

## Supplementary Information

### **A Photo- and Electrochemically- Active Porphyrin-Fullerene Dyad Electropolymer**

Miguel Gervaldo, Paul A. Liddell, Gerdenis Kodis, Bradley J. Brennan, Christopher R. Johnson, James W. Bridgewater, Ana L. Moore,\* Thomas A. Moore\* and Devens Gust\*

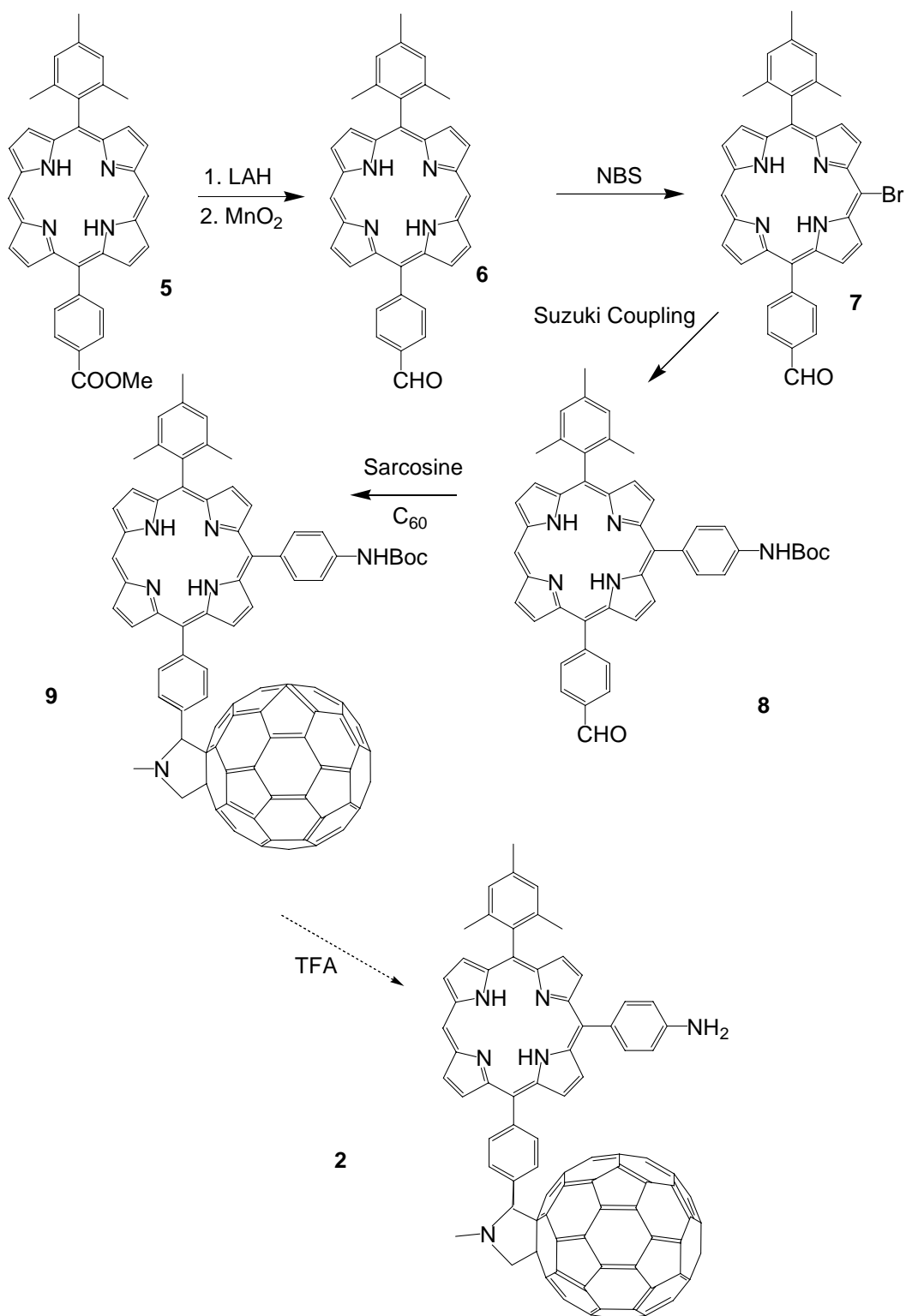
*Department of Chemistry and Biochemistry, Center for Bioenergy and Photosynthesis, Arizona State University, Tempe, AZ 85287*

#### **Synthesis**

Monomeric porphyrin-fullerene dyad **2** was synthesized as illustrated in Figure S1. Details for each compound are given below. <sup>1</sup>H NMR spectra were recorded on a Varian Unity spectrometer at 300 or Bruker 400 MHz spectrometer. Mass spectra were obtained on a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). Ultraviolet-visible ground state absorption spectra were measured on a Shimadzu UV2100U spectrometer.

**5-(4-Carboxymethylphenyl)-15-(2,4,6-trimethylphenyl)porphyrin (5).** This compound was prepared by an adaptation of a general procedure reported elsewhere.<sup>1</sup> A flask containing 1.76 g (12.0 mmol) of 2,2'-dipyrrromethane,<sup>2</sup> 0.89 mL (6.0 mmol) of mesitaldehyde, 0.98 g (6.0 mmol) of methyl 4-formylbenzoate and 1.2 L of chloroform was flushed with a stream of argon for 15 min. Boron trifluoride-diethyl etherate (0.84 mL, 13.0 mmol) was added to the reaction mixture and the solution was stirred in the dark for 30 min. A portion of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (4.0 g) was added and the stirring was continued for another 60 min. The reaction mixture was washed with sodium bicarbonate solution (×3) and concentrated by evaporation of the solvent at reduced pressure, and the residue was chromatographed on silica gel (dichloromethane/15-0% hexanes). The material isolated from the column was recrystallized from dichloromethane-methanol to give 1.03 g (22% yield) of the desired porphyrin **5**. <sup>1</sup>H NMR (300 MHz) δ -3.09 (2H, s, N-H), 1.85 (6H, s, Ar-CH<sub>3</sub>), 2.66 (3H, s, Ar-CH<sub>3</sub>), 4.14 (3H, s, -COOCH<sub>3</sub>), 7.32 (2H, s, Ar-H), 8.34 (2H, d, *J*=8 Hz, Ar-H), 8.49 (2H, d, *J*=8 Hz, Ar-H), 8.90 (2H, d, *J*=5 Hz, β-H), 9.00 (2H, d, *J*=5 Hz, β-H), 9.33 (2H, d, *J*=5 Hz, β-H), 9.38 (2H, d, *J*=5 Hz, β-H), 10.26 (2H, s, meso-H); MALDI-TOF-MS *m/z* calcd for C<sub>37</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub> 562.24, obsd 562.24.

**5-(4-Formylphenyl)-15-(2,4,6-trimethylphenyl)porphyrin (6).** A flask containing 200 mg (0.35 mmol) of 5-(4-carboxymethylphenyl)-15-(2,4,6-trimethylphenyl)porphyrin **5** and 70 mL of tetrahydrofuran was cooled to 5-10 °C before lithium aluminum hydride was added in small quantities. The progress of the reaction was followed by TLC (silica gel/dichloromethane). Once all the porphyrin ester had been consumed, ice was cautiously added to the reaction mixture. The solvent was distilled under reduced pressure and the residue was redissolved in dichloromethane. The resulting solution was dried over sodium sulfate and then concentrated by removal of all solvent through distillation at reduced pressure. The resulting porphyrin alcohol was dissolved in 50 mL of dichloromethane and stirred as small portions of activated manganese dioxide were added. The course of the reaction was followed by TLC (silica



**Figure S1.** Synthetic route for preparation of dyad **2**.

gel/dichloromethane). Once the conversion was complete, the reaction mixture was filtered through Celite<sup>®</sup> and the filtrate was concentrated by evaporation of the solvent at reduced pressure. The residue was chromatographed on silica gel (dichloromethane/15-5% hexanes) to give 157 mg (83% yield) of the expected porphyrin **6**. <sup>1</sup>H NMR (300 MHz) δ -3.09 (2H, s, N-H), 1.84 (6H, s, Ar-CH<sub>3</sub>), 2.66 (3H, s, Ar-CH<sub>3</sub>), 7.32 (2H, s, Ar-H), 8.32 (2H, d, *J*=8 Hz, Ar-H), 8.44 (2H, d, *J*=8 Hz, Ar-H), 8.90 (2H, d, *J*=4 Hz, β-H), 8.99 (2H, d, *J*=4 Hz, β-H), 9.34 (2H, d, *J*=5 Hz, β-H), 9.40 (2H, d, *J*=5 Hz, β-H), 10.28 (2H, s, meso-H), 10.41 (1H, s, -CHO); MALDI-TOF-MS *m/z* calcd for C<sub>36</sub>H<sub>28</sub>N<sub>4</sub>O<sub>1</sub> 532.23, obsd 532.22.

**10-Bromo-5-(4-formylphenyl)-15-(2,4,6-trimethylphenyl)porphyrin (7)**. To a flask containing 150 mg (0.282 mmol) of 5-(4-formylphenyl)-15-(2,4,6-trimethylphenyl)porphyrin (**6**) and 20 mL of chloroform was added 50 mg (0.282 mmol) of N-bromosuccinimide. The reaction mixture was stirred for 30 min under a nitrogen atmosphere. The solvent was evaporated at reduced pressure and the residue was chromatographed on silica gel (dichloromethane/hexanes 4:3 to 2:1) to give 119 mg (69% yield) of the monobrominated porphyrin **7**. <sup>1</sup>H NMR (300 MHz) δ -2.91 (2H, s, N-H), 1.83 (6H, s, Ar-CH<sub>3</sub>), 2.65 (3H, s, Ar-CH<sub>3</sub>), 7.31 (2H, s, Ar-H), 8.30 (2H, d, *J*=8 Hz, Ar-H), 8.37 (2H, d, *J*=8 Hz, Ar-H), 8.81 (2H, d, *J*=5 Hz, β-H), 8.85 (1H, d, *J*=2 Hz, β-H), 8.87 (1H, d, *J*=2 Hz, β-H), 9.25 (1H, d, *J*=6 Hz, β-H), 9.29 (1H, d, *J*=6 Hz, β-H), 9.69 (1H, d, *J*=6 Hz, β-H), 9.74 (1H, d, *J*=6 Hz, β-H), 10.14 (1H, s, meso-H), 10.40 (1H, s, -CHO); MALDI-TOF-MS *m/z* calcd for C<sub>36</sub>H<sub>27</sub>N<sub>4</sub>O<sub>1</sub>Br<sub>1</sub> 610.14, obsd 610.14.

**5-(4-Formylphenyl)-10-(4-*tert*-butylphenylcarbamate)-15-(2,4,6-trimethylphenyl)porphyrin (8)**. To a glass tube was added 110 mg (0.180 mmol) of 10-bromo-5-(4-formylphenyl)-15-(2,4,6-trimethylphenyl)porphyrin (**7**), 574 mg (1.80 mmol) of 4-(Boc-amino)benzeneboronic acid pinacol, 764 mg (3.60 mmol) of potassium phosphate tribasic and 35 mL of THF. The suspension was flushed with argon for 10 min, 21 mg (0.018 mmol) of tetrakis(triphenylphosphine)palladium(0) was added, and the argon flushing was continued. After 10 min the tube was sealed with a Teflon<sup>®</sup> screw plug and the reaction mixture was warmed to 68 °C for 17 h. Upon cooling, the reaction mixture was filtered through Celite<sup>®</sup>, the residue was washed well with dichloromethane, and the filtrate was concentrated by distillation at reduced pressure. The impure material was chromatographed on silica gel (hexanes/15-20% ethyl acetate) to give 114 mg (87% yield) of the desired porphyrin **8**. <sup>1</sup>H NMR (300 MHz) δ -2.94 (2H, s, N-H), 1.64 (9H, s, -CH<sub>3</sub>), 1.84 (6H, s, Ar-CH<sub>3</sub>), 2.64 (3H, s, Ar-CH<sub>3</sub>), 6.85 (1H, s, N-H), 7.30 (2H, s, Ar-H), 7.67 (2H, d, *J*=8 Hz, Ar-H), 8.13 (2H, d, *J*=8 Hz, Ar-H), 8.29 (2H, d, *J*=7 Hz, Ar-H), 8.40 (2H, d, *J*=7 Hz, Ar-H), 8.75 (1H, d, *J*=4 Hz, β-H), 8.80 (1H, d, *J*=5 Hz, β-H), 8.85 (1H, d, *J*=4 Hz, β-H), 8.88 (1H, d, *J*=5 Hz, β-H), 8.91 (1H, d, *J*=2 Hz, β-H), 8.93 (1H, s, *J*=2 Hz, β-H), 9.28 (1H, d, *J*=5 Hz, β-H), 9.33 (1H, d, *J*=5 Hz, β-H), 10.17 (1H, s, meso-H), 10.39 (1H, s, -CHO); MALDI-TOF-MS *m/z* calcd for C<sub>47</sub>H<sub>41</sub>N<sub>5</sub>O<sub>3</sub> 723, obsd 723.

**P-C<sub>60</sub> Dyad 9**. To a glass tube was added 100 mg (0.138 mmol) of 5-(4-formylphenyl)-10-(4-*tert*-butylphenylcarbamate)-15-(2,4,6-trimethylphenyl)porphyrin (**8**), 200 mg (0.276 mmol) of C<sub>60</sub>, 123 mg (1.38 mmol) of sarcosine and 40 mL of toluene. The suspension was flushed with argon for 10 min, the tube was sealed with a Teflon<sup>®</sup> screw plug and the reaction mixture was warmed to 110 °C for 16 h. The solvent was evaporated at reduced pressure and the residue was chromatographed on silica gel (carbon disulfide/dichloromethane/hexanes 100:85:15 to carbon disulfide/dichloromethane 1:2) to give 80 mg (39% yield) of dyad **9**. <sup>1</sup>H NMR (300 MHz) δ -3.03 (2H, s, N-H), 1.62 (9H, s, -CH<sub>3</sub>), 1.82(6H, s, Ar-CH<sub>3</sub>), 2.61 (3H, s, Ar-CH<sub>3</sub>), 3.10 (3H, s, N-CH<sub>3</sub>), 4.46 (1H, d, *J*=9 Hz, pyrrolid-H), 5.04 (1H, d, *J*=9 Hz, pyrrolid-H), 5.20 (1H, s, pyrrolid-H), 6.76 (1H, s, N-H), 7.24 (2H, s, Ar-H), 7.70 (2H, d, *J*=9 Hz, Ar-H), 8.07 (2H, d, *J*=8

Hz, Ar-H), 8.17 (2H, brd s, Ar-H), 8.24 (2H, d,  $J=7$  Hz, Ar-H), 8.66 (2H, d,  $J=4$  Hz,  $\beta$ -H), 8.77 (2H, d,  $J=5$  Hz,  $\beta$ -H), 8.80 (2H, d,  $J=5$  Hz,  $\beta$ -H), 9.22 (2H, d,  $J=4$  Hz,  $\beta$ -H), 10.07 (1H, s, meso-H); MALDI-TOF-MS  $m/z$  calcd for  $C_{109}H_{46}N_6O_2$  1470.37, obsd 1470.39.

**P-C<sub>60</sub> Dyad 2.** A solution comprised of 60 mg (0.041 mmol) of dyad **9** and 20 mL of trifluoroacetic acid was stirred under an argon atmosphere for 15 min. It was then diluted with dichloromethane (100 mL) and washed with water and then aqueous sodium bicarbonate until all the acid had been neutralized. The solvent was evaporated and the residue was chromatographed on silica gel (flash column, dichloromethane/carbon disulfide 3:1 to 6:1) to give 52 mg (93% yield) of dyad **2**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>)  $\delta$  -2.98 (2H, s, N-H), 1.86 (6H, s, Ar-CH<sub>3</sub>), 2.66 (3H, s, Ar-CH<sub>3</sub>), 3.17 (3H, s, N-CH<sub>3</sub>), 3.98 (2H, s, -NH<sub>2</sub>), 4.46 (1H, d,  $J=9$  Hz, pyrrolid.-H), 5.14 (1H, d,  $J=9$  Hz, pyrrolid.-H), 5.30 (1H, s, pyrrolid.-H), 7.01 (2H, d,  $J=8$  Hz, Ar-H), 7.27 (2H, s, Ar-H), 7.94 (2H, d,  $J=7$  Hz, Ar-H), 8.23 (2H, brd. s, Ar-H), 8.29 (2H, d,  $J=7$  Hz, Ar-H), 8.68 (2H, d,  $J=4$  Hz,  $\beta$ -H), 8.78 (2H, d,  $J=4$  Hz,  $\beta$ -H), 8.88 (2H, d,  $J=5$  Hz,  $\beta$ -H), 9.23 (2H, d,  $J=5$  Hz,  $\beta$ -H), 10.07 (1H, s, meso-H); MALDI-TOF-MS  $m/z$  calcd. for  $C_{104}H_{38}N_6$  1370.3, obsd. 1370.3; Uv/vis (CH<sub>2</sub>Cl<sub>2</sub>) 416, 511, 546, 586, 640, 703 nm.

### Electrochemical measurements

The voltammetric characterization of the redox processes for the molecules was performed with a CHI 600C potentiostat (CH Instruments) using a Pt disk working electrode, a Pt gauze counter electrode, and a silver wire pseudo-reference electrode in a conventional three-electrode cell. Indium tin oxide (ITO) electrodes (Delta Technologies) with a nominal resistance of 8–12  $\Omega/cm$  were also used as working electrodes. When ITO electrodes were used, the counter electrode was isolated from the monomer solution by a glass frit in order to avoid interference with the redox reactions occurring at the working electrode. Electrochemical studies were carried out in anhydrous dichloromethane (stored under molecular sieves and potassium carbonate) deoxygenated by bubbling with nitrogen, and containing 0.10 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte (tetra-*n*-butylammonium perchlorate was also used for FT-IR measurements). The working electrode was cleaned between experiments by polishing with a 0.3  $\mu m$  alumina slurry, followed by solvent rinses. After each voltammetric experiment, ferrocene was added to the solution, and the potential axis was calibrated against the formal potential of the ferrocenium/ferrocene redox couple (taken as 0.45 V vs SCE in dichloromethane).

Spectroelectrochemical experiments were carried out in a homemade cell built from a commercial UV-visible cuvette. An ITO-coated glass plate was used as the working electrode, the Pt counter electrode was isolated from the monomer solution by a glass frit, and a Ag wire was employed as the reference electrode. The cell was placed in the optical path of the sample light beam in a spectrophotometer. The background correction was obtained by subtracting from the raw spectrum the UV-vis spectrum of a blank cell (an electrochemical cell with an ITO working electrode that did not bear the polymer film) taken under conditions and parameters identical to those of the polymer experiment.

### Spectroscopic studies

**Steady-state spectroscopy.** Absorption spectra were measured on a Shimadzu UV-3101PC UV-vis-NIR spectrometer.

**IR spectroscopy.** For infrared spectra, a Bruker IFS 66V/S Fourier transform infrared spectrometer was used with an attenuated total reflectance sample holder and an evacuated

sample chamber. The polymer samples were deposited on ITO as was indicated in the electrochemistry section. The film-coated electrode, immersed in a porphyrin-free solution containing tetra-*n*-butylammonium hexafluorophosphate, was poised at each selected potential for 60 s. It was then removed from the electrolyte solution, rinsed with clean dichloromethane, and clamped against the ATR sample holder. The spectrometer sample compartment was evacuated prior to data measurement. In a second series of experiments, the same procedure was followed, but the electrolyte was tetra-*n*-butylammonium perchlorate.

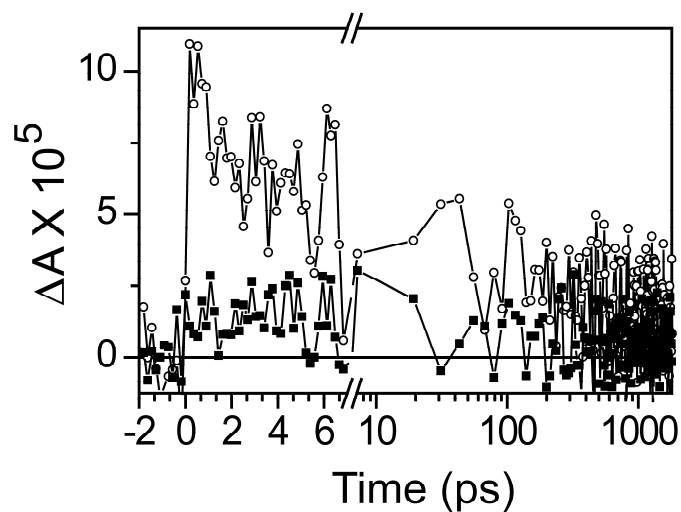
**Time-resolved fluorescence.** Fluorescence decay measurements were performed by the time-correlated single-photon-counting method employing an ultrafast laser and a streak camera. The 130 fs light pulses at 780-860 nm were generated by a mode-locked Ti:Sapphire laser (Mira 900, Coherent) pumped by a frequency-doubled Nd:YVO<sub>4</sub> laser (44% from an 18 W Verdi, Coherent). The repetition rate of the Ti:Sapphire laser was reduced to 4.75 MHz by a pulse picker (Model 9200, Coherent). The excitation light was frequency doubled, intensity adjusted using a continuously varied neutral density filter and focused on the sample. The spot diameter was ca. 300 μm. Fluorescence with polarization set to the magic angle was collected 90° to the excitation beam and focused on the entrance slit of a Chromex 250IS spectrograph, which was coupled to a Hamamatsu C5680 streak camera with a M5675 synchroscan sweep unit. The streak images were recorded on a Hamamatsu C4742 CCD camera and curvature corrected (corrections for shading and system detection sensitivity at different wavelengths were not performed). Instrument response function was ca. 5 - 20 ps.

**Transient absorption.** For the single kinetics transient absorption measurements, laser pulses of 100 fs at 800 nm were generated from an amplified, mode-locked Titanium Sapphire kilohertz laser system (Millennia/Tsunami/Spitfire, Spectra Physics). Part of the laser pulse energy was sent through an optical delay line and focused on to a 2 mm sapphire plate to generate a white light continuum for the probe beam, and light from this beam at < 850 nm was removed by a long-pass filter. The remainder of the pulse energy was used to pump an optical parametric amplifier (Spectra Physics) to generate excitation pulses, which were modulated using a mechanical chopper. The excitation beam wavelength was tuned to 600 nm (10 nm fwhm) or 590 nm and its intensity was adjusted using a continuously-variable neutral density filter. Both beams were focused on the sample to a 300 μm diameter spot. The polarization between the pump and the probe was set to the magic angle (54.7°). After passing through the sample, the probe beam was sent through a monochromator (SP150, Action Res. Corp.) and recorded by a diode detector (Model 2032, New Focus Inc.) and boxcar integrator (SR250, Stanford Research Systems). The instrument response function was ca. 200 fs.

Data analysis was carried out using locally written software (ASUFIT) developed in a MATLAB environment (Mathworks Inc.). Decay-associated spectra were obtained by fitting the transient absorption or fluorescence change curves over a selected wavelength region simultaneously as described by Eq 1 (parallel kinetic model),

$$\Delta A(\lambda, t) = \sum_{i=1}^n A_i(\lambda) \exp(-t / \tau_i) \quad (1)$$

where  $\Delta A(\lambda, t)$  is the observed absorption (or fluorescence) change at a given wavelength at time delay  $t$  and  $n$  is the number of kinetic components used in the fitting. A plot of  $A_i(\lambda)$  versus wavelength is called a decay-associated spectrum, and represents the amplitude spectrum of the  $i^{\text{th}}$  kinetic component, which has a lifetime of  $\tau_i$ . Random errors associated with the reported lifetimes obtained from fluorescence and transient absorption measurements were typically  $\leq 5\%$ .



**Figure S2.** Transient absorption kinetics at 880 nm for **poly1** on ITO-coated glass following excitation at 600 nm with 100 fs pulses. Decays shown were obtained with laser pulse fluences of  $28\mu\text{J}/\text{cm}^2$  (circles), and  $14\mu\text{J}/\text{cm}^2$  (squares).

### References

1. Yu, L. H.; Muthukumar, K.; Sazanovich, I. V.; Kirmaier, C.; Hindin, E.; Diers, J. R.; Boyle, P. D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *Inorg. Chem.* **2003**, *42*, 6629-6647.
2. Laha, J. K.; Dhanalekshmi, S.; Taniguchi, M.; Ambroise, A.; Lindsey, J. S. *Organic Process Research & Development* **2003**, *7*, 799-812.