Supporting Information

Solvent Dependence of Lateral Charge Transfer in a Porphyrin Monolayer

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1) Sample Preparation

Synthesis and characterization of the porphyrins can be found in previously published work.[1] Nanoparticulate SnO_2 films on FTO-coated glass (TEC 15, Hartford Glass) were prepared by a doctor-blading method using SnO_2 colloidal paste composed of ~15 nm diameter SnO_2 nanoparticles (Alfa Aesar, Nanoarc) prepared using a previously published procedure.[2] The paste consisted of 10% SnO_2 and 5% ethyl cellulose in a mixture of water, acetic acid, and α-terpineol. Using a double-layered mask of Scotch Magic Tape, films of ~8 μm were prepared prior to annealing in a programmable oven by ramping the temperature to 370 °C at 3 °C/minute, holding for 10 minutes, ramping to 470 °C at 3 °C/minute, holding for 30 minutes, and then slowly cooling. The transparent films were kept in a 120 °C oven until use.

The SnO_2 films on FTO were sensitized with a monolayer of porphyrin by soaking in a porphyrin / ethyl acetate solution for ~10 hours, and then rinsed in ethyl acetate. For pure monomer and dyad films, ~250 μM porphyrin solutions in ethyl acetate were used, while the 25:1 monomer/dyad ratio monolayers were prepared using a mixed porphyrin solution containing a 25:1 ratio of monomer to dyad. Previous analysis has shown that the surface monolayers are composed of the same ratio as that of the soaking solution.[1] Steady-state UV-visible spectroscopy was performed using a Shimadzu UV-2600 spectrophotometer. SnO_2 thickness was determined using a Tencor Alpha-step 200 profilometer.

2) Transient Absorption

An Edinburgh Instruments LP900 transient absorption spectrometer was used for data collection. The samples were photoexcited with an ~7 ns pulse at 515 nm which was generated by an optical parametric oscillator (OPO, Spectra Physics) that was pumped with the third harmonic (355 nm) of a Nd:YAG laser (Spectra Physics INDI-10). The probe was generated by a pulsed 450 W Xe arc lamp that was filtered to selectively probe at the desired wavelength. Dye-sensitized SnO_2 films were held at a 45° angle relative to the pump and probe illumination paths in a 1 cm path length cuvette containing the experimental solvent and 100 mM $LiClO_4$. The pump power was 1 mJ/pulse for recombination kinetic experiments, and 200-400 μJ/pulse for data collection with the 25:1 monomer-to-dyad films. At this pump power, less than 1 in 25 dyes are theoretically photoexcited when reflections and scattering are taken into account. Signal intensity was linear with pump power in this regime, and hole-hopping kinetics were independent of pump power.

3) Summary of Random-Walk Model

Kinetic values for electron self-exchange were obtained using a previously discussed model.[1] This model effectively simulates the transient absorption spectrum by incorporating the known rates of electron-hole recombination on a photoactive surface monolayer (found from the spectral profiles of the dyes) and the calculated electron self-exchange (lateral hole-hopping) rate using a standard hexagonal random-walk model. The intramolecular rate of hole transfer within the dyad was modeled as an instantaneous process, as it is observed experimentally to occur on the sub-nanosecond timescale in all solvents.

Using a randomized, hexagonally packed system of monomer and dyad in a 25:1 ratio, a random-walk scenario was analyzed where a randomly assigned molecule (monomer/dyad) was chosen to initiate a photo-induced electron injection into the semiconductor, thereby becoming the oxidized porphyrin radical cation (hole). This hole was allowed to randomly hop among the porphyrins until it reached a dyad, and the number of required hops was logged. This scenario was repeated with 10^6 randomized systems producing the probability curve for reaching a dyad as a function of number of hops, and is shown in Figure S1.
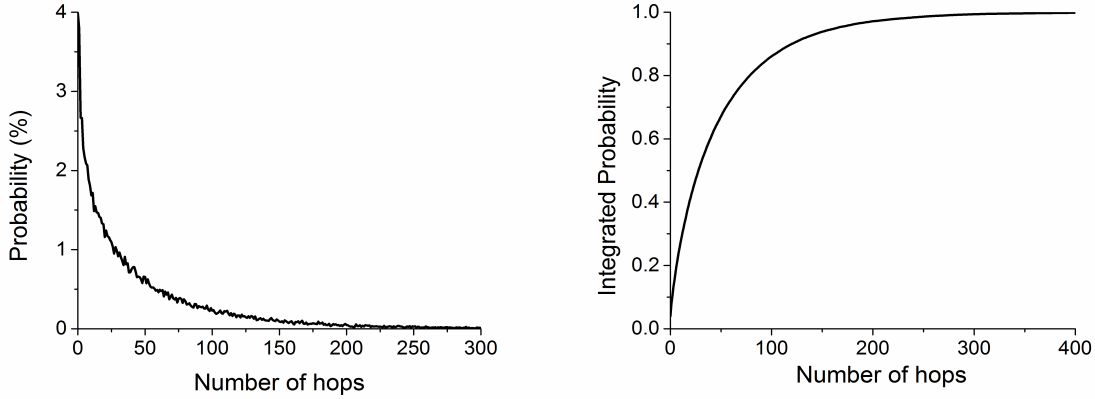

Figure S1: Random-walk probability curves. The probability density of reaching a dyad after each hop (left) and integrated probability (right). Data taken from reference S1.

The probability distributions from Figure S1 allow for modeling of the photoactive surface as a sum of monomers (M) which are some number of hops (n) from reaching a dyad as is shown in Equations S1-S3. For calculations, n was limited to 300, which effectively incorporates over 99% of the possible holes.

$$[M_{total}] = [M_1] + [M_2] + [M_3] + \ldots + [M_n] \tag{S1}$$

$$-\frac{d[M_n]}{dt} = \left[(\beta_M k_{rec,M}^{\beta_m} t^{\beta_M - 1} + k_{hop})[M_n] \right] - k_{hop}[M_{n+1}] \tag{S2}$$

$$-\frac{d[D]}{dt} = \left[(\beta_D k_{rec,D}^{\beta_D} t^{\beta_D - 1})[D] \right] - k_{hop}[M_1] \tag{S3}$$

Incorporation of the known charge-recombination parameters (stretched-exponential decay from the pure monomer and dyad films) with the random-walk probability distributions provides a means to determine the relative oxidized monomer and dyad populations as a function of time (Equation S2 and S3). The oxidized monomer species are separated by their total number of hops (n) from the dyad. In Equation S2, the change in population for oxidized monomer species which are n hops from a dyad is dependent on the initial population of M_n, the rate of recombination (stretched exponential decay), k_{hop}, and the population of M which is $n+1$ hops from the dyad. M_n decreases with recombination events, decreases as holes hop towards a dyad, and increases as the population transfers from M_{n+1} to M_n. The populations of M can be summed for any time period using Equation S1. In Equation S3, the change in population of dyad (D) is decreased with recombination events and increased as holes hop from the M_1 population which is only a single hop from the dyad. No further lateral charge transfer is considered once the hole is located on a dyad.

Using the populations of *M* and *D* at any point in time, and the known ratio of monomer and dyad transient absorption intensities at the observed wavelength (-3.5 at 560 nm), Equation S4 can simulate the transient absorption (ΔOD) signal with scaling factor *A* and can account for any minor offsets (*b*). The experimental transient absorption spectra were simulated from Equation S4 using the populations of *M* and *D* obtained as a function of the variable k_{hop}.

$$\Delta O D = A([M]_t + \varepsilon[D]_t) + b \tag{S4}$$

Limitations of the model. The derivations using stretched exponential recombination kinetics as the method of incorporating time into the model resulted in factors of $t^{\beta-1}$ in Equations S2 and S3. Since *β* must be between 0 and 1, this effectively puts time in the denominator. Thus, the calculations will break down at ultrafast time regimes where *t* is very small, generally on the femtosecond timescale. For our calculations, which are on orders of magnitude longer timescales, we exclude the first 1 ns of transient absorption kinetic data and start our calculations at *t* ~ 1 ns to place ourselves well within the time window where the equations converge and fit the data. Exclusion of the data does not affect our results, as the great majority of the transient absorption decay takes place on timescales that are orders of magnitude longer.
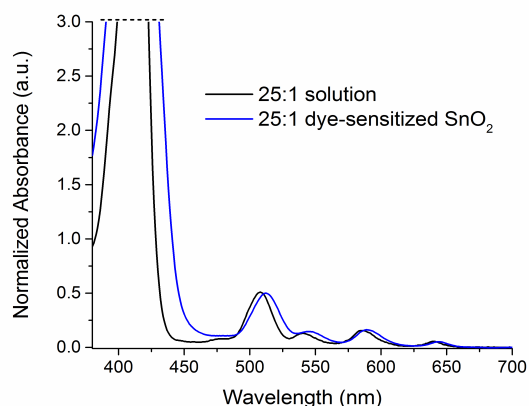

Figure S2. UV-visible spectra overlay of a 25:1 monomer-to-dyad ratio porphyrin solution in ethyl acetate (black) and the dry dye-sensitized SnO_2 film in air (blue).

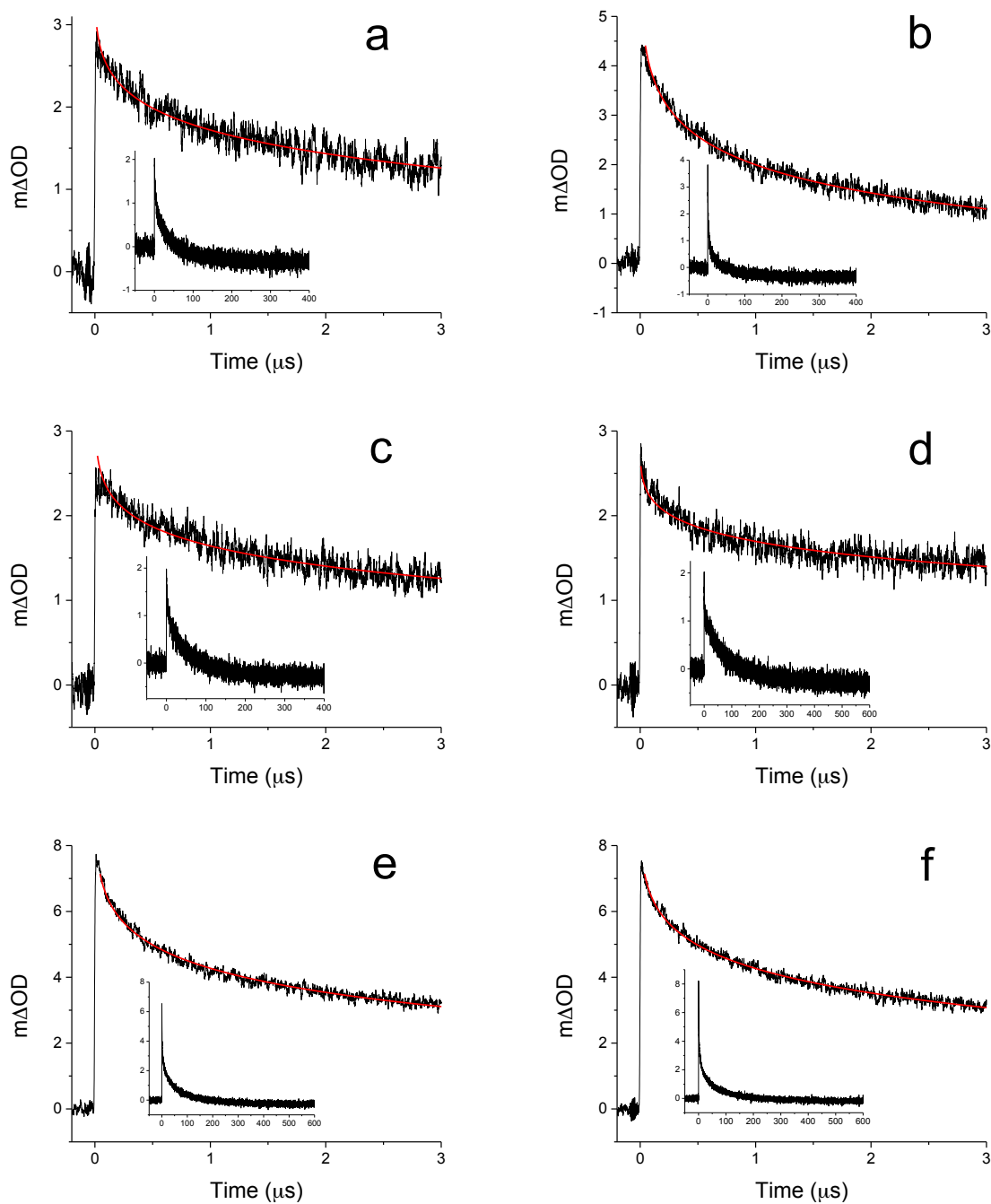Figure S3. Transient absorption spectra for monolayers of pure monomer in: a) H_2O, b) 75% H_2O / 25% ACN, c) 50% H_2O / 50% ACN, d) 25% H_2O / 75% ACN, e) ACN, and f) PC. Solvents incorporated 100 mM $LiClO_4$ as electrolyte, with solvent mixtures as volume %. Stretched exponential decay fits are shown in red, and the decay parameters are found in Table 1 of the main text. Insets show longer timescales.
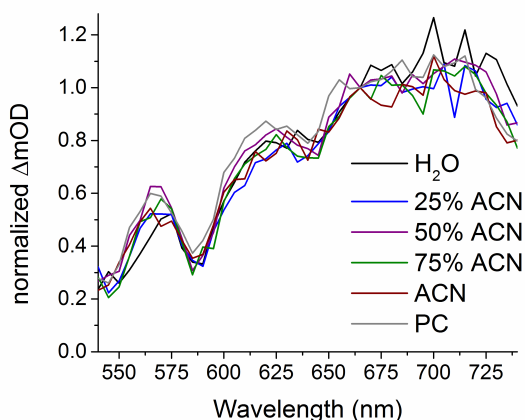
Figure S4. Transient absorption spectral map of monomer-sensitized SnO_2 electrodes in varying solvents containing 100 mM $LiClO_4$. Data obtained at 2 µs after photoexcitation at 515 nm, and normalized at 665 nm.
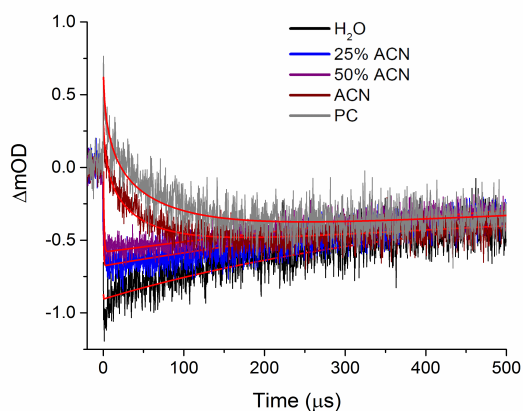

Figure S5. Transient absorption spectra of dye-sensitized SnO_2 electrodes with porphyrin monolayers containing a 25:1 monomer-to-dyad ratio in different solvents. Fits (red) were obtained using the model in the text and using kinetic parameters in Table 1 of the main text.

References

(1)   Brennan, B. J.; Durrell, A. C.; Koepf, M.; Crabtree, R. H.; Brudvig, G. W. Towards Multielectron Photocatalysis: A Porphyrin Array for Lateral Hole Transfer and Capture on a Metal Oxide Surface. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12728-12734.
(2)   Antoniuk-Pablant, A.; Terazono, Y.; Brennan, B. J.; Sherman, B. D.; Megiatto, J. D.; Brudvig, G. W.; Moore, A. L.; Moore, T. A.; Gust, D. A New Method for the Synthesis of β-Cyano Substituted Porphyrins and Their Use as Sensitizers in Photoelectrochemical Devices. *J. Mater. Chem. A* **2016**, *4*, 2976-2985.