Supporting Information for

Intramolecular Energy Transfer within Butadiyne-Linked

Chlorophyll and Porphyrin Dimer-Faced, Self-assembled Prisms

Richard F. Kelley^{†§}, Suk Joong Lee^{†§}, Thea M. Wilson^{†§}, Yasuyuki Nakamura[‡],

David M. Tiede^{§||}*, Atsuhiro Osuka[‡]*, Joseph T. Hupp^{†§}*, and Michael R. Wasielewski^{†§}*

[†]Department of Chemistry and

 $\ensuremath{^\$}\xspace$ Argonne-Northwestern Solar Energy Research (ANSER) Center

Northwestern University, Evanston IL 60208-3113

^{II}Chemistry Division, Argonne National Laboratory, Argonne IL 60439

[‡]Department of Chemistry, Graduate School of Science, Kyoto University,

Kyoto 606-8502, Japan

*Address Correspondence to this Author. E-mail: <u>m-wasielewski@northwestern.edu</u>, <u>j-hupp@northwestern.edu</u>, <u>osuka@bake.kuchem.kyoto-u.ac.jp</u>, <u>tiede@anl.gov</u>

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. High resolution fast atom bombardment and electrospray ionization mass spectra were obtained with the 70-SE-4F and Q-Tof Ultima mass spectrometers at the University of Illinois at Urbana-Champaign. 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

1,4-Bis[Zinc 2-octyl-1-dodecyl 3-ethyl-pyrochlorophyllide a-20-yl]-1,3-butadiyne (1) Zinc 2-octyl-1-dodecyl 3-ethyl-20-ethynyl-pyrochlorophyllide $a^{1}(10 \text{ mg}, 11 \text{ }\mu\text{mol})$, copper iodine (4 mg, 20 µmol), and N,N-diisopropylethylamine (7 mg, 50 µmol) were combined in 1 mL of dry, deoxygenated toluene. The green solution was then refluxed under nitrogen with stirring in the dark for 24 hrs. After cooling to room temperature, the solvent from the blue-green solution was removed using a rotary evaporator. The resulting residue was chromatographed on a SEC column using THF as the mobile phase. The chromatographed product was finally precipitated from hexanes to yield (1) (5 mg, 50 %). ¹H NMR (δ in CDCl₃ w/ pyridine-d5) 9.38, 9.05 (s, 2) H, 5- and 10- meso H), 5.00 (br s, 4 H, 13^2 -CH₂), 4.86 (q, 2 H, J = 7.6 Hz, 17-H), 4.08 (q, 4 H, J = 7.1 Hz, 17d-OCH₂-), 4.05 (dd, 2 H, J = 3.3, 6.8 Hz, 18-H), 3.85 (t, 4 H, J = 5.9 Hz, 3a-CH₂-), 3.65 (q, 8 H, J = 7.1 Hz, 8a-CH₂-), 3.61, 3.59, 3.17 (s, 6 H, 2-, 7- and 12-CH₃), 2.44 (m, 4 H, 17a-CH₂-), 1.83 (m, 4 H, 17b-CH₂-), 1.73 (d, 6 H, J = 7.1 Hz, 18-CH₃), 1.67, 1.65 (t, 6 H, J = 8.0 Hz, 3b- and 8b-CH₃), 1.57 (m, 2 H, branched alkyl -CH(CH₂-)₂), 1.22-1.10 (br m, 64 H, branched alkyl -CH₂-), 0.85 (m, 6 H, J = 6.2 Hz, branched alkyl -CH₃). HRMS-FAB (m/z): $[M]^+$ calcd for C₁₁₀H₁₄₆N₈O₆Zn₂, 1802.9948; found, 1802.9951.

4-(4-Bromo-phenylethynyl)pyridine (LL-1). To a solution of 4-ethynylpyridine (206 mg, 2.00 mmol) and 1,4-dibromobenzene (1.415 g, 6.00 mmol) in triethylamine (25 mL), $Pd(PPh_3)_2Cl_2$ (70 mg, 100 µmol) and CuI (15 mg, 79 µmol) was added. The resulting mixture was refluxed for 24 hr. After cooling to RT, the solvent was removed on a rotary evaporator. The residue was then dissolved in methylcyclohexane, washed with H₂O, and dried over MgSO₄. Following the solvent removal using a rotary evaporator, the resulting product was purified by silica gel chromatography using methylcyclohexane / MeOH (9.5/0.5) as the mobile phase to afford LL-1

(372 mg, 72% yield). ¹H NMR (δ in CDCl₃): 8.58 (d, J = 6.1 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.39 (d, 2H), 7.35 (d, 2H). HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₃H₈BrN, 256.9840; found, 256.9902

1,3,5-Tris[2-{4-(2-(4-pyridyl)ethynyl)phenyl}ethynyl]benzene (LL). To a solution of 1,3,5-triethynylbenzene²(45 mg, 0.30 mmol) and 4-(4-bromo-phenylethynyl)-pyridine (310 mg, 1.21 mmol) in triethylamine (15 mL), Pd(PPh₃)₄ (24 mg, 21 µmol) and CuI (7.5 mg, 0.035 mmol) was added. The reaction mixture was then refluxed for 2 days. Following solvent removal using a rotary evaporator, the residue was dissolved in EtOAc and washed with sat NH₄Cl solution (aq) and H₂O. The solution was dried over MgSO₄ and the solvent was again removed. The resulting crude product was chromatographed on a silica gel column using methylcyclohexane / MeOH (9:1) as the mobile phase to yield LL (120 mg, 59%). ¹H NMR (CDCl₃): 8.63 (d, J= 6.1 Hz, 6H), 7.68 (s, 3H), 7.55 (s, 12H), 7.41 (d, J = 6.1 Hz, 6H). HRMS-ESI (m/z): [M+H]⁺ calcd for C₅₁H₂₇N₃, 681.2205; found, 681.2275.

Optical Spectroscopy

Femtosecond transient absorption measurements were performed with the following apparatus: A Spectra-Physics Millenium V frequency-doubled CW Nd:YVO₄ laser was used to pump a Coherent MIRA Ti:sapphire oscillator. The 110 fs, 856-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 frequencydoubled 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 μ J/pulse. Two 5% reflective beam splitters were placed

in the output path to generate two 828-nm beams for white light generation. The remaining 856nm light was frequency doubled by using a 1-mm-type I LBO crystal to give 428-nm 120-fs, 75µJ pulses.³ The 856-nm light from the first 5% beam splitter was passed through a waveplatepolarizer 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 856-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 856-nm light from the second 5% beam splitter was used to create a second white light continuum by focusing the 856-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.⁴ The first stage contains a Type II BBO crystal, which was pumped with about 20 µJ of 428-nm light focused into the crystal with a 300 mm f.l. lens. After removal the IR idler beam and residual 428-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 428 nm pump light. The final amplified pulse energy was ~7.5 μ J/pulse after filtering out the residual 428-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.³ The instrument was outfitted with a CCD array detector (Ocean Optics PC2000) for simultaneous collection of spectral and kinetic data.⁵

Fluorescence lifetime measurements were made using a Hamamatsu C4780 picosecond fluorescence lifetime measurement system, consisting of a C4334 Streakscope[™] and a C4792-01 synchronous delay generator. The excitation light source was supplied by a home-built cavity-

dumped Ti:Sapphire laser⁶ 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.

Association constants for 1₃-SL₂

The equilibrium constants applicable to the three species model, Figure S1 are defined as follows:

$$K_{12} = [1 - SL_2]/[1][SL]^2$$
(1)

$$K_{32} = [1_3 - SL_2]/[1]^3 [SL]^2$$
⁽²⁾

$$K_{32\leftrightarrow 12} = \left(K_{12}\right)^3 / K_{32} \tag{3}$$

The titration data, Figure S2, were fit to a three chromophore model using multivariate factor analysis (SPECFIT V3.0),⁷ Figure S3, to yield the stability constants $K_{12} = (1.14 \pm 0.05) \times 10^7$ M⁻² and $K_{32} = (2.27 \pm 0.09) \times 10^{24}$ M⁻⁴. From these stability values, the equilibrium constant for the exchange between the two species was determined to be $K_{32\leftrightarrow 12} = 6.53 \times 10^{-4}$ M⁻². These results suggest that the 1₃-SL₂ prism is fully formed and stable after the stoichiometric addition of 2/3 equivalents of SL and that the prismatic assembly is maintained under the conditions used for the photophysical measurements.

Acknowledgment

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

spectrometer was purchased in part with a grant from the National Science Foundation, Division of Biological Infrastructure (DBI-0100085).



Figure S1. Schematic representation of the three colored species model used for fitting the **1-SL** titration data. K_{32} and K_{12} are the stability constants for the **1₃-SL**₂ prism and the **1-SL**₃ open complex, respectively. $K_{32} \leftrightarrow_{12}$ is the equilibrium constant for the exchange between the two species.



Figure S2. Titration of 1 with SL in toluene ([1] = 1.27×10^{-5} M).



Figure S3. Speciation profile derived from the spectrophotometric titration of 1 with SL using a three colored species model.



Figure S4. Small Angle X-ray Scattering (scattering intensity versus q^2) for 1₃-SL₂. Inset: small angle scattering for the 1₃-SL₂ model. Guinier fits to the data are also shown.





Figure S5. Small Angle X-ray Scattering (scattering intensity versus q^2) for **1₃-LL**₂. Inset: small angle scattering for the **1₃-LL**₂ model. Guinier fits to the data are also shown.

Figure S6. Small Angle X-ray Scattering (scattering intensity versus q^2) for **2₃-LL₂**. Inset: small angle scattering for the **2₃-LL₂** model. Guinier fits to the data are also shown.



Figure S7. Time resolved fluorescence data for 1_3 -SL₂ in toluene following excitation with 400 nm, 120 fs laser pulses monitored from 714 to 726 nm. The fit to the data is also shown.



Figure S8. Time resolved fluorescence data for 2_3 -SL₂ in toluene following excitation with 400 nm, 120 fs laser pulses monitored from 716 to 728 nm. The fit to the data is also shown.



Figure S9. Time resolved fluorescence data for 1_3 -LL₂ in toluene following excitation with 400 nm, 120 fs laser pulses monitored at from 729 to 741 nm. The fit to the data is also shown.



Figure S10. Time resolved fluorescence data for 2_3 -LL₂ in toluene following excitation with 400 nm, 120 fs laser pulses monitored at from 730 to 742 nm. The fit to the data is also shown.





Figure S12. Transient absorption spectra used to estimate the extinction coefficient of the $S_1 \rightarrow S_n$ absorbance for 1₃-SL₂, 1₃-LL₂, 2₃-SL₂, and 2₃-LL₂ in toluene. The red lines are the constant $S_1 \rightarrow S_n$ extinction coefficients used in the Förster energy transfer rate calculations given in the main text.

Table S1. Effect on the calculated Förster energy transfer rate of reducing the magnitude of the $S_1 \rightarrow S_n$ extinction coefficients by comparing all four estimates as presented by the red, green, blue, and cyan lines in Figure S12.

	1 ₃ -SL ₂ Chl Prism Small (Toluene)					Forster		Experimental
	d	η	κ²	$ au_{Fluor}$	Φ_{Fluor}	k _{Energy} Transfer	τ _{Energy} Transfer (ps)	τ _{Energy Transfer} (ps)
estimate 1	17.3	1.496	1	1.19	0.07	9.68E+10	10.3	6.2
estimate 2	17.3	1.496	1	1.19	0.07	7.26E+10	13.8	
estimate 3	17.3	1.496	1	1.19	0.07	4.84E+10	20.7	
estimate 4	17.3	1.496	1	1.19	0.07	2.42E+10	41.3	
	1 ₃ -LL ₂ Cł	nl Prism Lar	rge (To	luene)				
estimate 1	28.3	1.496	1	1.10	0.08	6.36E+09	157.3	14.6
estimate 2	28.3	1.496	1	1.10	0.08	4.77E+09	209.7	
estimate 3	28.3	1.496	1	1.10	0.08	3.18E+09	314.6	
estimate 4	28.3	1.496	1	1.10	0.08	1.59E+09	629.1	
	2 3-SL ₂ P	orphyrin Pr	ism La	rge (Tolue	ene)			
estimate 1	17.3	1.496	1	1.36	0.14	9.07E+11	1.1	4.8
estimate 2	17.3	1.496	1	1.36	0.14	6.80E+11	1.5	
estimate 3	17.3	1.496	1	1.36	0.14	4.54E+11	2.2	
estimate 4	17.3	1.496	1	1.36	0.14	2.27E+11	4.4	
	2 3 -LL 2 P	orphyrin Pri	ism La	rge (Tolue	ene)			
estimate 1	28.3	1.496	1	1.33	0.15	5.20E+10	19.2	18.4
estimate 2	28.3	1.496	1	1.33	0.15	3.90E+10	25.6	
estimate 3	28.3	1.496	1	1.33	0.15	2.60E+10	38.4	
estimate 4	28.3	1.496	1	1.33	0.15	1.30E+10	76.9	

References:

(1)Kelley, R. F.; Tauber, M. J.; Wasielewski, M. R. Angew. Chem., Int. Ed. 2006, 45, 7979-7982.

(2)Mongin, O.; Papamicael, C.; Hoyler, N.; Gossauer, A. J. Org. Chem. 1998, 63, 5568-5580.

(3)Lukas, A. S.; Miller, S. E.; Wasielewski, M. R. J. Phys. Chem. B 2000, 104, 931-940.

(4)Greenfield, S. R.; Wasielewski, M. R. Opt. Lett. 1995, 20, 1394-1396.

(5)Giaimo, J. M.; Gusev, A. V.; Wasielewski, M. R. J. Am. Chem. Soc. 2002, 124, 8530-8531.

(6)Pshenichnikov, M. S.; de Boeij, W. P.; Wiersma, D. A. Opt. Lett. 1994, 19, 572-574.

(7); Version 3.0.38 ed.; Spectra Software Associates: Marlborough, MA, 2006.