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Supplementary Material

Towards multielectron photocatalysis: a porphyrin array for lateral hole transfer and capture on a metal oxide surface

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Experimental

Synthesis

5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-nitrophenyl) porphyrin was prepared using the method developed by Lindsey and co-workers.[1] A flask containing 800 mL chloroform was sparged with nitrogen for 10 min, 616 mg (4.08 x 10^{-3} mol) 4-nitrobenzaldehyde was added, and the mixture was sonicated. Ethanol (2 mL) and 1.21 g (4.11 x 10^{-3} mol) 2,3,5,6-tetrafluorophenyl dipyrromethane were added. Under vigorous stirring, 350 μL (2.84 x 10^{-3} mol) BF_3-etherate was added, and the reaction was kept in the dark under a nitrogen atmosphere. After 80 min, 2.30 g (1.01 x 10^{-2} mol) DDQ and a small amount of sodium bicarbonate were added, and the mixture was stirred overnight. The crude reaction was filtered through a pad of silica, eluted with dichloromethane, and the filtrate was dried by distillation under reduced pressure. The crude solid was chromatographed on silica using chloroform as eluent to yield 434 mg of a mixture of the desired *opp* di-nitro isomer (~90%) compound which co-eluted with the *adj* isomer (~10%). This purple-red solid was used without further purification.

5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-aminophenyl) porphyrin. To 100 mL of glacial acetic acid was added 428 g (5.04 x 10^{-4} mol) 5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis(4-nitrophenyl) porphyrin mixed with the *adj* isomer. Tin(II) chloride dihydrate (1.82 g, 8.07 x 10^{-3} mol) was added along with 20 mL concentrated aqueous HCl. The green solution was stirred at 50 ˚C in a closed environment with a balloon of nitrogen to limit loss of HCl. After 7 h, 2 mL of HCl was added, and the reaction stirred for an additional 15 hr. The reaction was cooled on an ice bath, and 20 mL of aqueous ammonia, 200 mL water, and 400 mL chloroform were added. Sodium bicarbonate was added until the porphyrin extracted into the organic phase. The mixture was placed in a separatory funnel and the organic phase isolated. The aqueous phase was then extracted with 100 mL ethyl acetate. The chloroform and ethyl acetate extractions were washed with aqueous sodium bicarbonate, combined, and distilled under reduced pressure. The crude product was purified by silica gel chromatography using a mixture of chloroform and ethyl acetate as eluent (gradient 2% to 10% ethyl acetate in chloroform). Combined fractions were distilled under reduced pressure to obtain the desired product as a purple-red solid (261 mg, 66%).

^{1}H NMR (400 MHz, DMSO, δ) 9.09 (d, *J* = 4.9 Hz, 4H), 9.03 (d, *J* = 4.9 Hz, 4H), 8.49 (tt, *J* = 10.1 Hz, *J* = 7.9 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 4H) 7.02 (d, *J* = 8.3 Hz, 4H), 5.64 (s, 4H), -2.86 (s, 2H).

HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{44}H_{25}F_8N_6$, 789.2008; found, 789.2004.

5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-carbomethoxyphenyl) porphyrin (H_2PF_8-ester) was prepared using the method developed by Lindsey and co-workers.[1] A flask containing 800 mL chloroform was sparged with nitrogen for 15 min, 670 mg (4.08 x 10^{-3} mol) methyl-4-formylbenzoate was added, and the mixture was sonicated. Ethanol (2 mL) and 1.21 g (4.11 x 10^{-3} mol) 2,3,5,6-tetrafluorophenyl dipyrromethane were added. With vigorous stirring, 350 μL (2.84 x 10^{-3} mol) BF_3-etherate was added, and the reaction was kept in the dark under a nitrogen atmosphere. After 90 min, 2.30 g (1.01 x 10^{-2} mol) DDQ and a small amount of sodium bicarbonate were added, and the mixture was stirred overnight. The crude reaction was filtered through a pad of silica, eluted with dichloromethane, and the filtrate was dried by distillation under reduced pressure. The crude solid was chromatographed on silica using

dichloromethane/toluene 4:1 and fractions collected. Pure fractions were combined and dried by distillation under reduced pressure to obtain the desired product as a purple-red solid (417 mg, 24%).
^{1}H NMR (400 MHz, $CDCl_3$, δ) δ 8.89 (d, *J* = 4.8 Hz, 4H), 8.85 (d, *J* = 4.9 Hz, 4H), 8.51 – 8.43 (m, 4H), 8.35 – 8.28 (m, 4H), 7.61 (tt, *J* = 9.6 Hz, *J* = 8.0 Hz, 2H), 4.12 (s, 6H), -2.83 (m, 2H).
HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{48}H_{27}F_8N_4O_4$, 875.1899; found, 875.1908.

5,15-bis-(2,3,5,6-tetrafluorophenyl)-10-(4-carbomethoxyphenyl)-20-(4-carboxyphenyl) porphyrin (H_2PF_8-acid). To a flask was added 411 mg (4.70 x 10^{-4} mol) 5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-carbomethoxyphenyl) porphyrin to a mixture of 200 mL tetrahydrofuran and 40 mL methanol. A solution of 680 mM KOH in water was prepared, and 3.5 mL (2.38 x 10^{-3} mol KOH) was added to the porphyrin solution. The reaction was stirred at 50 ˚C under a nitrogen atmosphere for 4 h, and then quenched with aqueous citric acid. The mixture was placed in a separatory funnel, 200 mL water was added, and the mixture was extracted with 300 mL chloroform. The organic layer was collected, dried by distillation under reduced pressure, and the crude product was purified by chromatography on silica gel using dichloromethane containing 3% methanol. The desired product was obtained along with starting material as purple-red solids. The reaction was repeated using the recovered starting material in a mixture of 100 mL tetrahydrofuran, 25 mL methanol, and 1.5 mL of the KOH solution. Identical reaction conditions and workup allowed for addition desired product to be obtained as a purple-red solid (226 mg, 56%).
UV-visible: λ_{max}(ethyl acetate)/nm 412 (ε, $dm^3\ mol^{-1}\ cm^{-1}$ 375 000), 508 (20 300), 540 (4 800), 585 (6 000), 640 (2 200).
^{1}H NMR (400 MHz, DMSO, δ) 13.32 (s, 1H), 9.17 (d, *J* = 4.1 Hz, 4H), 8.92 (m, 4H), 8.49 (tt, *J* = 10.4 Hz, *J* = 8.0 Hz, 2H), 8.40 (d, *J* = 10.4 Hz, 8H), 4.04 (s, 3H), -3.05 (s, 2H).
HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{47}H_{25}F_8N_4O_4$, 861.1743; found, 861.1739.

5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-trifluoroacetamidophenyl) porphyrin. To a solution of 237 mg (3.00 x 10^{-4} mol) 5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-aminophenyl) porphyrin in 125 mL ethyl acetate was added 500 μL diisopropylethylamine and 285 μL (1.65 x 10^{-3} mol) trifluoroacetic anhydride. The solution was stirred for 24 h, then placed in a separatory funnel and washed with aqueous sodium bicarbonate and water. The organic layer was collected, dried with sodium sulfate, filtered, and the solvent evaporated under reduced pressure to obtain the desired product as a purple-red solid (280 mg, 95%).
^{1}H NMR (400 MHz, DMSO, δ) 11.73 (s, 2H), 9.18 (d, *J* = 3.6 Hz, 4H), 8.96 (d, *J* = 4.6 Hz, 4H), 8.51 (tt, *J* = 10.1 Hz, *J* = 8.2 Hz, 2H), 8.33 (d, *J* = 8.4 Hz, 4H) 8.19 (d, *J* = 8.4 Hz, 4H), -3.01 (s, 2H).
HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{48}H_{23}F_{14}N_6O_2$, 981.1654; found, 981.1656.

5,15-bis-(2,3,5,6-tetrafluorophenyl)-10-(4-trifluoroacetamidophenyl)-20-(4-aminophenyl) porphyrin. To a flask was added 350 mg (3.57 x 10^{-4} mol) 5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-trifluoroacetamidophenyl) porphyrin to a mixture of 200 mL tetrahydrofuran and 50 mL methanol. A solution of 970 mM KOH in water was prepared, and 3 mL (2.82 x 10^{-3} mol KOH) was added to the porphyrin solution. The reaction was stirred at 50 ˚C under a nitrogen atmosphere for 2 h. The reaction was placed in a separatory funnel, 200 mL brine was added, and the mixture extracted with 150 mL dichloromethane and then 50 mL ethyl acetate. The organic extracts were washed with water, combined, and dried by distillation under reduced pressure. The crude product was purified by chromatography on silica gel using chloroform eluent containing ethyl acetate (starting 5%, ending 10%). The desired product was obtained along with starting material as purple-red solids. The reaction was repeated using the recovered starting material in a mixture of 100 mL tetrahydrofuran, 25 mL methanol, and 2 mL of the KOH solution. Identical reaction conditions and workup allowed for additional desired product to be obtained as a purple-red solid (185 mg, 59%).

^{1}H NMR (400 MHz, DMSO, δ) 9.04 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.82 (m, 4H), 8.26 (d, *J* = 8.4 Hz, 2H), 8.23 (s, 1H), 8.00 (m, 4H), 7.60 (tt, *J* = 9.8 Hz, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.07 (s, 2H), -2.79 (s, 2H).

HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{46}H_{24}F_{11}N_6O$, 885.1831; found, 885.1837.

Zn-5,15-bis-(2,3,5,6-tetrafluorophenyl)-10-(4-trifluoroacetamidophenyl)-20-(4-aminophenyl) porphyrin. To a solution of 165 mg (1.87 x 10^{-4} mol) 5,15-bis-(2,3,5,6-tetrafluorophenyl)-10-(4-trifluoroacetamidophenyl)-20-(4-aminophenyl) porphyrin in 60 mL dichloromethane was added a solution of 820 mg zinc(II) acetate dihydrate (3.74 x 10^{-3} mol) in 20 mL methanol. The reaction was stirred overnight, then placed in a separatory funnel and 10 mL ethyl acetate was added for solubility. The reaction mixture was washed with water, aqueous sodium bicarbonate, and then water. The organic layer was collected and dried by distillation under reduced pressure to obtain the desired product as a purple-red solid (172 mg, 97%).

^{1}H NMR (400 MHz, DMSO, δ) 11.69 (s, 1H), 9.00-8.97 (m, 6H), 8.85 (dd, *J* = 4.4 Hz, *J* = 1.1 Hz, 2H), 8.44 (tt, *J* = 10.3 Hz, *J* = 7.8 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 5.55 (s, 2H).

HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{46}H_{22}F_{11}N_6OZn$, 947.0965; found, 947.0946.

Zn-5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-trifluoroacetamidophenyl) porphyrin ($ZnPF_8$-amide). To a solution of 35 mg (3.57 x 10^{-5} mol) 5,15-bis-(2,3,5,6-tetrafluorophenyl)-10,20-bis-(4-trifluoroacetamidophenyl) porphyrin in 30 mL dichloromethane was added a solution of 160 mg zinc(II) acetate dihydrate (7.29 x 10^{-4} mol) in 10 mL methanol. The reaction was stirred overnight, then placed in a separatory funnel. The reaction mixture was washed with water, aqueous sodium bicarbonate, and then water. The organic layer was collected and dried by distillation under reduced pressure to obtain the desired product as a purple-red solid (32 mg, 86%).

UV-visible: λ_{max}(ethyl acetate)/nm 399 (ε, dm^3 mol^{-1} cm^{-1} 49 300), 420 (553 000), 551 (19 600), 593 (4 200).

^{1}H NMR (400 MHz, DMSO, δ) 11.70 (s, 2H), 9.02 (d, *J* = 4.5 Hz, 4H), 8.88 (d, *J* = 4.7 Hz, 4H), 8.45 (tt, *J* = 10.5 Hz, *J* = 7.9 Hz, 2H), 8.27 (d, *J* = 8.3 Hz, 4H), 8.15 (d, *J* = 8.3 Hz, 4H).

HRMS–API (*m/z*): M^+ calcd. for $C_{48}H_{20}F_{14}N_6O_2Zn$, 1042.0716; found, 1042.0728.

Dyad-ester. To a mixture of 34 mg (3.95 x 10^{-5} mol) 5,15-bis-(2,3,5,6-tetrafluorophenyl)-10-(4-carbomethoxyphenyl)-20-(4-carboxyphenyl) porphyrin in 25 mL dichloromethane was added 100 μL thionyl chloride. The solution was stirred under nitrogen atmosphere in the dark for 4 h, and then was dried by distillation under reduced pressure. A solution of 29 mg (3.06 x 10^{-5} mol) Zn-5,15-bis-(2,3,5,6-tetrafluorophenyl)-10-(4-trifluoroacetamidophenyl)-20-(4-aminophenyl) porphyrin in 20 mL dichloromethane with 100 μL pyridine was added to the reaction flask, and

the reaction mixture was stirred overnight in the dark under a nitrogen atmosphere. The reaction mixture was then placed in a separatory funnel and was washed with water, aqueous sodium bicarbonate, and then water. The organic layer was collected and dried by distillation under reduced pressure. The crude material was purified by chromatography on silica gel using dichloromethane containing 2% ethyl acetate as eluent. Fractions were collected, combined, and dried under reduced pressure to obtain the desired product as a purple-red solid (41 mg, 75%).
^{1}H NMR (400 MHz, CD_3COCD_3, δ) 10.71 (s, 1H), 10.42 (s, 1H), 9.25 (br d, *J* = 4.5 Hz, 2H), 9.22 (br d, *J* = 4.5 Hz, 2H), 9.16-9.10 (m, 8H), 9.03-9.01 (m, 4H), 8.66 (d, *J* = 8.2 Hz, 2H), 8.56 (d, *J* = 8.1 Hz, 2H), 8.52-8.47 (m, 6H), 8.35 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.3 Hz, 2H), 8.25-8.22 (m, 2H), 8.20-8.06 (m, 4H), 4.11 (s, 3H), -2.76 (s, 2H).
HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{93}H_{44}F_{19}N_{10}O_4Zn$, 1789.2530; found, 1789.2460.

Dyad-acid. To a solution of 40 mg (2.23×10^{-5} mol) Dyad-ester in 15 mL tetrahydrofuran was added 7 mL methanol and 2.5 mL of an aqueous solution containing 10% KOH. The reaction was stirred for 3 hr at 40 ˚C in the dark under a nitrogen atmosphere. The reaction was transferred to a separatory funnel and quenched with an aqueous solution of citric acid (1 g citric acid in 50 mL water). Ethyl acetate (30 mL) was added, the organic layer was washed twice with water, and then dried under reduced pressure. The crude material was redissolved in 20 mL dichloromethane containing 850 μL diisopropylethylamine, and 200 μL trifluoroacetic anhydride was added. The reaction was stirred overnight in the dark under a nitrogen atmosphere. The reaction mixture was transferred to a separatory funnel and the organic layer was washed with 20 mL of an aqueous solution containing 1% KOH. The aqueous layer was extracted with 10 mL ethyl acetate. The organic extracts were combined and washed with dilute aqueous citric acid, water, and then dried by distillation under reduced pressure. The crude material was purified by column chromatography on silica gel using dichloromethane containing 10% ethyl acetate and 5% ethanol as eluent. Fractions were collected, combined, and dried by distillation under reduced pressure to obtain the desired product as a purple-red solid (20 mg, 50%).
UV-visible: λ_{max}(ethyl acetate)/nm 421 (ε, $dm^3\ mol^{-1}\ cm^{-1}$ 761 000), 508 (25 600), 550 (25 200), 588 (10 700), 640 (2 300).
^{1}H NMR (400 MHz, CD_3COCD_3, δ) 10.72 (s, 1H), 10.42 (s, 1H), 9.25 (br d, *J* = 4.3 Hz, 2H), 9.22 (br d, *J* = 4.2 Hz, 2H), 9.15-9.10 (m, 8H), 9.04 (br d, *J* = 4.5 Hz, 2H), 9.02 (d, *J* = 4.7 Hz, 2H), 8.64 (d, *J* = 8.3 Hz, 2H), 8.56 (d, *J* = 8.2 Hz, 2H), 8.53 (d, *J* = 8.2 Hz, 2H), 8.50 (d, *J* = 8.5 Hz, 2H), 8.47 (d, *J* = 8.4 Hz, 2H), 8.35 (d, *J* = 8.5 Hz, 2H), 8.32 (d, *J* = 8.5 Hz, 2H), 8.25-8.22 (m, 2H), 8.20-8.05 (m, 4H), -2.75 (s, 2H).
HRMS–API (*m/z*): $[M + H]^+$ calcd. for $C_{92}H_{42}F_{19}N_{10}O_4Zn$, 1775.2373; found, 1775.2400.

Characterization. Proton NMR spectra were obtained on a 400 MHz instrument, with chemical shifts reported as δ ppm from an internal TMS standard. Assignments were aided by correlation with COSY spectra. Mass spectrometry was performed on an Agilent G6550A Q-TOF LC/MS with API by direct injection.

Surface coverage analysis. The number of SnO_2 nanoparticles in each film was estimated using the manufacturer's average spherical particle size of 16 nm, the experimentally determined volume of the film, and the amount of void space within each film. The visible area was obtained by taking a picture and using CorelDraw software for analysis, and the thickness was determined by profilometry. The void space was estimated as the volume composed of the polymer stabilizer and residual trapped solvent during the sintering process. The latter was estimated by assuming that 95% of the colloid solvent (water, acetic acid) evaporated prior to sintering, and that a residual 5% was trapped within the polymer/nanoparticle film while sintering. It was further estimated that 5% of the nanoparticle particle surface area was composed of inter-particle connections. The number of porphyrins bound to the surface was experimentally determined by leaching of a prepared monolayer into an alkaline organic solution, with UV-visible spectroscopy and the extinction coefficients used for calculations. The leaching experiment is described above. The porphyrins were modeled as freely-rotating molecules extending normal from the nanoparticle surface, with each occupied block covering 3.24 nm^2 (H_2PF_8-acid and Dyad-acid in mixed monolayers) or 4.67 nm^2 (Dyad-acid monolayer) as determined from a calculated molecular structure with MM2 energy minimization. Using the experimentally determined dye amounts, estimated surface area, and an estimation of the area covered by each dye molecule, it was determined that ~86% +/- 4% of full monolayer coverage was formed, and did not vary significantly with different ratios of surface-bound dyes.

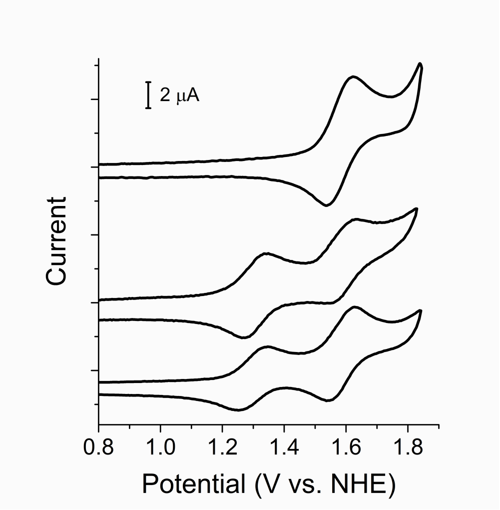

Figure S1. Electrochemistry. H_2PF_8-ester (top), $ZnPF_8$-amide (middle) and Dyad-ester (bottom). Electrolyte consisted of 100 mM tetra-*n*-butylammonium hexafluorophosphate in dichloromethane. Data obtained using 50 mV/sec scan rate.

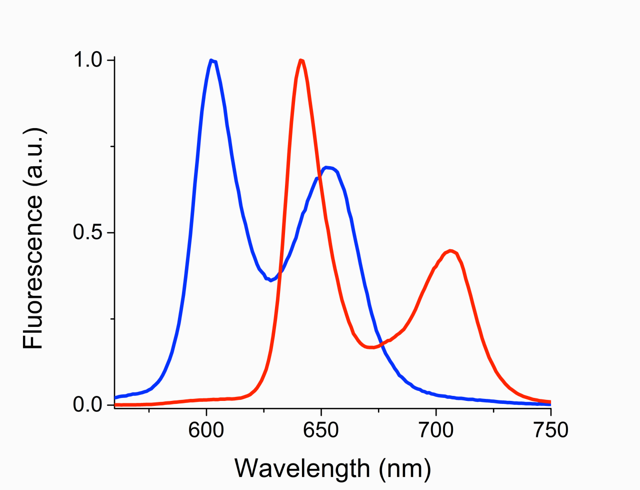

Figure S2. Fluorescence spectra of H_2PF_8-ester (red) and $ZnPF_8$-amide (blue) in acetonitrile. Excitation of the porphyrins was at 508 nm (H_2PF_8) and 553 nm ($ZnPF_8$) at absorbance values below 0.09.

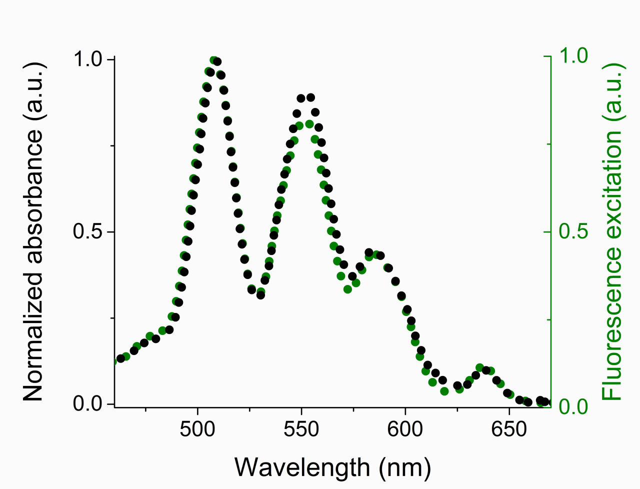

Figure S3. Energy Transfer. The absorbance spectrum (black) and fluorescence excitation spectrum (green) of dilute Dyad-ester in acetonitrile. Fluorescence excitation spectrum obtained by monitoring the freebase porphyrin emission at 710 nm.

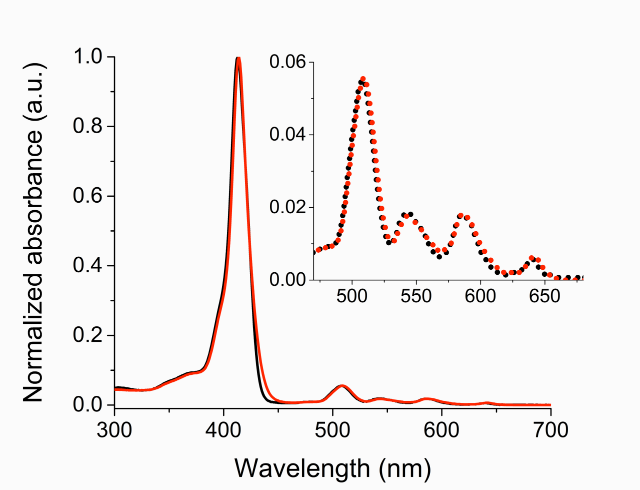

Figure S4. Absorbance of H_2PF_8-acid:Dyad-acid 5:1 ratio dye solution in ethyl acetate (black) and desorbed dye solution (red) obtained from leaching of 5:1 dye ratio SnO_2 electrode in THF/methanol/KOH(aq) solution. Inset highlights the Q-band region. The slight shift in the absorption spectra is due to the different solvent system used for the measurements.

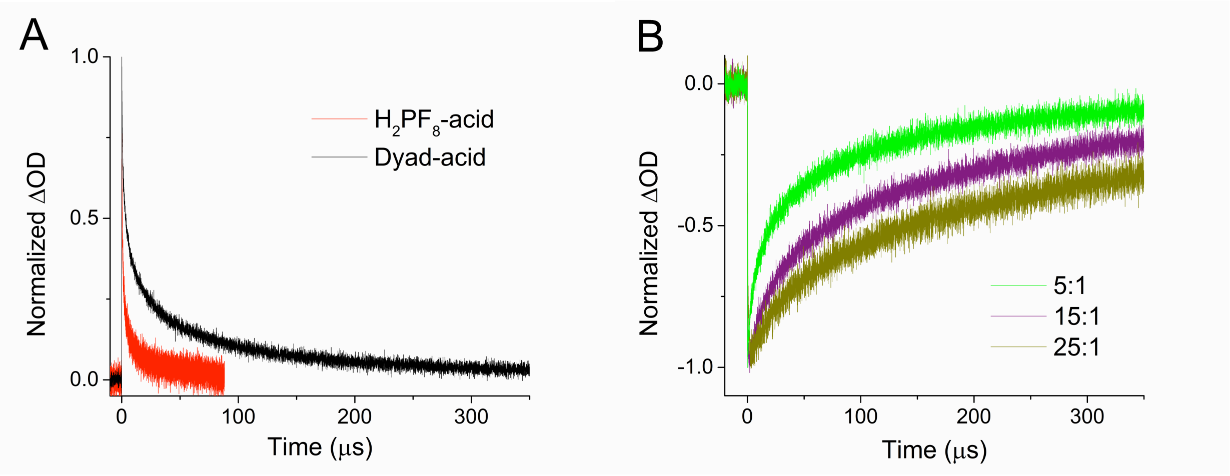

Figure S5. Transient absorption traces for H_2PF_8-acid and Dyad-acid (A) and varying H_2PF_8-acid: Dyad-acid ratios (B). Samples were excited at 515 nm and probed at 470 nm (A) and 560 nm (B). Electrolyte consisted of 200 mM $NaClO_4$ (aq).

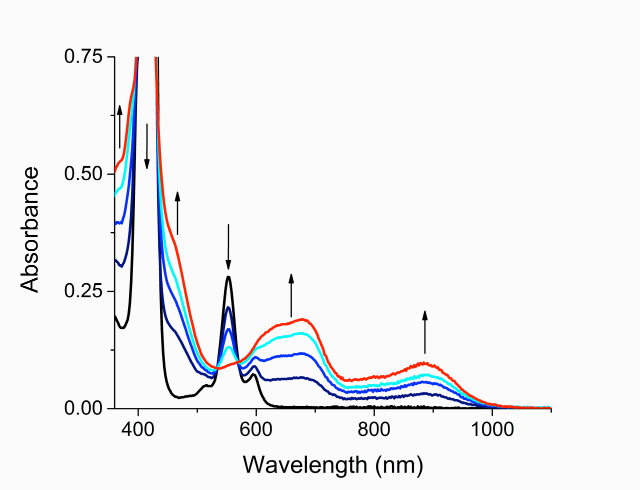

Figure S6. Spectroelectrochemistry of ZnPF$_8$-amide. Performed in acetonitrile solvent containing 100 mM TBAPF$_6$ as electrolyte at 1.49 V vs. NHE. Spectra obtained prior to applied potential (black) and after equilibrium of first oxidized state (red). At intervals of time prior to complete oxidation, spectra were obtained corresponding to partially oxidized solutions containing a mixture of starting material and oxidized species (navy, blue, and cyan).

Sample derivation for differential equations

$$y(t) = e^{-(kt)^{\beta}}$$

$$y(t) = e^{-(k^{\beta}t^{\beta})}$$

$$\ln[y(t)] = -k^{\beta}t^{\beta}$$

$$\frac{\partial y}{y(t)} = -\beta k^{\beta}t^{\beta-1}\partial t$$

$$\frac{\partial y}{\partial t} = -\beta k^{\beta}t^{\beta-1}y(t)$$

The example above shows the differentiation of the stretched exponential function used to fit the recombination processes, where y(t) can be either [M$_n$] or [D].

(1) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.