 1.01-1.35 (m, 72H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 186.20, 185.94, 185.68, 185.63, 149.93, 149.83, 149.04, 148.84, 148.66, 148.53, 147.89, 147.53, 143.62, 142.15, 141.39, 140.00, 139.61, 138.02, 136.68, 136.48, 136.35, 135.79, 135.65, 135.02, 134.15, 134.05, 133.70, 132.85, 132.79, 132.39, 131.68, 131.52, 130.54, 130.28, 130.21, 130.04, 129.79, 129.45, 129.18, 129.10, 129.02, 128.96, 128.37, 128.20, 128.07, 127.83, 127.59, 127.44, 127.33, 127.04, 125.44, 125.31, 120.54, 120.42, 120.05, 119.89, 118.97, 49.39,

48.88, 36.03, 35.91, 35.77, 35.71, 35.49, 35.40, 35.34, 29.70, 29.65, 29.62, 29.59, 29.53 ppm. FT-IR (ATR): *v* = 3224.7 (w), 2998.2 (w), 2951.7 (m), 2862.6 (w), 1670.6 (w), 1588.7 (m), 1549.6 (w), 1483.4 (w), 1451.4 (m), 1405.4 (w), 1387.0 (w), 1358.8 (s), 1321.3 (w), 1295.2 (m), 1255.4 (m), 1202.7 (w), 1087.1 (m), 1026.2 (s), 997.2 (w), 942.3 (w), 929.1 (w), 879.3 (w), 837.6 (w), 810.6 (w), 736.3 (m), 695.9 (m), 627.1 (m), 530.6 (w), 517.3 (w) cm⁻¹. MALDI-TOF-MS (dithranol): 1484.19 ([M]⁺). ESI-TOF-MS (25% CH₂Cl₂ in methanol): calcd for [C₁₀₃H₁₁₃N₄O₅]⁺: 1485.8705; found: 1485.8712 ([M + H]⁺).



(4-PhBn)₂OxP-BODIPY (BODIPY-OxP in main manuscript). A solution of (4-PhBn)₂OxP-CHO (300 mg, 0.20 mmol) and pyrrole (542 mg, 0.56 mL, 8.075 mmol, 40.0 equiv.) in CH₂Cl₂ (10 mL) was degassed by bubbling with N_2 for 15 minutes in the dark. The solution was stirred for 1 h at room temperature under N_2 in the presence of TFA (2.3 mg, 1.54 uL, 0.02 mmol, 0.1 equiv.). CH₂Cl₂ (10 mL) then DDQ (92 mg, 0.40 mmol, 2 equiv.) were added and the reaction mixture was stirred for 30 minutes. Et₃N (82 mg, 0.113 mL, 0.80 mmol, 4.0 equiv.) was then added and the solution was stirred for a further 15 minutes. Boron trifluoride diethyl etherate (344 mg, 0.30 mL, 2.42 mmol, 12.0 equiv.) was then added. The reaction mixture was stirred overnight (16 h) at room temperature then reaction completion was confirmed using thin layer chromatography (SiO₂; CH₂Cl₂:n-hexane, 1:1, v/v). Water was then added to the reaction mixture followed by extraction with CH_2Cl_2 . The CH_2Cl_2 phase was washed twice with water, dried over anhydrous Na_2SO_4 and the solvent evaporated yielding a crude green product which was purified by flash column chromatography (SiO₂; CH₂Cl₂:n-hexane, 1:1, v/v). Product containing fractions were combined and solvents removed under reduced pressure yielding the title compound as a reddish-orange (Yield: 150 mg, 45 %). UV/Vis (CH₂Cl₂): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 258 (80900), 488 (114700) nm. ¹H NMR (300 MHz, CDCl₃): δ = 9.54 (s, 1H), 9.28 (s, 1H), 7.92 (s, 1H), 7.58-7.61 (m, 4H), 7.27-7.41 (m, 13H), 7.21-7.23 (m, 1H), 6.81-7.09 (m, 12H), 6.43-6.64 (m, 4H), 6.12 (s, 1H), 5.90 (d, J = 7.7 Hz, 2H), 5.71 (d, J = 15.8 Hz, 1H), 5.06 (s, 1H), 4.71 (d, J = 14.3 Hz, 1H), 4.50 (d, J = 14.3 Hz, 1H), 4.22 (d, J = 15.8 Hz, 1H), 1.13-1.38 (m, 72H) ppm.¹³C NMR (76

MHz, CDCl₃): δ = 186.36, 186.19, 185.88, 153.50, 151.05, 148.69, 148.46, 147.80, 147.61, 147.15, 146.51, 146.33, 146.31, 146.28, 142.26, 142.22, 141.59, 141.04, 140.36, 140.34, 140.04, 139.06, 139.03, 137.15, 136.99, 136.56, 136.02, 135.58, 135.56, 135.52, 135.34, 135.31, 135.00, 134.96, 134.56, 134.05, 134.01, 133.98, 132.90, 132.88, 132.85, 132.51, 132.48, 132.05, 132.01, 131.93, 131.89, 131.86, 131.55, 131.53, 131.16, 130.99, 130.60, 130.45, 130.18, 129.97, 129.96, 129.92, 128.96, 128.45, 128.25, 127.86, 127.68, 127.59, 127.11, 126.89, 126.35, 126.08, 124.63, 120.60, 120.52, 120.47, 119.76, 119.69, 119.65, 119.43, 118.70, 115.79, 114.41, 114.19, 113.58, 113.57, 113.54, 112.77, 50.43, 50.40, 50.37, 49.90, 49.47, 49.46, 49.42, 35.75, 35.61, 35.39, 35.33, 35.27, 34.53, 30.10, 29.80, 29.57, 29.49 ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ = -143.6 (m), -147.7 (m) ppm. FT-IR(ATR): *v* = 3625.8 (w), 2953.7 (m), 2865.8 (w), 1714.0 (w), 1575.7 (m), 1532.2 (w), 1483.1 (w), 1452.2 (w), 1436.4 (w), 1385.4 (m), 1359.0 (m), 1329.4 (w), 1386.2 (w), 1255.0 (w), 906.7 (w), 885.8 (w), 873.5 (w), 841.8 (w), 817.2 (m), 744.4 (m), 722.9 (w), 696.3 (w), 659.6 (w), 629.0 (w), 531.4 (w), 491.2 (w) cm⁻¹; MALDI-TOF-MS (dithranol): 1646.80 ([M]⁺). ESI-TOF-MS (25% CH₂Cl₂ in methanol): calcd for [C₁₁₁H₁₁₈BF₂N₆O₄]⁺: 1647.9270; found 1647.9298 ([M + H]⁺)

3.0 ¹H-NMR Titration of BODIPY-OxP with Fluoride Anions



Figure S1. 1H NMR titration of BODIPY-OxP with tetrabutylammonium fluoride in CDCl₃. Equivalency fo fluoride anions is give at each spectrum. Resonances due to calix[4]pyrrole NH groups gradually broaden eventually being unobservable due to hydrogen bonding with fluoride anions. Binding site is depicted in the scheme below:



4.0 Femtosecond Transient Absorption Spectroscopy of Control Compounds.



Fig. S2. Fs-TA spectra at the indicated delay times of (a) BODIPY control and (b) OxP control in DCB. Decay associated spectra are shown on the right hand panel.

5.0 Chemical Analytical Spectra



¹H NMR Spectrum of (4-PhBn)₂OxP-CHO

¹³C NMR Spectrum of (4-PhBn)₂OxP-CHO



MALDI-TOF-MS Spectrum of (4-PhBn)₂OxP-CHO



ESI-TOF-MS Spectrum of (4-PhBn)₂OxP-CHO BPHO4PCH0 #1 RT: 0.04 AV:1 NL: 2.27E7 T: FTMS + p ESIFul ms [200000030000000]



UV-Vis Spectrum of (4-PhBn)₂OxP-CHO



¹H NMR Spectrum of (4-PhBn)₂OxP-BODIPY



¹³C NMR Spectrum of (4-PhBn)₂OxP-BODIPY



¹⁹F NMR Spectrum of (4-PhBn)₂OxP-BODIPY



MALDI-TOF-MS Spectrum of (4-PhBn)₂OxP-BODIPY



ESI-TOF-MS Spectrum of (4-PhBn)₂OxP-BODIPY



6.0 References

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