# Supplementary Information

## Comparison of Silatrane, Phosphonic Acid, and Carboxylic Acid Functional Groups for Attachment of Porphyrin Sensitizers to $TiO_2$ in Photoelectrochemical Cells

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**General analytical methods.** Mass spectrometry was performed by the MALDI-TOF method using a Voyager DE STR from Applied Biosystems. $^1$H NMR spectra were obtained in deuterated chloroform using a 400 MHz instrument with tetramethylsilane as internal reference. Proton assignments were aided by the use of COSY experiments. Profilometry was used to determine sample thicknesses using a calibrated Sloan Dektak II Profilometer.

Electrochemistry was performed using a CH Instruments 650C or 760D electrochemical workstation with a standard 3-electrode cell setup using a platinum gauze counter electrode, pseudo Ag/AgCl reference electrode, and platinum working electrode in dichloromethane solvent containing 100 mM tetra-butylammonium hexafluorophosphate as the electrolyte. Potentials are referenced to SCE using the ferrocene / ferrocenium redox couple as an internal standard.[S1]

**Steady-state spectroscopy.** UV–Visible-NIR spectroscopy was performed using a Shimadzu UV-2550 UV–Visible spectrophotometer. Steady-state fluorescence spectra were measured using a Photon Technology International MP-1 spectrometer and corrected for detection system response. Excitation was provided by a 75 W xenon-arc lamp and single grating monochromator. Fluorescence was detected 90° to the excitation beam via a single grating monochromator and an R928 photomultiplier tube having S-20 spectral response and operating in the single photon counting mode. FT-IR-ATR was performed using a Nicolet 380 FT-IR with Smart Orbit single reflection ATR attachment equipped with diamond substrate.

**Time-resolved fluorescence**. Fluorescence decay kinetics was measured using the time-correlated single-photon counting (TCSPC) technique. The excitation source was a fiber supercontinuum laser based on a passive modelocked fiber laser and a high-nonlinearity photonic crystal fiber supercontinuum generator (Fianium SC450). The laser provides 6-ps pulses at a repetition rate variable between 0.1 – 40 MHz. The laser output was sent through an Acousto-Optical Tunable Filter (Fianium AOTF) to obtain excitation pulses at the desired wavelength of 520 nm. Fluorescence emission was collected at 90° and detected using a double-grating monochromator (Jobin-Yvon, Gemini-180) and a microchannel plate photomultiplier tube (Hamamatsu R3809U-50). The polarization of the emission was 54.7° relative to that of the excitation. Data acquisition was done using a single photon counting card (Becker-Hickl, SPC-830). The IRF had a FWHM of 50 ps, as measured from the scattering of the sample at the excitation wavelength. The data was fitted with a sum of exponentials decay model at a single wavelength using ASUFIT.

**Transient absorption**. Nanosecond transient absorption measurements were made with excitation from an optical parametric oscillator driven by the third harmonic of a Nd:YAG laser (Ekspla NT342B). The pulse width was ~4-5 ns, and the repetition rate was 10 Hz. The detection portion of the spectrometer (Proteus) was manufactured by Ultrafast Systems. The instrument response function was ca. 4.8 ns.

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 the equation below (parallel kinetic model), 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.

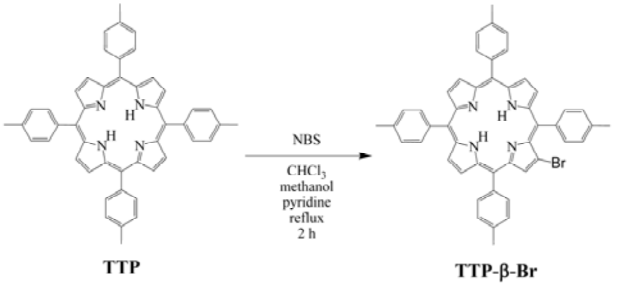
$$\Delta A(\lambda,t)=\sum_{i=1}^{n} A_i(\lambda)\exp(-t/\tau_i)$$

A plot of $A_i(\lambda)$ versus wavelength is called a decay-associated spectrum (DAS), and represents the amplitude spectrum of the $i^{\text{th}}$ kinetic component, which has a lifetime of $\tau_i$. Evolution-associated difference spectra (EADS) were obtained by global analysis of the transient absorption data using a kinetic model consisting of sequentially interconverting species, e.g. $1\rightarrow 2\rightarrow 3\rightarrow\ldots$ . The arrows indicate successive mono-exponential decays with increasing time constants, which can be regarded as the lifetimes of each species. Associated with each species is a lifetime and a difference spectrum. Each EADS corresponds in general to a mixture of states and does not portray the spectrum of a pure state or species. This procedure enables us to visualize clearly the evolution of the transient states of the system. Random errors associated with the reported lifetimes obtained from fluorescence and transient absorption measurements were typically ≤ 5%.

**Materials.** All reagents and chemicals were obtained from commercial sources unless noted. Dichloromethane, hexanes, toluene, tetrahydrofuran, and triethylamine were distilled prior to use. Acetonitrile (Omnisolv grade) was stored on 4Å molecular sieves. Silica gel chromatography was performed using 230-400 mesh silica gel (Silicycle, Siliflash F60). Fluorinated tin oxide (FTO, TEC 15, 12-14 Ω/sq) on silica glass was obtained from Hartford Glass.

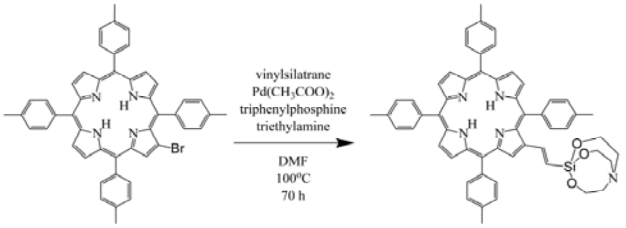
**Synthesis.** The 5, 10, 15, 20-tetrakis (4-methylphenyl)porphyrin (TTP), TTP-β-formyl, and TTP-β-COOMe were synthesized according to literature procedures.[S2,3] The TTP-β-COOH was prepared by hydrolysis of TTP-β-COOMe using a method similar to that described by Wang et al.[S4] Vinylsilatrane was obtained from Gelest and purified by the following procedure. The sticky solid was dissolved in dichloromethane, and the solution washed with water. The organic layer was filtered through a sintered frit, and the material was precipitated from the filtrate by adding hexanes and filtered to yield a white powder.

**General procedure for porphyrin metalations.** Unless otherwise stated, zinc metalation of porphyrins was performed by adding porphyrin and 5-10 equivalents of zinc(II) acetate dihydrate to a 5:1 solution of dichloromethane / methanol. The solution was heated for 30 min and then allowed to stir overnight under a nitrogen atmosphere. The organic layer was washed with distilled water, saturated aqueous sodium bicarbonate, and again with distilled water, and the solvent was distilled under reduced pressure. All reactions went to completion.



**TTP-β-Br.** In a dry round bottom flask was dissolved 260 mg TTP ($3.9 \times 10^{-4}$ mol) in a mixture of 130 mL chloroform, 1 mL pyridine, and 200 μL anhydrous methanol. The reaction mixture was stirred and heated to reflux under a nitrogen atmosphere. Over a 2 h period, N-bromosuccinimide was added in increments totalling 80 mg ($4.5 \times 10^{-4}$ mol). After an additional

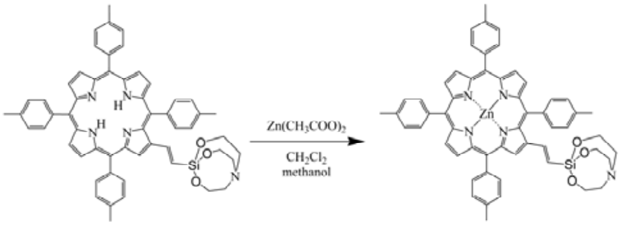
2 h at reflux, the reaction mixture was cooled to room temperature and washed with water, and the solvent was removed under reduced pressure. The crude material was precipitated from a solution of dichloromethane and methanol by distillation of dichloromethane under reduced pressure, and the precipitated porphyrin products were obtained by filtration. The product was purified by chromatography on silica gel (activated by heating overnight at 100°C) using a 3:2 mixture of hexanes / dichloromethane as eluent (115 mg, 39%). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.91-8.75 (7H, m, *β*-H), 8.1-8.04 (6H, m, Ar-H), 7.95 (2H, d, *J*=8 Hz, Ar-H), 7.56-7.51 (8H, m, Ar-H), 2.70 (12H, s, Ar-$CH_3$), -2.85 (2H, s, NH). MALDI-TOF-MS m/z calcd for $C_{48}H_{37}BrN_4$ 750.2, obsd 750.2.



TTP-β-Br

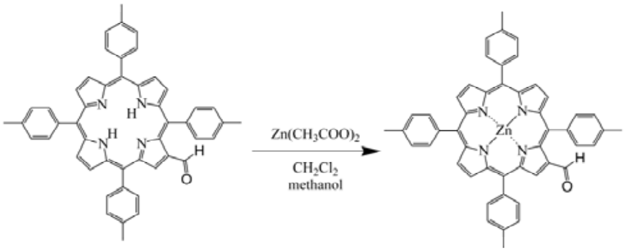
TTP-β-sil

**TTP-β-sil.** In a dry round bottom flask was dissolved 81 mg TTP-β-Br ($1.1 \times 10^{-4}$ mol), 48 mg vinylsilatrane **4** ($2.4 \times 10^{-4}$ mol), 8.5 mg palladium(II) acetate ($3.8 \times 10^{-5}$ mol), 30 mg triphenylphosphine ($1.1 \times 10^{-4}$ mol), and 200 μL triethylamine in 30 mL DMF. The reaction mixture was kept under a nitrogen atmosphere and heated to 100°C for 70 h. After cooling, the solvent was distilled under reduced pressure. The crude products were purified by column chromatography on silica gel. The TTP and brominated starting material were flushed from the column using dichloromethane as the eluent. Addition of 1% methanol to the dichloromethane eluent eluted the desired porphyrin. The solid was sonicated in a 50:50 methanol/water solution and filtered to yield the desired porphyrin product (21 mg, 22%). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.06 (1H, s, *β*-H), 8.85-8.83 (2H, m, *β*-H), 8.75 (2H, s, *β*-H), 8.70 (1H, d, *J*=5 Hz, *β*-H) 8.64 (1H, d, *J*=5 Hz, *β*-H), 8.09-7.99 (8H, m, Ar-H), 7.54-7.48 (8H, m, Ar-H), 7.06 (1H, d, *J*=18 Hz, *β*-CH), 6.65 (1H, d, *J*=18 Hz, CH-Si), 3.82 (6H, t, *J*=6 Hz, O-$CH_2$), 2.83 (6H, t, *J*=6 Hz, N-$CH_2$), 2.69 (12H, m, Ar-$CH_3$), -2.67 (2H, br s, NH). MALDI-TOF-MS m/z calcd for $C_{56}H_{51}N_5O_3Si$ 869.4, obsd 869.2.



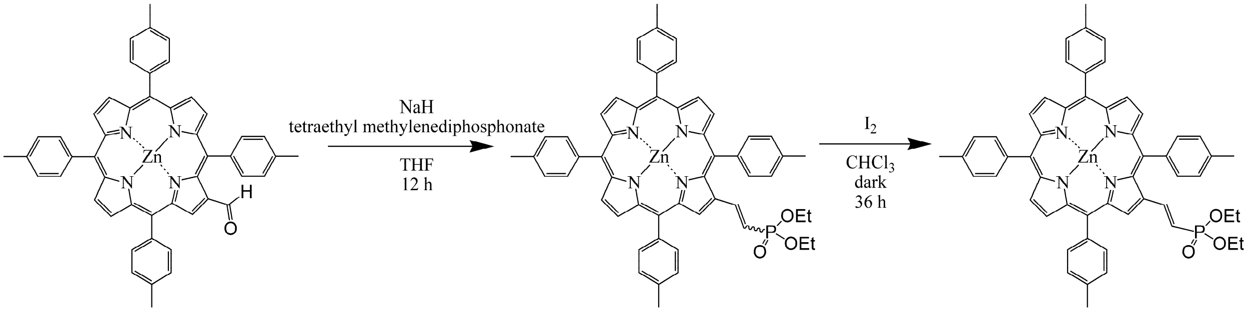
**TTP-β-sil** **Zn-TTP-sil**

**Zn-TTP-sil.** TTP-β-sil was metalated using the general metalation procedure. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.11 (1H, s, *β*-H), 8.91-8.88 (4H, m, *β*-H), 8.85 (1H, d, *J*=4 Hz, *β*-H) 8.77 (1H, d, *J*=4 Hz, *β*-H), 8.07 (4H, d, *J*=8 Hz, Ar-H), 8.02 (2H, d, *J*=8 Hz, Ar-H), 7.98 (2H, d, *J*=8 Hz, Ar-H), 7.52-7.48 (8H, m, Ar-H), 7.04 (1H, d, *J*=18 Hz, *β*-CH), 6.52 (1H, d, *J*=18 Hz, CH-Si), 3.81 (6H, t, *J*=6 Hz, O-CH$_2$), 2.82 (6H, t, *J*=6 Hz, N-CH$_2$), 2.69 (12H, m, Ar-CH$_3$). MALDI-TOF-MS m/z calcd for $C_{56}H_{49}N_5O_3SiZn$ 931.3, obsd 931.4.



**TTP-β-formyl** **Zn-TTP-β-formyl**

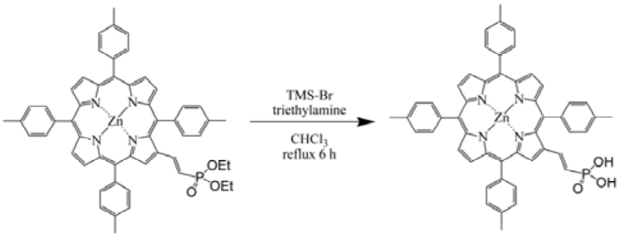
**Zn-TTP-β-formyl.** TTP-β-formyl was metalated using the general metalation procedure. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.56 (1H, s, *β*-H), 9.36 (1H, s, CHO), 8.97-8.91 (6H, m, *β*-H), 8.11-8.04 (8H, m, Ar-H), 7.57-7.53 (8H, m, Ar-H), 2.71-2.70 (12H, m, Ar-CH$_3$). MALDI-TOF-MS m/z calcd for $C_{49}H_{36}N_4OZn$ 760.2, obsd 760.2.



**Zn-TTP-β-formyl** **Zn-TTP-PO(OEt)$_2$**

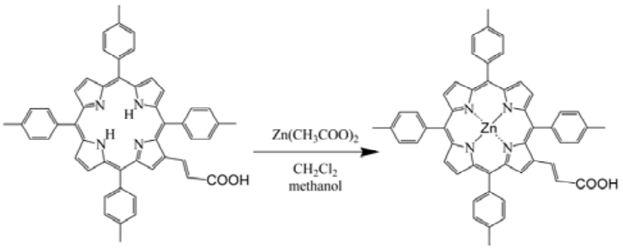
**Zn-TTP-PO(OEt)$_2$.** This substance was prepared following a modification of a procedure described by Bonfantini et al.[S3] A dry round bottom flask containing 40 mL of distilled THF was flushed with nitrogen while 37 mg sodium hydride ($9.3 \times 10^{-4}$ mol) was added.

The solution was cooled in an ice bath and 69 mg of Zn-TTP-β–formyl ($9.1 \times 10^{-5}$ mol) and 120 μL of tetraethyl methylenediphosphonate ($4.8 \times 10^{-4}$ mol) were added. A small amount of additional sodium hydride was added to remove some water contamination in the solvent. The reaction mixture was stirred under a nitrogen atmosphere at room temperature overnight, and then quenched using a saturated ammonium chloride solution. The reaction mixture was placed in a separatory funnel with chloroform and a brine solution. The organic layer was separated and washed with water and the solvent was then removed by distillation under reduced pressure. The crude product was dissolved in a mixture of dichloromethane and methanol, and the dichloromethane removed by distillation under reduced pressure. The porphyrin was precipitated by addition of water, and then removed by filtration. The crude material was purified by column chromatography on silica gel using 2% methanol in dichloromethane as eluent to obtain 36 mg of a cis/trans mixture containing the desired porphyrin. The mixture was dissolved in 25 mL of chloroform and 8 mg of $I_2$ ($3.2 \times 10^{-5}$ mol) was added. The reaction mixture was stirred for 36 h under a nitrogen atmosphere in the dark. The mixture was transferred to a separatory funnel and quenched by adding excess aqueous sodium bisulfite. The organic layer was separated and washed with water, and the solvent was removed by distillation under reduced pressure. Demetalation by acidic solutions during workup required re-metalation using the general metalation procedure, and 35 mg of the desired porphyrin was isolated (43%). $^{1}H$ NMR (400 MHz, $CDCl_3$, $^{31}P$ decoupled ) δ 8.89-8.75 (7H, m, *β*-H), 8.08-8.02 (6H, m, Ar-H), 7.68 (2H, d, *J*=8 Hz, Ar-H), 7.53 (2H, d, *J*=8 Hz, Ar-H), 7.47-7.44 (4H, m, Ar-H), 6.97 (2H, br d, *J*=7 Hz, Ar-H), 6.34 (1H, br d, *J*=17 Hz, β-CH), 5.19 (1H, br d, *J*=17 Hz, CH-P), 3.06 (4H, broad, P-$CH_2$), 2.75 (3H, s, Ar-$CH_3$), 2.645 (3H, s, Ar-$CH_3$), 2.640 (3H, s, Ar-$CH_3$), 2.35 (3H, s, Ar-$CH_3$), 0.86 (6H, t, $CH_3$). MALDI-TOF-MS m/z calcd for $C_{54}H_{47}N_4O_3PZn$ 894.3, obsd 894.4.



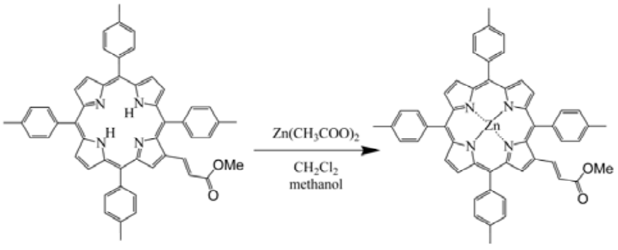
**Zn-TTP-PO(OEt)$_2$**　　**Zn-TTP-PO$_3$H$_2$**

**Zn-TTP-PO$_3$H$_2$.** This porphyrin was prepared following a procedure by Muthukumaran et al.[S5] In a dry round bottom flask was dissolved 37 mg of Zn-TTP-PO(OEt)$_2$ ($4.1 \times 10^{-5}$ mol) and 200 μL triethylamine ($1.4 \times 10^{-3}$ mol) in 25 mL chloroform. The vessel was placed under a nitrogen atmosphere and 150 µL bromotrimethylsilane was added dropwise. A reflux condenser was attached and the solution was heated to reflux under a nitrogen atmosphere for 6 h. The reaction mixture was cooled and washed with brine, dilute citric acid, and then water. The solvent was removed by distillation under reduced pressure, and the crude material was determined to be partially demetalated. The crude product was remetalated using a modified version of the general metalation procedure where after the bicarbonate wash, the organic layer was washed with a dilute solution of polyphosphoric acid (~3% w/w). After metalation the product was determined to be >95% pure (35 mg, 100 %). MALDI-TOF-MS m/z calcd for $C_{50}H_{39}N_4O_3PZn$ + 1(H) 839.2, obsd 839.3.



**TTP-β-COOH** **Zn-TTP-COOH**

**Zn-TTP-COOH.** Metalation of TTP-β-COOH was performed using a modified version of the general porphyrin metalation procedure wherein a dilute aqueous citric acid wash was performed after the bicarbonate wash in order to reprotonate the carboxylate group. MALDI-TOF-MS m/z calcd $C_{51}H_{38}N_4O_2Zn$ 802.2, obsd 802.2.



**TTP-β-COOMe** **Zn-TTP-COOMe**

**Zn-TTP-COOMe.** Metalation of TTP-β-COOMe was performed using the general porphyrin metalation procedure. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.08 (1H, s, *β*-H), 8.94-8.89 (6H, m, *β*-H), 8.08-8.05 (6H, m, Ar-H), 7.95 (2H, d, *J*=8Hz, Ar-H), 7.55-7.51 (8H, m, Ar-H), 7.37 (1H, d, *J*=15Hz, *β*-CH), 6.48 (1H, d, *J*=15Hz, CH), 3.73 (3H, s, O-$CH_3$), 2.72 (3H, s, Ar-$CH_3$), 2.70 (3H, s, Ar-$CH_3$), 2.69 (6H, s, Ar-$CH_3$). MALDI-TOF-MS m/z calcd for $C_{52}H_{40}N_4O_2$ Zn 816.2, obsd 816.3.

**$TiO_2$ colloid.** The colloid was prepared using a modified procedure from Kang et al.[S6] A solution of 26 mL distilled water and 8.5 mL glacial acetic acid was cooled in an ice bath. Separately, 1 mL of isopropanol and 4 mL of titanium isopropoxide (Alfa Aesar 97%) were mixed, and the mixture was then added dropwise to the cooled solution with stirring. A reflux condenser was attached, and the mixture was heated at 110 $^oC$ for 4.5 h. After cooling, 32 mL of the opaque colloid was transferred to a Teflon® container and placed in an acid digestion vessel autoclave (Parr – model 4744). The vessel was heated in an oven at 200 $^oC$ for 12 h and then allowed to cool to room temperature. The colloid was re-dispersed into solution using a sonic horn (Branson Sonic Power - Sonifier cell disruptor - model 350) with continuous sonication for 2 min, a 50/50 pulse for 2 min, and continuous sonication for 1 min to fully disperse the material. The colloid was placed in a round bottom flask and concentrated to 4.2 mL (4.6 grams) using a rotary evaporator under reduced pressure. The concentrated colloid was mixed with 120 mg each of PEG (Fluka - 17500 MW with bisphenol-A) and PEO (Aldrich – 100000 MW). Another ~0.8 mL water was added to decrease the viscosity. The colloidal solution was stirred overnight to insure homogeneity.

**Preparation and characterization of $TiO_2$ electrodes.** A glass sheet with a transparent, conductive FTO layer was rinsed with acetone, water, and ethanol. An area on the substrate was then defined using Scotch® transparent tape (51 $\mu$m thick). The nanoparticle colloidal solution was spread over the FTO and tape mask using a glass rod. The resulting film was dried overnight in air. The tape was removed, and the films were heated in an oven at 450 $^oC$ for 1 h. Profilometry was used to determine the thickness of $TiO_2$ electrodes prepared using the above procedure. The results showed a narrow thickness range that varied between 3 μm and 3.2 μm.

**Sensitization of $TiO_2$.** Porphyrins were dissolved in toluene (~0.2 mM), and electrodes were soaked at 90 $^oC$ for 1 h, rinsed in toluene and acetonitrile, and then dried in air. Sensitization of $TiO_2$ with Zn-TTP-COOH at lower surface coverage used an identical procedure with soakings of 5 and 8 minutes.

**Counter electrodes for DSSC.** Platinized FTO (Pt/FTO) glass for use as electrodes in regenerative-type photoelectrochemical cells were prepared as follows using conductive FTO glass (Hartford Glass, TEC 15). Holes were drilled in the glass for future electrolyte introduction. A diamond burr and high speed rotary tool were used to place two holes on opposite corners of the glass. FTO was cleaned with distilled water, acetone, and ethanol, and then dried in air. A drop of 10 mM hexachloroplatinic acid ($H_2PtCl_6$) in anhydrous ethanol was placed on the conductive side of the FTO glass, which was then dried in air. The FTO was heated in air at 450°C for 1 h, during which time a nearly transparent Pt/PtO film formed.

**DSSC fabrication.** Dye sensitized $TiO_2$ electrodes were shaped into ~1 cm × 1 cm electrodes. DSSC fabrication involved sealing a sensitized electrode to a platinized counterelectrode (Pt/FTO) in a face-to-face design using a heat-sealable polymer (Solaronix, Surlyn®, 25 μm) to confine the active area of the electrodes and act as a high-resistance spacer between them. The Pt/FTO holes were used as the corners of the heat-seal polymer frame. The sensitized electrode was placed on top, and the polymer melted on a hotplate. After cooling, the electrolyte was introduced via the holes in the platinized FTO. Electrolyte consisted of 100 mM LiI, 50 mM $I_2$, 650 mM 1-butyl-3-methylimidazolium iodide,[4b] and 50 mM 4-*t*-butylpyridine in an 85:15 acetonitrile:valeronitrile solvent mixture. A thin microscope slide cover glass was used to cover the holes and limit solvent evaporation.

**DSSC testing.** Devices were connected to a programmable Keithley 2400 Sourcemeter linked to a computer via a National Instruments USB-6009 communication board, and all data were acquired by programs written using LabView 7.1 software. A 450 W Osram® xenon arc lamp with a Jobin Yvon single-grating monochromator was used for illumination at specific wavelengths. Light intensity was measured at each wavelength tested using a calibrated silicon diode detector (Newport Corp. model 818-UV) to obtain the power density spectrum. Current vs. wavelength measurements were obtained in 4 nm increments. Photocurrent was determined by subtracting the average dark current from the average light current. AM1.5G illumination was obtained using the xenon arc lamp with added filter (Newport Oriel model 81094) to simulate the AM1.5G solar spectrum. The lamp output was calibrated to 1000 $W/m^2$ using a Daystar Solar Meter. Current-voltage measurements were obtained by scanning an applied potential using a Keithley 2400 Sourcemeter.

**Dye leaching study.** The $TiO_2$ electrodes were sensitized with porphyrin using the procedure described above. Porphyrin was leached from the sensitized electrode surface using an alkaline solution consisting of a mixture of THF / methanol / 0.5% aqueous $Cs_2CO_3$ (w/w) in a 10:5:2 ratio. Electrodes were soaked at room temperature for 20 min and rinsed with a THF / water solution followed by an acetonitrile wash. For 'cured' electrodes, $TiO_2$ was sensitized as described and then heated at ~80 °C for 1 h in a solution of acetonitrile containing 0.6% water.

**Supporting information figures:**

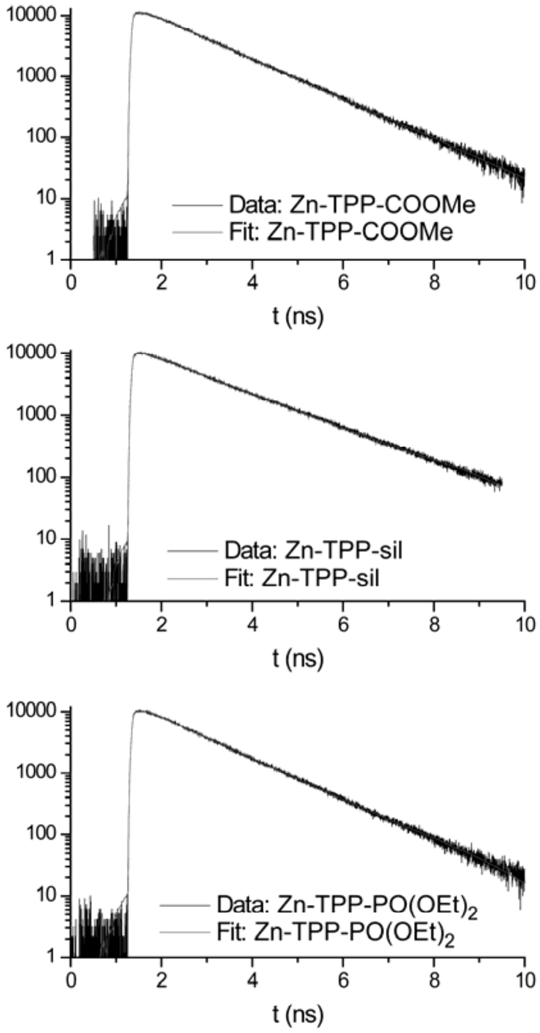


**Figure S1.** Fluorescence lifetimes determined using the single photon timing method. Experiments were performed in dichloromethane with excitation at 550 nm (*A* ~0.3) and emission detected at 660 nm. The data were fitted to the sum of two exponential components:

Zn-TTP-COOMe: $\tau$ = 1.32 ns (95.5 %) and 0.34 ns (4.5%).
Zn-TTP-sil: $\tau$ = 1.56 ns (89%) and 0.29 ns (11%).
Zn-TTP-PO(OEt)$_2$: $\tau$ = 1.30 ns (94%) and 0.44 ns (6%).

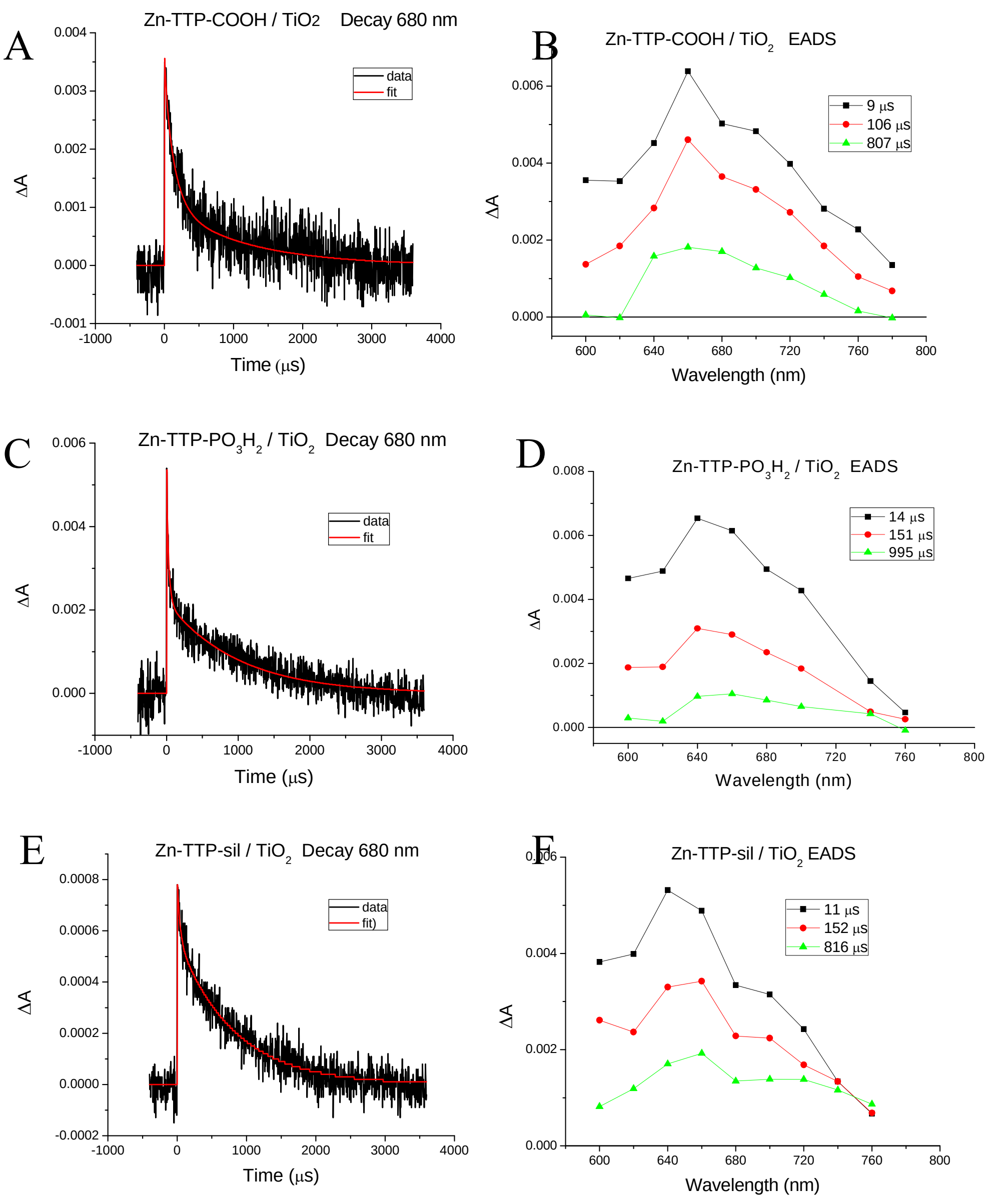


**Figure S2.** Transient absorbance decay at 680 nm and evolution associated decay spectra (EADS) for Zn-TTP-COOH / $TiO_2$ (A and B), Zn-TTP-$PO_3H_2$ / $TiO_2$ (C and D), and Zn-TTP-sil / $TiO_2$ (E and F). Dyes on $TiO_2$ were analyzed in a solution of 100 mM $LiClO_4$ and 50 mM 4-*t*-butyl pyridine in a mixture of 85:15 acetonitrile and valeronitrile solvent. The electrodes were pumped at 560 nm and probed between 600 and 780 nm. The decay data are shown in black along with the best-fit line using a three-component exponential decay (red). EADS components are shown in the short (black), medium (red) and long timeframe (green).

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