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Supporting Information for

Fast Energy Transfer Within a Self-Assembled Cyclic Porphyrin Tetramer

by

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Experimental Section.

Materials and General Procedures. Chemicals were obtained from commercial sources and used without further purification. All reactions were performed under N_2 using inert-atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. Column chromatography was carried out with 230-400 mesh silica gel from Sorbent Technologies. Absorbance and fluroescence spectra were obtained using Varian Cary 5000 UV-Vis-NIR and ISA Instruments Fluorolog spectrophotometers, respectively. NMR spectra were recorded on either a Mercury 400 (400.168 MHz for ^{1}H) or an Inova 500 (499.773 for ^{1}H, and 125.669 MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million downfield from tetramethylsilane with solvent resonances as internal standards. Low-resolution laser desorption mass spectra were obtained with a PE Voyager DE-Pro MALDI-TOF mass spectrometer using dithranol as a matrix from the Integrated Molecular Structure Education Research Center (IMSERC) at Northwestern University. High-resolution fast atom bombardment (FAB-HR) mass spectra were obtained with the 70-SE-4F mass spectrometer at the University of Illinois at Urbana-Champaign.

[10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (1). Dipyrromethane[1] (500 mg, 3.4 mmol) and 2,6-di(n-hexoxy)benzaldehyde[2] (1042 mg, 3.4 mmol) were dissolved in 600 mL of CH_2Cl_2 . The resulting solution was degassed for 10 min at RT. Trifluoroacetic acid (165 μL) was slowly added and the resulting mixture was allowed to reflux for 8 h under N_2 atmosphere.

One gram of 2,3-dicyano-5,6-dichloro-parabenzoquinone was then added and the reaction mixture was refluxed for another 1 h. After cooling, 3.5 mL of pyridine was added. The precipitate was filtered off and the volatiles were removed under reduced pressure. The resulting residue was purified by silica-gel column chromatography (Hexanes/Dichloromethane (1:1 v/v)) to afford pure 10,20-bis[2,6-di(n-hexoxy)phenyl]porphin. The purple solid was then metallated with zinc(II) acetate to afford pure **1** (452 mg, 29 %). ^{1}H NMR ($CDCl_3$): δ 10.14 (s, 2 H), 9.26 (d, $^3J_{H\text{-}H}$ = 5.2 Hz, 4 H), 8.96 (d, $^3J_{H\text{-}H}$ = 5.2 Hz, 4 H), 7.05 (t, $^3J_{H\text{-}H}$ = 8.5 Hz, 2 H), 7.01 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4 H), 3.83 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 8 H), 0.90 (m, 8 H), 0.50 (m, 16 H), 0.40 (m, 8 H), 0.23 (m, 12 H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.03, 151.35, 149.42, 132.81, 129.29, 120.62, 114.55, 105.15, 104.01, 68.71, 30.88, 28.72, 25.12, 22.16, 13.58. MS (MALDI-TOF) *m/z* 927.1 (Calcd *m/z* 926.6 for M^+).

[5-bromo-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (2). A solution of **1** (928 mg, 1 mmol) and pyridine (0.5 mL) in chloroform (184 mL) was cooled down to -5°C and degassed for 10 min. N-Bromosuccinimide (175 mg) was added all at once. After the stirring for 15 min, the reaction mixture was poured into 200 mL of water. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness in vacuo to afford a deep purple oil which was purified by silica-gel column chromatography (Hexanes/Dichloromethane (1.5:1 v/v)) to afford **2** (65 mg, 64%). ^{1}H NMR ($CDCl_3$): δ 10.09 (s, 1 H), 9.72 (d, $^3J_{H\text{-}H}$ = 4.2 Hz, 2 H), 9.27 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 2 H), 8.99 (d, $^3J_{H\text{-}H}$ = 4.2 Hz, 2 H), 8.98 (d, $^3J_{H\text{-}H}$ = 4.3 Hz, 2 H), 7.71 (t, $^3J_{H\text{-}H}$ = 8.6 Hz, 2 H), 7.02 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4 H), 3.84 (t, $^3J_{H\text{-}H}$ = 6.1 Hz, 8 H), 0.92 (m, 8 H), 0.45 (m, 16H), 0.32 (m, 8 H), 0.20 (m, 12 H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.24, 151.25, 151.17, 150.17, 149.03, 132.57, 132.45, 132.37, 131.80, 130.06, 121.29, 113.78, 105.50, 103.79, 68.83, 30.96, 28.77, 25.03, 22.15, 13.64. MS (MALDI-TOF) *m/z* 1005.5 (Calcd *m/z* 1005.5 for M^+).

[5-(4-ethynylpyridyl)-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (EPZn). A solution of **2** (100 mg, 0.10 mmol), 4-ethynylpyridine[3] (23 mg, 0.22 mmol), tetrahydrofuran (5 mL), and diethylamine (1 mL) was degassed for 10 min. CuI (2.0 mg, 11 mol %) and $Pd(PPh_3)_4$ (2.6 mg, 2.3 mol %) was added and the mixture was refluxed for 2 days under N_2 atmosphere in the dark. Solvent was removed under vacuum and the residue was purified by silica-gel chromatography (Hexanes/Tetrahydrofuran (7:3 v/v)) to afford **EPZn** (32 mg, 31 %). ^{1}H NMR (toluene-d_8 with 10 molar equivalents pyridine-d_5): δ 9.83 (d, $^3J_{H\text{-}H}$ = 4.4, 2 H), 9.73 (s, 1 H), 9.20 (d, $^{3}J_{\text{H-H}}$ = 4.4 Hz, 2 H), 9.08 (d, $^{3}J_{\text{H-H}}$ = 4.4 Hz, 2 H), 9.02 (d, $^{3}J_{\text{H-H}}$ = 4.4 Hz, 2 H), 8.46 (d, $^{3}J_{\text{H-H}}$ = 4.6 Hz, 2 H), 7.70 (t, $^{3}J_{\text{H-H}}$ = 8.1 Hz, 2 H), 7.36 (d, $^{3}J_{\text{H-H}}$ = 4.4 Hz, 2 H), 6.98 (d, $^{3}J_{\text{H-H}}$ = 8.8 Hz, 4 H), 3.71 (t, $^{3}J_{\text{H-H}}$ = 6.6 Hz, 8 H), 0.92 (m, 16 H), 0.79 (m, 8 H), 0.43 (m, 8 H), 0.27 (t, $^{3}J_{\text{H-H}}$ = 7.3, 12 H). ^{13}C{^{1}H} NMR (toluene-d8 with10 molar equivalents pyridine-d5): δ 161.07, 152.67, 152.15, 151.21, 150.58, 149.87, 133.14, 132.77, 132.13, 131.97, 130.82, 130.41, 122.54, 114.59, 107.92, 105.84, 100.19, 96.91, 92.96, 68.99, 31.56, 29.56, 25.72, 22.81, 14.13. MS (FAB): *m/z* 1025.4798 (Calcd *m/z* 1025.4798 for M^{+}).

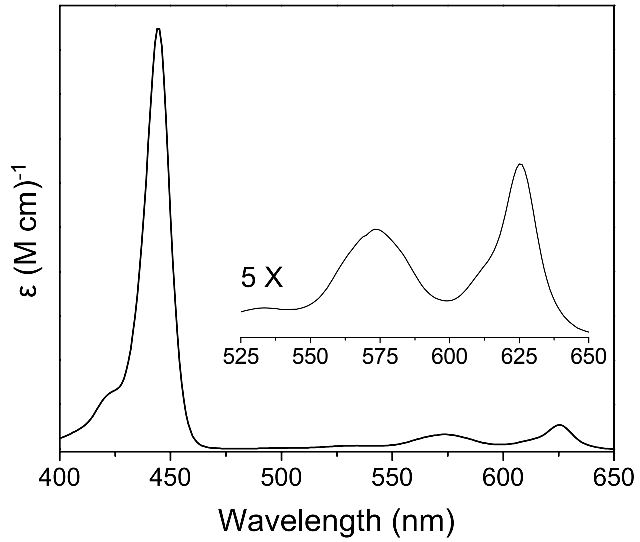


Figure S1. Ground-state electronic absorption spectrum of **EPZn** in pyridine. Peak positions: 444 nm (Soret), 573 nm (Q_x), 625 nm (Q_y).

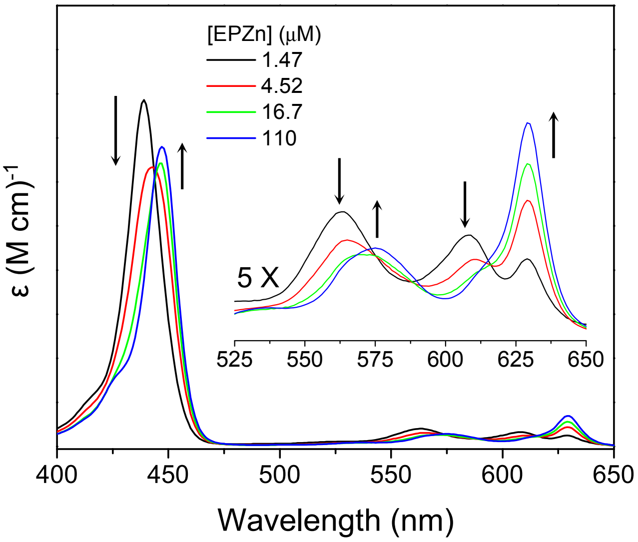


Figure S2. Ground-state electronic absorption spectra of **EPZn** in dry toluene. Arrows show the direction of change in absorption with increasing porphyrin concentration. Peak positions at [EPZn] = 110 μM: 447 nm (Soret), 575 nm (Q_x), 629 nm (Q_y).

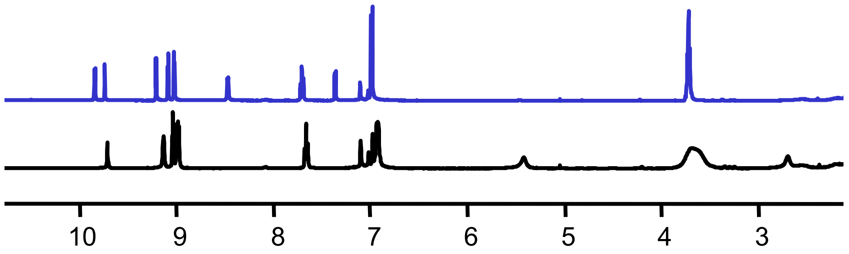


Figure S3. ^{1}H NMR spectra (2.4 to 10.8 ppm) of **EPZn** in toluene-d_8 (black) and in toluene-d_8 with 10 molar equivalents pyridine-d_5 (blue).

Solution X-ray scattering experimental methods.

Solution X-ray scattering measurements were carried out at Beamline 12-1D at the Advanced Photon Source at Argonne National Laboratory. Detailed descriptions of procedures used for X-ray scattering measurements and coordinate-based analyses have been reported previously.[4,5,6] Briefly, a double-crystal Si (1 1 1) monochromator and a two-dimensional mosaic CCD detector were used in the data collection. The X-ray energy was set and the sample detector distances where adjusted to obtain scattering in two different q-ranges: 10 keV for 0.01 $\text{Å}^{-1} < q < 0.43\ \text{Å}^{-1}$ and 20 keV for 0.1 $\text{Å}^{-1} < q < 2.4\ \text{Å}^{-1}$. Here, $q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of X-rays and 2θ is the scattering angle.

The sample solutions were prepared immediately prior to measurement. The solutions were injected into a glass capillary (0.2 mm diameter), which was positioned in the beam path. Five 1-second scans were averaged for each solvent blank (dry toluene or dry toluene with pyridine) and sample to obtain the solvent and sample scattering patterns. The solute scattering intensity was obtained by subtracting the scattering pattern obtained from the solvent blank from the entire sample scattering intensity.

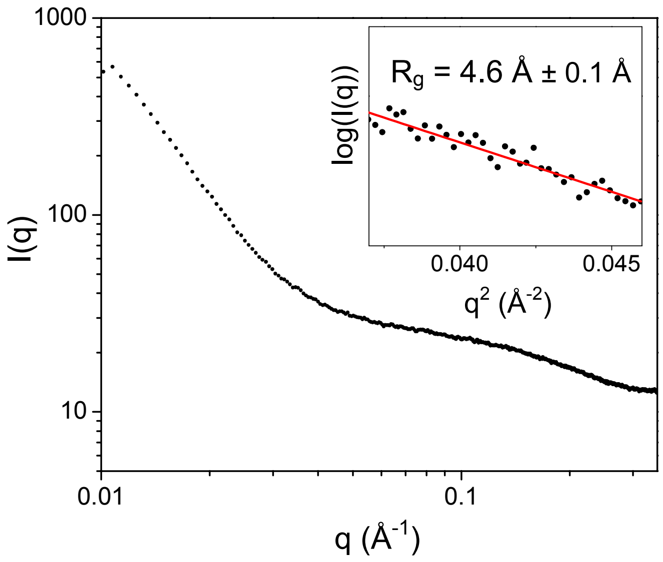


Figure S4. Experiment scattering intensity, $I(q)$, versus scattering vector, q, data for **EPZn** in dry toluene with 2 molar equivalents pyridine. Inset: Scattering intensity versus q^2. Guinier fit to the data is also shown.

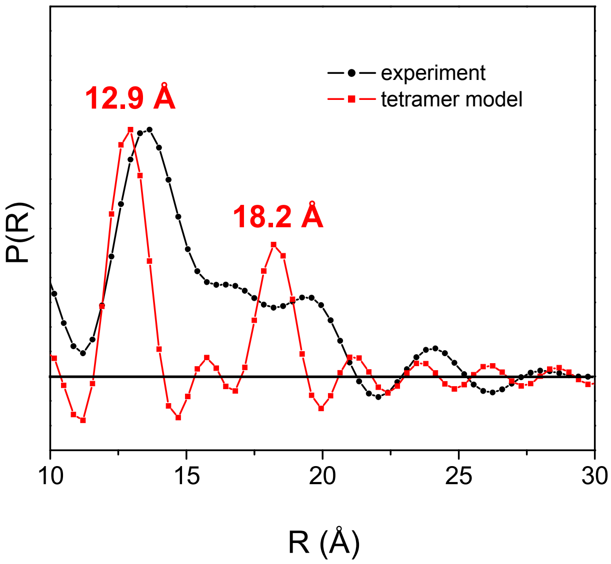
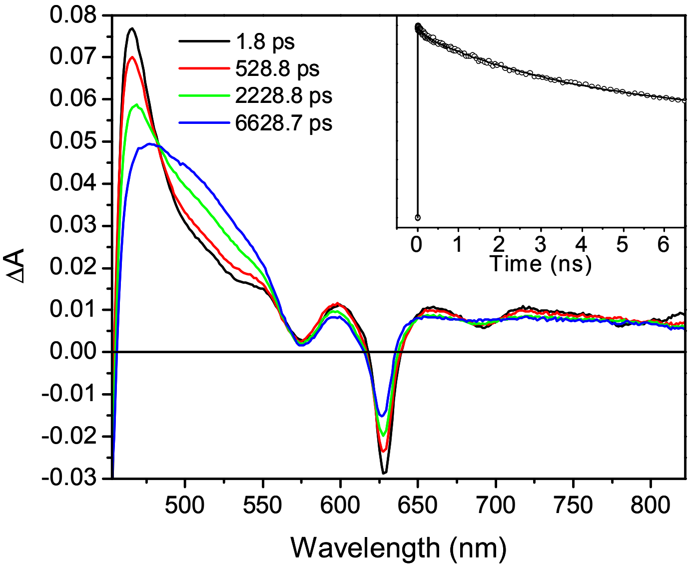


Figure S5. Experiment and model pair-distribution plots, calculated from corresponding X-ray scattering intensity versus q (Å^{-1}) plots. The tetramer model is calculated from Zn-Zn interactions only. Model peaks are indicated.

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.[7] 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

Figure S6. Transient absorption spectra of **EPZn** in pyridine following excitation with 632 nm, 120 fs laser pulses. Inset: transient absorption kinetics of ^{1*}**EPZn** monitored at 467 nm. The nonlinear least-squares fit to the data is also shown.



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.[8] 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 of 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.[7] The instrument was outfitted with a CCD array detector (Ocean Optics PC2000) for simultaneous collection of spectral and kinetic data.[9]

Femtosecond transient anisotropy measurements were performed with the following configuration: the polarization of the probe light in the transient absorption apparatus was set to 45° with respect to the pump light before reaching the sample. After passing through the irradiated sample, the probe beam was split into purely parallel and perpendicular polarization components using a polarization beamsplitter cube. Data for both pump-probe orientations were simultaneously detected by dual channel spectrometer (DS 2000 and ADC2000-PCI+, Ocean Optics). The anisotropy decays were then calculated as follows:

$$r(t) = \frac{I_{Parallel}(t) - GI_{Perpendicular}(t)}{I_{Parallel}(t) + 2GI_{Perpendicular}(t)}$$

where $I_{Parallel}(t)$ and $I_{Perpendicular}(t)$ correspond to the intensity of the transient absorption features when the pump-probe orientations are parallel and perpendicular, respectively. The factor G is defined as $I_{Perpendicular}(t)/I_{Parallel}(t)$ and was used to correct for differences in the sensitivities of the detection system for vertically and horizontally polarized light. Kinetic analyses of the data were performed at several wavelengths using a Levenberg-Marquardt nonlinear least squares fit to a

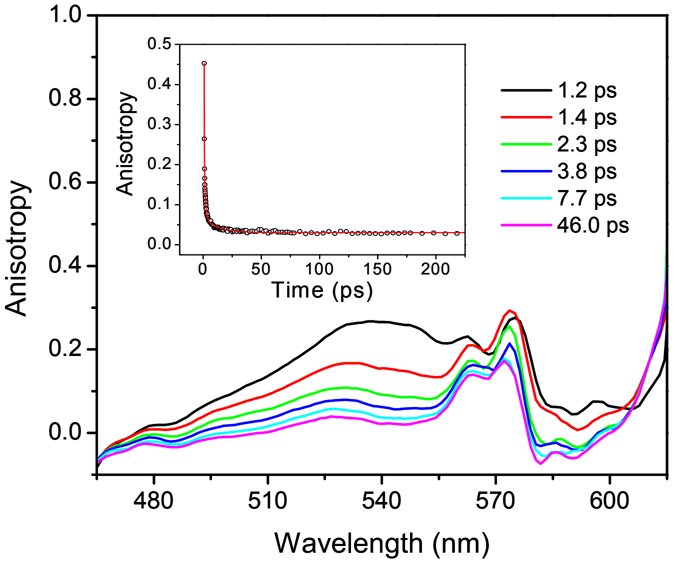


Figure S7. Transient absorption anisotropy spectra of **EPZn** in dry toluene following excitation with 632 nm, 120 fs laser pulses. Inset: transient anisotropy kinetic for ^{1*}**EPZn** at 535 nm (◦◦◦◦). Nonlinear least-squares fit to the data is also shown (—).

general sum-of-exponentials function with an added Gaussian to account for the finite instrument response.

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-

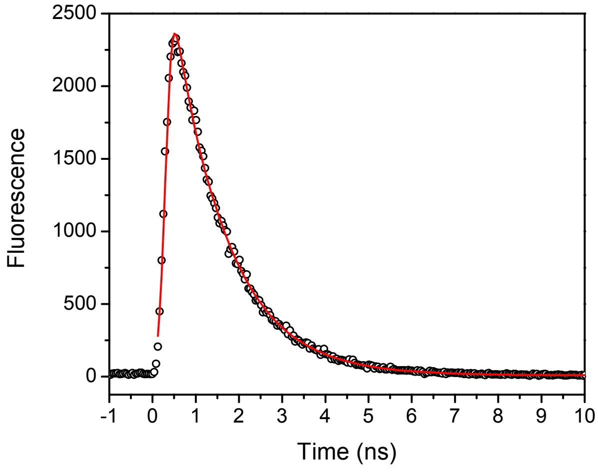


Figure S8. Time resolved fluorescence data for **EPZn** in pyridine following excitation with 400 nm, 120 fs laser pulses monitored at 880 nm. The fit to the data is also shown.

dumped Ti:Sapphire laser[10] 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.

Acknowledgement

High-resolution fast atom bombardment mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, at the 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).

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