

Photoinduced electron transfer from rail to rung within a self-assembled oligomeric porphyrin ladder†

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}

Received (in Berkeley, CA, USA) 10th August 2009, Accepted 24th November 2009

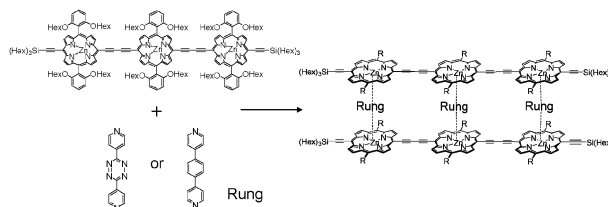
First published as an Advance Article on the web 8th December 2009

DOI: 10.1039/b916392a

Photoinduced electron transfer in a self-assembled supramolecular ladder structure comprising oligomeric porphyrin rails and ligated dipyridyltetrazine rungs was characterized by transient absorption spectroscopy and transient direct current photoconductivity to be mainly from an oligomer (rail) to the center of a terminal tetrazine (rung), with the remaining hole being delocalized on the oligomer and subsequent charge recombination in 0.19 ns.

Highly conjugated porphyrin oligomers¹ show interesting photophysical properties such as reasonably long singlet excited-state lifetime (~ 1 ns) and exciton delocalization² among the porphyrin subunits and therefore are potentially useful for light-harvesting applications. These oligomers can self-assemble into higher order structures³ that may facilitate chromophore immobilization and spacing control on photoelectrodes, similar to other self-assembled supramolecular structures on surfaces.⁴ Once the immobilized supramolecular chromophores absorb photons, charges are expected to be separated, then collected. Designing systems that work for solar-to-electricity conversion requires fundamental understanding of charge separation in such systems. Here we report charge-separation studies of a self-assembled oligomeric porphyrin ladder structure featuring redox-active rungs (3,6-di-4-pyridyl-1,2,4,5-tetrazine, DPT). The studies employed absorption, fluorescence, transient absorption spectroscopies, and transient direct current photoconductivity (TDCP). In the ladder structure, butadiyne-linked porphyrin trimers (rails) and tetrazine species (rungs) are the electron donors and acceptors, respectively. We observed that in the photoexcited ladder, an electron generally transfers from the trimer to a single tetrazine at one end of the ladder, with the remaining hole delocalized over three porphyrins. The electron and hole recombine in 0.19 ns.

Scheme 1 illustrates the ladder formation of the trimer^{1b,3a,d} with DPT via reversible coordination of nitrogen atoms of pyridine by porphyrinic Zn(II) sites. Fig. 1 shows the UV-vis spectra of the formation of ladder **L1** in toluene. Upon addition of DPT, the Q-band absorption of the trimer



Scheme 1

red-shifts and is sharpened as a result of coplanarization of the porphyrin subunits, leading to stronger electronic coupling among the subunits. Observation of five isosbestic points at 440 nm, 473 nm, 490 nm, 503 nm and 752 nm, respectively, indicates all-or-nothing ladder formation as a result of the equilibrium between the trimer and **L1**.^{1b} (These points would be absent if intermediate structures formed to an appreciable extent.) The observed DPT : trimer binding stoichiometry (2 : 3) is consistent with formation of **L1**. Titration of the trimer with the redox-inert rung, 1,4-bis(4-pyridyl)-benzene (ladder **L2**), yields the same spectral behavior.

The fluorescence of **L1** is dramatically quenched (ESI†, Fig. S1) due to incorporation of the redox-active DPT (nonemissive) while that of **L2** is readily observed. Photoinduced electron transfer (ET) from the trimer to the electron-accepting tetrazine species is the major fluorescence quenching pathway. The excited-state oxidation potential of the planarized trimer in **L1** is determined to be -1.47 V (vs. Fc^+/Fc).⁵ The ground-state reduction potential of DPT in solution is -1.22 V (ESI†, Fig. S3b). Thus, electron transfer is energetically favorable from the excited trimer to DPT.

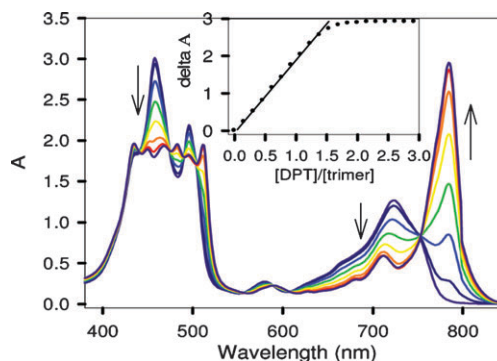


Fig. 1 Spectrophotometric titration of the trimer ($C = 1.9 \times 10^{-5}$ M) with DPT in toluene. Inset: absorbance change at 780 nm showing stoichiometric coordination of DPT.

^a Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA. E-mail: j-hupp@northwestern.edu; Fax: +1 847-491-7713; Tel: +1 847-467-3347

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

† Electronic supplementary information (ESI) available: Details of experiments and calculations. See DOI: 10.1039/b916392a

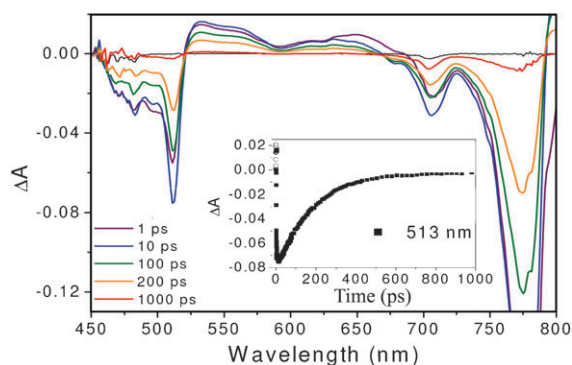


Fig. 2 Transient spectra of **L1** in toluene, excited at 700 nm. The kinetics of ground-state recovery at 513 nm (inset) is fit by a single exponential with a lifetime of 0.19 ± 0.01 ns attributed to charge recombination.

Femtosecond transient absorption spectroscopy (fsTA) was used to study electron transfer and charge recombination in **L1**. Due to similar broad absorption of the excited states of cationic and neutral trimers, direct assignment of absorption peaks to the ET process was difficult, and thus the ET rate was not directly determined from TA. The broad absorption in the visible region for the cationic and neutral butadiyne-linked dimers has indeed been observed experimentally and calculated theoretically.⁶ We estimate that the ET process is complete within a few tens of ps based on fluorescence quenching.⁷ Forward ET is rapid relative to the lifetime of the charge-separation (CS) state (0.19 ns, see below).

The lifetime of the CS state of **L1** was determined by monitoring the kinetics of ground-state recovery, see Fig. 2 for TA spectra and the kinetics at 513 nm (inset). Upon excitation at 700 nm, the transient spectra show a broad absorption of the excited and/or cationic states in the 530–650 nm region, and bleaches in the B and Q band regions corresponding to depopulation of the ground state. Stimulated emission also contributed to the bleach at 770 nm. The ground-state bleach kinetics at 513 nm show a main component that decays exponentially in 0.19 ± 0.01 ns, much faster than the 1.3 ns ground-state recovery for **L2** (ESI†, Fig. S4). The **L1** pathway is attributed to charge recombination.

To gain more insight into charge separation in **L1**, we utilized transient direct current photoconductivity (TDCP).⁸ This technique measures the vectorial change of dipole moment due to optical excitation and subsequent reactions and thus provides information about both the distance and the direction of charge separation.^{8,9} For molecules or assemblies lacking charge-transfer behavior, TDCP reports on polarizability differences between the ground and excited states.^{2a} Fig. 3 shows TDCP responses for **L1** and **L2** in toluene, based on 532 nm excitation. Since **L2** does not undergo charge separation upon photoexcitation, the TDCP signal is similar to that of the trimer and can be fit by a three-state model with ground-state, singlet and triplet excited-state polarizabilities.^{2a,10}

The photoresponse of **L1** shows a distinctly different negative-going peak from that of **L2** and can be fit using a two-state model with dipoles for the ground (zero Debye, by symmetry) and CS states. To rationalize the fitting, parameters

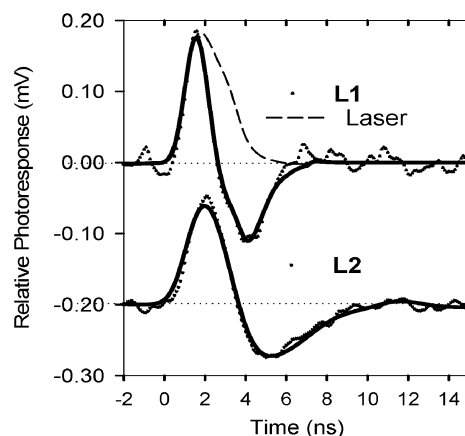


Fig. 3 TDCP signals of ladders **L1** and **L2**. The signal sizes are scaled by absorbed energy. **L2** is vertically offset for clarity. Excitation wavelength is 532 nm. Solid lines = data fits.

based on structural information were used. Qualitatively, we expect very small signals when lifetimes are short relative to the laser pulse (~ 2 ns). On the other hand, we expect large signals if the charge-separation distance is large. Given the modest, but not tiny, signal amplitudes observed here, both factors appear to be at work. The dipole moment of the CS state (and therefore the dipole moment *change* relative to the ground state) was found to be $\Delta\mu_{CS} = \mu_{CS} - \mu_G = 81 \pm 7$ D, based on a CS state lifetime of 0.19 ns. The rotational diffusion time (τ_r) was found to be 5.5 ± 0.5 ns, on the same time-scale for similar structures.¹¹ The value for $\Delta\mu_{CS}$ corresponds to a charge-separation distance of 17 ± 1.5 Å, assuming transfer of a full electronic charge. Notably this distance considerably exceeds the distance from the center of an individual porphyrin subunit to the center of an immediately appended DPT subunit; see Fig. 4.

Insight into the apparent discrepancy is provided by TDCP-based assessment of the excitation correlation factor, β , corresponding to the cosine of the angle, θ , between the $S_0 \rightarrow S_2$ transition dipole and the charge-separation-based change in dipole moment. Electron transfer from a single porphyrin subunit (hypothetically) to an immediately appended DPT rung would yield $\theta = 90^\circ$ and $\beta = 0$. Instead we find that signals can be most satisfactorily fit with $\beta = 0.9 \pm 0.1$, corresponding to a θ value of between 0 and roughly 40° . Combining θ and the CS distance, we find (Fig. 4) that the

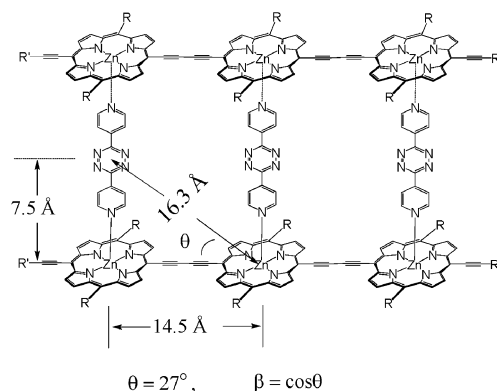


Fig. 4 Distances and angles in ladder **L1**.

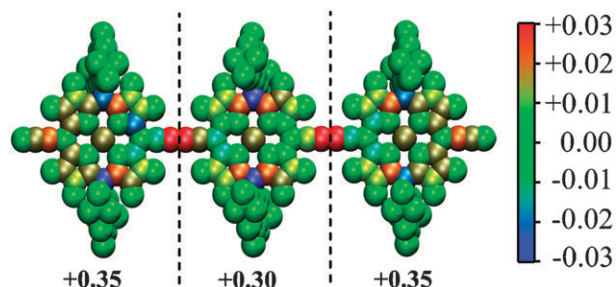


Fig. 5 Distribution of positive charge (+1) on the trimer cation after subtracting the charge density of the neutral trimer, indicating the delocalized nature of the positive charge on the trimer cation.

results can be rationalized if an electron is primarily transferred to one of the two available terminal DPT rungs¹² and if the remaining hole is symmetrically delocalized over one of the two available trimeric porphyrin rails.

Electronic structure calculations of neutral and cationic trimers were performed to provide information on the charge distribution after ET. Fig. 5 shows the distribution of positive charge on the cationic trimer after subtracting charge density for the neutral trimer. The +1 charge is symmetrically distributed over three porphyrin rings and two butadiyne bridges with the center of the excess charge located on the trimer center, consistent with the delocalized nature of holes on ethyne-linked porphyrin oligomers.^{2e,13} The delocalization description is consistent with the conclusions reached above based on TDCP-derived CS distance and direction measurements.

In summary, we find that reversible, photoinduced charge separation occurs *via* an oxidative quenching mechanism within a supramolecular ladder assembly comprising trimeric porphyrin rails (excited-state electron donors) and dipyriddy-tetrazine rungs (electron acceptors). TDCP measurements reveal that the CS distance is much greater and the CS angle much shallower than expected based on geometrically orthogonal electron transfer from a single porphyrin subunit to an immediately axially appended tetrazine rung. Instead, the experimental measurements and related electronic structure calculations are consistent with electron transfer chiefly to a terminal rung and delocalization of the remaining hole symmetrically on a trimeric porphyrin rail.

We thank Dr Karen Mulfort for providing a sample of DPT. We thank the Korean Electric Power Research Institute (KEPRI), and the Office of Science, U.S. Department of Energy (Grants DE-FG02-87ER13808 and DE-FG02-99ER14999) for financial support of this work. GCS and MAR acknowledge the DOE ANSWER EFRC (DE-SC0001785) grant.

Notes and references

- (a) D. Kim and A. Osuka, *Acc. Chem. Res.*, 2004, **37**, 735–745; (b) P. N. Taylor and H. L. Anderson, *J. Am. Chem. Soc.*, 1999, **121**, 11538–11545; (c) S. M. LeCours, H. W. Guan, S. G. DiMaggio, C. H. Wang and M. J. Therien, *J. Am. Chem. Soc.*, 1996, **118**, 1497–1503.

- (a) C. She, J. E. McGarrah, S. J. Lee, J. L. Goodman, S. T. Nguyen, J. A. G. Williams and J. T. Hupp, *J. Phys. Chem. A*, 2009, **113**, 8182–8186; (b) V. S. Y. Lin and M. J. Therien, *Chem.–Eur. J.*, 1995, **1**, 645–651; (c) P. J. Angiolillo, H. T. Uyeda, T. V. Duncan and M. J. Therien, *J. Phys. Chem. B*, 2004, **108**, 11893–11903; (d) R. Shediach, M. H. B. Gray, H. T. Uyeda, R. C. Johnson, J. T. Hupp, P. J. Angiolillo and M. J. Therien, *J. Am. Chem. Soc.*, 2000, **122**, 7017–7033; (e) K. Susumu and M. J. Therien, *J. Am. Chem. Soc.*, 2002, **124**, 8550–8552; (f) J. J. Piet, P. N. Taylor, B. R. Wegewijs, H. L. Anderson, A. Osuka and J. M. Warman, *J. Phys. Chem. B*, 2001, **105**, 97–104; (g) J. J. Piet, P. N. Taylor, H. L. Anderson, A. Osuka and J. M. Warman, *J. Am. Chem. Soc.*, 2000, **122**, 1749–1757; (h) P. J. Angiolillo, V. S. Y. Lin, J. M. Vanderkooi and M. J. Therien, *J. Am. Chem. Soc.*, 1995, **117**, 12514–12527.
- (a) H. L. Anderson, *Inorg. Chem.*, 1994, **33**, 972–981; (b) S. J. Lee and J. T. Hupp, *Coord. Chem. Rev.*, 2006, **250**, 1710–1723; (c) R. F. Kelley, S. J. Lee, T. M. Wilson, Y. Nakamura, D. M. Tiede, A. Suka, J. T. Hupp and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2008, **130**, 4277–4284; (d) S. J. Lee, K. L. Mulfort, J. L. O'Donnell, X. B. Zuo, A. J. Goshe, P. J. Wesson, S. T. Nguyen, J. T. Hupp and D. M. Tiede, *Chem. Commun.*, 2006, 4581–4583.
- (a) C. M. Drain, A. Varotto and I. Radivojevic, *Chem. Rev.*, 2009, **109**, 1630–1658; (b) T. Milic, J. C. Garno, J. D. Bateas, G. Smeureanu and C. M. Drain, *Langmuir*, 2004, **20**, 3974–3983.
- The excited-state redox potential $E_{ES}^{0/+1} = E^{0/+1} - {}^1E_{00} = 0.10 - 1.57 = -1.47$ V. $E^{0/+1}$ and E_{00} were measured in CH_2Cl_2 for planarized trimer, see Fig. S2 and S3 in ESI†.
- (a) D. P. Arnold, G. A. Heath and D. A. James, *J. Porphyrins Phthalocyanines*, 1999, **3**, 5–31; (b) G. J. Wilson and D. P. Arnold, *J. Phys. Chem. A*, 2005, **109**, 6104–6113.
- Assuming less than 1% remaining fluorescence due to redox quenching, we calculated the ET rate to be faster than 13 ps.
- (a) K. N. Grzeskowiak, S. N. Smirnov and C. L. Braun, *J. Phys. Chem.*, 1994, **98**, 5661–5664; (b) S. N. Smirnov and C. L. Braun, *J. Phys. Chem.*, 1994, **98**, 1953–1961; (c) S. N. Smirnov and C. L. Braun, *Rev. Sci. Instrum.*, 1998, **69**, 2875–2887.
- (a) K. A. Walters, Y. J. Kim and J. T. Hupp, *Inorg. Chem.*, 2002, **41**, 2909–2919; (b) F. W. M. Vanhelmont, R. C. Johnson and J. T. Hupp, *Inorg. Chem.*, 2000, **39**, 1814–1816; (c) F. W. M. Vanhelmont and J. T. Hupp, *Inorg. Chem.*, 2000, **39**, 1817–1819.
- The singlet and triplet polarizability changes for excitation of **L2** are 650 ± 120 Å³ and 90 ± 30 Å³, respectively.
- (a) τ_r is defined as rotational diffusion time which is usually measured by fs fluorescence anisotropy (FA) techniques when TDCP signals originate from dipole change. τ_r for **L1** falls in the time region of >5 ns, and therefore is too long to be determined unambiguously by FA techniques which typically measure processes faster than 5 ns, see Table 1 in ref. 11b. In ref. 11b, the relative ratio of τ_r for dimer-ladder (**12Bpy2**) and dimer (**1**) is 2.7 : 1 (3.4 ns *versus* 1.28 ns). Assuming a similarly relative ratio for trimer-ladder and trimer (2.24 ns), τ_r for trimer-ladder is estimated to be ~ 6 ns which agrees with the fitting of TDCP data. See ESI† for more discussion. When TDCP signals originate from the change of polarizability, τ_r can be shortened by a few times that of the defined rotational diffusion time depending on molecular symmetry, as is the case in ref. 2a; (b) S. Easwaramoorthi, S. Y. Jang, Z. S. Yoon, J. M. Lim, C. W. Lee, C. L. Mai, Y. C. Liu, C. Y. Yeh, J. Vura-Weis, M. R. Wasielewski and D. Kim, *J. Phys. Chem. A*, 2008, **112**, 6563–6570.
- Because the TDCP signals scale as the square of the effective charge-transfer distance, it is difficult to measure short distances (or to pick up contributions to the total signal that entail transfer over short distances, e.g. from the porphyrin rail to the center tetrazine unit). Consequently, we cannot rule out the possibility that a small minority of the assemblies transfer charge to the central, rather than peripheral, tetrazine. On the other hand, if we assume a statistical redistribution of charge (*i.e.* one-third of the time the electron transfers to the central tetrazine) we end up with unphysical distances (*i.e.* too large) for the rail-to-peripheral rung charge-transfer distance.
- H. L. Anderson, *Chem. Commun.*, 1999, 2323–2330.