

Supporting Information for

**Photoinduced Electron Transfer From Rail to Rung in a Self-assembled
Porphyrin Oligomeric Ladder**

by

Chunxing She,^{ab} Suk Joong Lee,^{ab} James E. McGarrah,^a Josh Vura-Weis,^{ab} Michael R. Wasielewski,^{ab} Hanning Chen,^{ab} George C. Schatz,^{ab} Mark A. Ratner^{ab} and Joseph T. Hupp^{*ab}

^a Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

^b Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

*To whom correspondence should be addressed. E-mail: j-hupp@northwestern.edu,
Tel: (847) 467-3347. Fax: (847) 491-7713

Experimental section

Materials. Synthesis and characterization of trimer has been published in a previous publication.¹ 3,6-di-4-pyridinyl-1,2,4,5-tetrazine and 1,4-bis(4-pyridyl)benzene are synthesized according to published procedures.²

Electrochemistry. Cyclic voltametry and square wave voltametry were performed using a platinum electrode in dried dichloromethane (HPLC grade) or 1,2-difluorobenzene (Aldrich, 98%). Tetra-n-butylammonium hexafluorophosphate (TBAPF₆, Fluka, ≥98.0%) was dried at 120 °C overnight before use. The solutions were deoxygenated by N₂. All voltages are relative to the internal reference ferrocenium/ferrocene (Fc⁺/Fc) redox couple.

Absorption and emission spectroscopy. All photophysical measurements were made at ambient in spectroscopic grade toluene. Absorption spectra were collected on a CARY 5000 UV-vis-NIR spectrophotometer. Emission spectra were collected on a Jobin-Yvon Fluorolog 3 fluorimeter using a red sensitive Hamamatsu R928 photomultiplier tube.

Transient absorption 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, 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 μJ/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.³ 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.⁴ 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. Pump energy at the sample was 1 μJ/pulse, and the transient spectra were taken at magic angle. 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

TDCP measurements. All measurements were performed with instrumentation described previously.⁶ The experimental protocol was nearly identical to that for the previously reported transient DC photocurrent spectroscopy studies done in displacement current mode. A 1000 V potential was applied across a 0.35 mm gap between two electrodes. The samples were excited at 532 nm with an OpoTek Vibrant OPO laser pumped with the third harmonic of a Quantel Brilliant Nd:YAG laser (10 Hz, ~ 2 ns fwhm). Laser beam profiles were collected with a 25 GHz Si photodiode (ET-2000 from Electron Optical Technology, Inc.). Solutions were purged with N₂ for 15-20 minutes before excitation. Reported values are averages from 2-4 energy-corrected data sets. A typical data set comprised 10 to 20 measurements, each of them an average of 256 shots.

TDCP analysis. The methodology of TDCP data analysis has been fully detailed elsewhere,⁷ and is only briefly summarized here. The transient voltage, $v(t)$, which is measured across the load resistor R in the circuit described in Scheme 1, results from the displacement current, dQ/dt (where Q is charge), i.e. $v(t) = R dQ/dt$. The equation for time variation in the system is as follows:

$$v(t) + \tau_{RC} \frac{dv(t)}{dt} = RS \frac{dP}{dt} \quad (3)$$

where we introduce the RC time constant, τ_{RC} , and S the surface area of the parallel measuring plates in the capacitance cell. It is instructive to consider the time evolution of the signal in a simplified two-state case where we only consider the polarizability change. In a self-assembled ladder (**L1**), charge transfers instantaneously (relative to laser pulse) from symmetric porphyrin trimer with zero ground state dipole moment to the tetrazine ligand, resulting in a charge-separation state. The evolving transient voltage, $v(t)$, in response to laser excitation in an electric field can be expressed as:^{8d}

$$v(t) + \tau_{RC} \frac{dv(t)}{dt} = G(\mu_s^*)^2 \left[\frac{e^{-t/\tau_{eff}}}{\tau_{eff}} - \frac{e^{-t/\tau_F}}{\tau_F} \right] \quad (4)$$

In eq. 4, G is a constant experimental factor detailing the contributions of solvent and E in the experiment, τ_{eff} equals $\tau_F^{-1} + \tau_r^{-1}$ where τ_r is the rotational diffusion time. μ_s^* is the permanent dipole moment for the charge-separation state.

The RC time constant was determined to be 0.37 ns by fits of experimental TDCP measurements of 4-dimethylamino-4-nitrostilbene (DMANS) in toluene as a standard, according to previously published work.^{8a}

Analysis of the TDCP signal was aided by a fitting program kindly provided by Professor Sergei Smirnov at NMSU. Two states (ground and charge-transfer states) were treated in the program for **L1** while three states were treated for **L2**: ground state (G), singlet excited state (S), and triplet excited state (T).

If we assume a charge-separation distance of 7.5 Å and the excitation correlation factor $\beta = 0$ (see molecular structure in Fig. 4), we would obtain a rotational diffusion time of 0.55 ± 0.1 ns which is too fast for rotation of molecular dipole with the size of 3~4 nm in diameter. Therefore, we ruled out the possibility that electron transfers to ONLY the tetrazine in the center of ladder **L1** while hole is delocalized on the trimer. In the analysis of relatively small TDCP signal for **L1** due to the short lifetime (~0.2 ns) of the CT-state, however, we could not rule out the possibility that 10% electron transfers to the tetrazine in the center of ladder **L1** because of relatively small signal. Statistically, there is 67% probability for electron to transfer to the tetrazine at the terminals of ladder **L1**, all other factors (e.g. electronic coupling) being equal.

Electronic structure calculations. The molecular geometries of both neutral and cationic trimers were optimized using DFT, as implemented in the CP2K atomistic simulation package,⁸ with the gradient-corrected Perdew-Burke-Ernzerhof (PBE) exchange-correlation term.⁹ To alleviate the computational burden for this rather large system with 227 atoms, the norm-conserving Gaussian-type Goedecker-Teter-Hutter (GTH) pseudopotential¹⁰ was employed to describe effectively the interaction between valence electrons and an atom's frozen core, which is composed of its nucleus and core electrons. The numbers of valence electrons for hydrogen, carbon, nitrogen, oxygen and zinc are 1, 4, 5, 6 and 12, respectively. To include different spin multiplicity, spin-dependent and spin-independent wavefunctions were used for cationic and neutral trimers, respectively, with double-zeta valence polarization Gaussian basis set (DZVP).

Single point energy calculation was performed at the optimized geometries. The HOMO-LUMO gap was calculated to be 1.32 eV for neutral trimer, in good agreement with experimental measurement (Q band $\lambda_{max} = 1.71$ eV).

The Mulliken population analysis was performed to calculate atomic partial charges for both compounds. The change of electron population on each atom as a result of photo-induced electron transfer can be readily obtained by subtracting partial charges in neutral trimer from those in cationic trimer. The +1 charge distribution in cation was visualized in VMD molecular graphics program¹¹ (Fig. 5). Each of the two terminal subunits gains 0.35 elementary

charge, whereas the central subunit gains slightly less 0.30 elementary charge, suggesting the nearly equal sharing of the positive charge in cation.

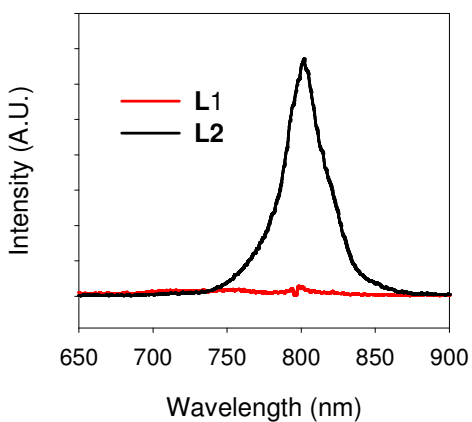


Fig. S1. Relative luminescence of ladders: trimer+3,6-di-4-pyridyl-1,2,4,5-tetrazine (**L1**) and trimer+1,4-bis(4-pyridyl)-benzene (**L2**) excited at 800 nm with identical optical density (0.05 OD). Scattering of excitation was subtracted.

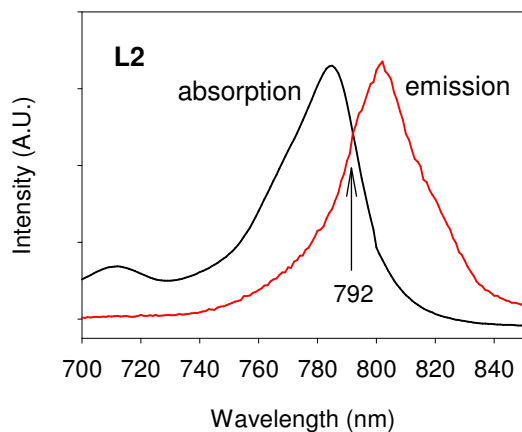


Fig. S2. Normalized absorption and emission spectra of ladder trimer+1,4-bis(4-pyridyl)-benzene (**L2**). The wavelength at the cross points is 792 nm. This cross point is used to estimate E_{00} ($=1240 \text{ nm eV}^{-1} / 792 \text{ nm} = 1.57 \text{ eV}$) of trimer-tetrazine.

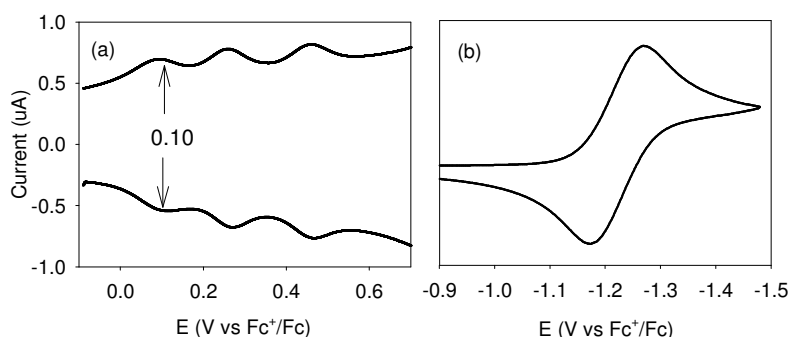


Fig. S3. (a) Square wave voltammetry of **L1** in CH_2Cl_2 . The first oxidation potential is 0.10 V vs. Fc^+/Fc for the planarized trimer. (b) Cyclic voltammetry of 3,6-di-4-pyridyl-1,2,4,5-tetrazine (DPT) in 1,2-difluorobenzene. The reduction potential for DPT is -1.22 V. The electrolyte used is 0.1 M TBAPF_6 .

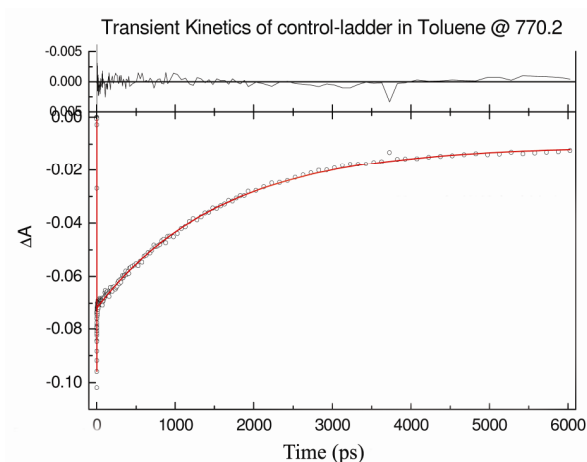


Fig. S4. Ground state recovery kinetics of **L2** at 770 nm. The main component of ground-state recovery occurs in 1.3 ns through excited state decay.

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