Photoinjection of High Potential Holes into $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ Nanoparticles by Porphyrin Dyes

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Supporting Information

ABSTRACT: Excited-state hole injection into the valence band of $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ nanoparticles (NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$) was investigated through sensitization with zinc porphyrin dyes using simulated solar irradiance. The $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ nanoparticles were prepared by a flux-mediated synthesis and found to have an average particle size of $\sim 10\text{--}15\text{ nm}$ by DLS and TEM. The zinc 4-(10,15,20-tris(4-pyridinyl)-porphyrin-5-yl)phenylphosphonic acid (**D1**) and its analogue, in which the pyridine groups are methylated (**D2**), were synthesized and found to have excited-state reduction potentials appropriate for p-type dye sensitization of the nanoparticles. The dye-sensitized NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ exhibited fluorescence quenching consistent with electron transfer from the NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ to the dye; forward and recombination rates were obtained by transient absorption measurements. Hole injection times of 8 ps and $<100\text{ fs}$ were observed for **D1** and **D2**, respectively. Nanoparticulate films of $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ were prepared and evaluated in dye-sensitized solar cells under simulated solar irradiance (AM 1.5 G, 100 mW/cm^2). Measurable photocurrents and open-circuit potentials (V_{oc}) of 200 and 110 mV were observed using **D1** and **D2**, respectively.

INTRODUCTION

Anthropogenic activity and especially the massive burning of fossil fuels has a deleterious effect on the global ecosystem.¹ Owing to the magnitude of the solar energy reaching the earth, development of a technology that is capable of efficiently converting sunlight into electricity or highly energetic fuels is an appealing prospect.² In this connection, photoelectrochemical dye-sensitized solar cells (DSSCs) have attracted growing interest since the seminal contribution by Grätzel and O'Regan in 1991.³ Currently, two general classes of DSSC designs can be distinguished. The first (n-DSSC) is based on the sensitization of a wide-band-gap n-type semiconductor oxide (e.g., TiO_2 , SnO_2 , or ZnO). Photoinduced electron injection from the excited photosensitizer into the oxide conduction band is followed by electron transmission by a conductor through the load and to a nonphotochemically active cathode. A mediator in solution transports electrons from the cathode to regenerate the oxidized dye at the photoanode. So far, photoconversion efficiencies up to 13% have been achieved.⁴ The second class of DSSC uses a p-type metal oxide such as NiO , Cu(I) -containing oxides, zinc cobalt oxide,⁵ or doped diamond (p-DSSC). In these devices, photoinduced hole injection into the valence band (VB) of the semiconductor of a photocathode initiates the overall electron flow. Thus far, they have achieved a maximum energy conversion efficiency of around 1.3%.⁶

These same concepts may be used in the design of photoelectrosynthetic systems that use visible light to split water into oxygen and hydrogen, or that produce other fuels or chemicals. Such systems are generally inefficient because of the great challenge of generating the necessary photopotential.⁷ However, if both efficient photocatalytic n-DSSC type anodes and p-DSSC type photocatalytic cathodes were available, one can envision their use in a tandem-type photoelectrosynthetic cell for water splitting.⁸ Such a cell would be based on a two-cell configuration,^{9,10} wherein water is oxidized by catalysts at the photoanode and hydrogen is produced by catalysts at the photocathode. In principle, such cells could be very efficient because the overall power conversion efficiency of a tandem cell is higher than the Shockley–Queisser limitation for a single junction cell.¹¹ In a tandem photoelectrosynthetic cell, electron flow is analogous to that in the Z scheme of natural oxygenic photosynthesis, but the thermodynamics are fundamentally different in that a properly designed tandem cell better matches the absorption spectra of the sensitizers to the solar spectrum, thereby nearly doubling the rate of light absorption. Optimally designed sensitizers would cover the solar spectrum from the

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near UV to about 750 nm for one photoelectrode and from 750 nm to about 1100 nm for the second photoelectrode.¹²

The principle of operation of a p-type semiconductor sensitized by organic dyes is illustrated in Scheme 1a. Light

Scheme 1. (a) Schematic of the Processes Involved in Hole Photoinjection in a System of a Chromophore and a p-Type Semiconductor.^a (b) Schematic of a p-DSSC Showing the Electron Transfer Processes Involved in the Operation of the Photoelectrochemical Cell, As Described in the Text

^aIn (a), the numbers on the arrows represent the order in which the processes occur: 1 - light absorption, 2 - hole injection, 3 - electron recombination.

excitation (step 1) of the sensitizer (S), forms the excited state (S^{*}), which decays by hole injection into the valence band of the p-type semiconductor to form the charge separated state (step 2). In this case, because there is no “wiring” to take the hole or electron away from the interface, they must recombine following step 3. Scheme 1b illustrates the pathway followed by a hole in a p-DSSC photoelectrochemical cell. Upon light absorption (step 1), the sensitizer excited state (S^{*}) injects a hole into the valence band of the semiconductor, leading to the reduction of the sensitizer (S^{•-}) (step 2). The injected holes diffuse to the back side of the transparent conducting electrode, pass into the external circuit, and reach the counter electrode, where they oxidize the redox mediator (M/M^{•+}) (step 4). This mediator reacts with the reduced sensitizer to restore the ground state of the sensitizer (step 5).¹³ In a photoelectrosynthetic application, a catalyst may be linked to or otherwise associated with the sensitizer so that useful synthetic chemistry is carried out at each electrode. In this case, an alternative pathway at the photocathode is reduction of the catalyst by the sensitizer excited state, followed by hole injection into the semiconductor by the oxidized sensitizer.

In this work, we describe the synthesis and characterization of Cu₅Ta₁₁O₃₀ nanoparticles (NP-Cu₅Ta₁₁O₃₀) and their ability

to accept high-potential holes into their valence band from a photoexcited porphyrin. Such nanoparticles may be suitable candidates for construction of tandem cells. In these cells, the photocathode would take advantage of the well-known high hole mobility of the copper(I)-based semiconductors like Cu₂O¹⁴ and CuNb₃O₈,¹⁵ as compared to the significantly lower charge carrier mobility in the commonly used NiO.¹⁶ This current investigation concerns primarily the fundamental understanding of the energetics and charge injection of this new dye–semiconductor combination.

EXPERIMENTAL SECTION

Materials. Dichloromethane (anhydrous, 99.5%), anhydrous methanol (99.8%), propionic acid, 4-pyridinecarboxaldehyde, 4-bromobenzaldehyde, triethylamine, diethyl phosphite, zinc acetate dihydrate, iodomethane, bromotrimethylsilane, tetrakis(triphenylphosphine)palladium (0), and ammonium hexafluorophosphate were purchased from Sigma-Aldrich and used without further purification. Pyrrole was purchased from Sigma-Aldrich and distilled prior to use. Silica gel (SiliaFlash F60 40–63 μm) used for column chromatography was purchased from SiliCycle. Dichloromethane, hexane, ethyl acetate, methanol, acetone, tetrahydrofuran, acetonitrile, and chloroform for synthesis and column chromatography were distilled. Toluene and dimethylformamide for synthesis were dried over activated 4 Å molecular sieves. Copper sulfate (anhydrous, 99%), ascorbic acid (99.9%), tantalum pentachloride (99.9%), and copper chloride (99%) were purchased from Alfa Aesar and used without further purification.

Structural Characterization. Mass spectra were obtained with a Bruker Microflex LRF matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF), equipped with a 60 Hz laser, using α-cyano-4-hydroxycinnamic acid (αCN), sinapinic acid (SA), or (1E,3E)-1,4-diphenylbuta-1,3-diene (DPB) as a matrix. The reported mass is the most abundant isotope observed. Calculated values are listed after the experimental result for comparison. The ¹H NMR spectra were taken on a Varian spectrometer at 400 MHz. Samples were prepared using deuterated solvents and with 0.03% tetramethylsilane as an internal standard.

Synthesis of Dyes. Scheme S1 shows the synthetic strategy followed for the preparation of the porphyrin sensitizers.

5-(4-Pyridinyl)dipyrromethane (1). Compound 1 was synthesized following a published procedure.¹⁷ Portions of 4-pyridinecarboxaldehyde (2.0 g, 18.7 mmol, 1.8 mL) and pyrrole (18.8 g, 281 mmol, 20 mL) were added to a 100 mL round-bottom flask equipped with an air-cooled condenser. The mixture was purged with argon for 20 min and heated at 85 °C under argon and stirred for 24 h. The resulting dark red solution was first purified using silica gel column chromatography (hexane:ethyl acetate 1:1) and further purified by crystallization from hexane:dichloromethane (DCM). The first crop of crystals was light brown (1.0 g) and the second was brown (1.2 g), giving an overall yield of 2.2 g (1.0 mmol, 53% yield). ¹H NMR δ ppm (CDCl₃): 8.48 (d, *J* = 6.0 Hz, 2H), 8.16 (s, 2H), 7.12 (d, *J* = 6.0 Hz, 2H), 6.73 (m, 2H), 6.17 (dd, *J* = 2.9, 5.8 Hz, 2H), 5.89 (m, 2H), 5.45 (s, 1H).

5,10,15-Tris(4-pyridinyl)-20-(4-bromophenyl)-porphyrin (2). In a 250 mL round-bottom flask were placed 1 (2.0 g, 8.58 mmol), 4-pyridinecarboxaldehyde (0.46 g, 4.29 mmol), and 4-bromobenzaldehyde (0.79 g, 4.29 mmol). Propionic acid (70 mL) was added, and the flask was equipped with a condenser. The reaction was refluxed at 140 °C for 45 min and then cooled

to room temperature. The propionic acid was removed by distillation under reduced pressure, and the mixture was dissolved in DCM. The organic solution was washed with a saturated sodium bicarbonate solution ($\times 4$) to neutralize any remaining acid. The organic layer was dried over Na_2SO_4 . The solvent was removed under reduced pressure, and the mixture was purified by silica gel column chromatography (4% MeOH:DCM) to yield a purple solid (175 mg, 0.252 mmol, 5.5% yield). ^1H NMR δ ppm (CDCl_3): 8.99 (d, $J = 4.0$ Hz, 6H), 8.83 (d, $J = 4.8$ Hz, 2H), 8.77 (m, 6H), 8.08 (d, $J = 4.0$ Hz, 6H), 7.99 (d, $J = 8.2$ Hz, 2H), 7.84 (d, $J = 8.2$ Hz, 2H), -2.96 (s, 2H). MALDI-TOF: m/z obsd. 695.14 calc. for $\text{C}_{41}\text{H}_{26}\text{BrN}_7$ 695.14.

4-(10,15,20-Tris(4-pyridinyl)-porphin-5-yl)phenylphosphonic Acid Diethyl Ester (3). Compound 2 (160 mg, 0.23 mmol) was dissolved in dry toluene (100 mL), triethylamine (20 mL), and diethyl phosphite (0.65 g, 4.60 mmol, 0.6 mL). The solution was purged with argon for 20 min, and tetrakis(triphenylphosphine)palladium(0) (53 mg, 0.046 mmol) was added quickly. The reaction was stirred under argon at 80°C for 18 h. The solvent was removed by distillation under reduced pressure, and the mixture was purified using silica gel column chromatography (2% MeOH:18% acetone:DCM). Compound 3 was obtained in 23% yield (40 mg, 0.053 mmol). ^1H NMR δ ppm (CDCl_3): 9.06 (d, $J = 5.6$ Hz, 6H), 8.85 (m, 8H), 8.33 (dd, $J = 4.0, 7.9$ Hz, 2H), 8.24 (dd, $J = 7.9, 13.1$ Hz, 2H), 8.16 (d, $J = 5.6$ Hz, 6H), 4.40 (m, 4H), 1.53 (t, $J = 7.1, 7.1$ Hz, 6H) -2.89 (s, 2H). MALDI-TOF: m/z obsd. 753.27 calc. for $\text{C}_{45}\text{H}_{36}\text{N}_7\text{O}_3\text{P}$ 753.26.

Zinc 4-(10,15,20-Tris(4-pyridinyl)-porphin-5-yl)phenylphosphonic Acid Diethyl Ester (D1E). In a 100 mL round-bottom flask, compound 3 (40 mg, 0.053 mmol) and $\text{ZnOAc} \cdot 2\text{H}_2\text{O}$ (117 mg, 0.53 mmol) were dissolved in THF (20 mL) and DCM (20 mL). The round-bottom flask was equipped with a condenser, and the reaction mixture was refluxed at 60°C for 12 h. The solvent was removed by distillation under reduced pressure. The mixture was redissolved in DCM and washed with H_2O three times. The organic solution was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The mixture was purified using silica gel column chromatography (10% MeOH:DCM) to yield a purple solid (14.1 mg, 0.0173 mmol, 32% yield). ^1H NMR δ ppm (DMSO): 9.01 (d, $J = 5.6$ Hz, 6H), 8.81 (m, 8H), 8.35 (dd, $J = 3.8, 8.0$ Hz, 2H), 8.21 (d, $J = 5.6$ Hz, 6H), 8.14 (dd, $J = 8.0, 13.0$ Hz, 2H), 4.28 (m, 4H), 1.42 (t, $J = 7.1, 7.1$ Hz, 6H). MALDI-TOF: m/z obsd. 815.18 calc. for $\text{C}_{45}\text{H}_{34}\text{N}_7\text{O}_3\text{PZn}$ 815.18.

Zinc 4-(10,15,20-Tris(4-pyridinyl)-porphin-5-yl)phenylphosphonic Acid (D1). D1E (5 mg, 6.1 μmol) was dissolved in chloroform (10 mL) and triethylamine (17 μL). The solution was heated at 60°C in a flask bearing a condenser, and trimethylsilyl bromide (TMS-Br) (14.1 mg, 92.1 μmol , 12 μL) was added. The reaction mixture was refluxed for 18 h. The solvent was removed under reduced pressure, and the product was extracted using DCM: H_2O . The organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed by distillation under reduced pressure. The final product was obtained in a 100% yield (5 mg, 6.14 μmol). ^1H NMR δ ppm (DMSO): 9.14 (s, 6H), 8.90 (m, 4H), 8.87 (d, $J = 4.7$ Hz, 2H), 8.83 (d, $J = 4.7$ Hz, 2H), 8.43 (s, 6H), 8.28 (dd, $J = 3.3, 8.0$ Hz, 2H), 8.12 (dd, $J = 7.9, 12.8$ Hz, 2H). MALDI-TOF: m/z obsd. 759.15 calc. for $\text{C}_{41}\text{H}_{26}\text{N}_7\text{O}_3\text{PZn}$ 759.11.

Zinc 4-(10,15,20-Tris(4-(N-methylpyridiniumyl)-porphin-5-yl)phenylphosphonic Acid Diethyl Ester (D2E). D1E (20 mg,

0.025 mmol) was dissolved in dry dimethylformamide (DMF) (10 mL), and the solution was purged with argon for 10 min. Methyl iodide (5.2 mg, 0.037 mmol, 2.3 μL) was added, and the reaction mixture was heated at 100°C for 1 h and then cooled to room temperature and stirred for 12 h. The solvent was removed by distillation under reduced pressure, and the mixture was extracted using DCM: H_2O . The aqueous layer was removed and concentrated by distillation of the solvent under reduced pressure. Anion exchange with NH_4PF_6 yielded porphyrin with hexafluorophosphate counterions, thus, increasing the solubility of the porphyrin in organic solvents. The mixture was cooled to 0°C , and the product precipitated out of solution. The water was removed by filtration to give a purple solid (21.5 mg, 0.0349 mmol, 100%). ^1H NMR δ ppm (DMSO): 9.42 (d, $J = 6.3$ Hz, 6H), 9.04 (m, 4H), 8.98 (d, $J = 4.7$ Hz, 2H), 8.92 (m, 8H), 8.35 (dd, $J = 3.7, 7.7$ Hz, 2H), 8.18 (dd, $J = 7.8, 13.0$ Hz, 2H), 4.71 (s, 9H), 4.30 (m, 4H), 1.43 (t, $J = 7.0, 7.0$ Hz, 6H). MALDI-TOF: m/z obsd. 860.42 calc. for $\text{C}_{48}\text{H}_{43}\text{N}_7\text{O}_3\text{PZn}^{3+}$ 860.24.

4-(10,15,20-Tris(4-(N-methylpyridiniumyl)-porphin-5-yl)phenylphosphonic Acid (7). D2E (5 mg, 5.8 μmol) was dissolved in acetonitrile (10 mL) and triethylamine (0.02 mL) and heated to 65°C . TMS-Br (13.3 mg, 0.087 mmol, 15 μL) was added, and the reaction mixture was refluxed for 12 h. The reaction conditions both cleaved the phosphonate esters and removed the zinc from the macrocycle. A green solid precipitated, and the solvent was removed under reduced pressure. The solid was resuspended in H_2O and washed with DCM. The H_2O was then removed under reduced pressure to yield a green solid (5 mg, 5.8 μmol , 100%). Compound 7 was used immediately to reintroduce the zinc without further purification. MALDI-TOF: m/z obsd. 742.30 calc. for $\text{C}_{44}\text{H}_{37}\text{N}_7\text{O}_3\text{P}^{3+}$ 742.27.

Zinc 4-(10,15,20-Tris(4-(N-methylpyridiniumyl)-porphin-5-yl)phenylphosphonic Acid (D2). In a 50 mL round-bottom flask, compound 7 (5 mg, 6 μmol) was dissolved in H_2O (5 mL) and THF (10 mL). $\text{ZnOAc} \cdot 2\text{H}_2\text{O}$ (26 mg, 0.119 mmol) was added, and the flask was equipped with a condenser. The reaction was refluxed for 2 h. The solvent was removed by distillation under reduced pressure, and the mixture was crystallized in H_2O :acetone. The crystals were filtered and rinsed with cold acetone to yield a green solid (5 mg, 6 μmol , 100%). ^1H NMR δ ppm (DMSO- D_2O): 9.22 (s, 6H), 9.01 (d, $J = 19.2$ Hz, 8H), 8.80 (s, 6H), 8.20 (m, 4H), 4.65 (s, 9H). MALDI-TOF: m/z obsd. 804.34 calc. for $\text{C}_{44}\text{H}_{35}\text{N}_7\text{O}_3\text{PZn}^{3+}$ 804.18.

High-Resolution Transmission Electron Microscopy.

TEM micrographs were collected using a Philips CM200 TEM at 200 kV, Cs 1.2 mm, PTP resolution: 0.25 nm; focused probe: 0.5 nm; and imaging modes: TEM/STEM. TEM micrographs were analyzed using Digital Micrograph software.¹⁸

Dynamic Light Scattering. Dynamic light scattering (DLS) data were taken on a Malvern Zetasizer Nano S with the detector 173° from the incident beam and a laser wavelength of 633 nm. Intensity by number was used for expressing the particle size distribution of the dispersion of nanoparticles. The particle size is determined using the velocity of Brownian motion and the Stokes–Einstein equation

$$d = \frac{kT}{3\pi\eta D} \quad (1)$$

where d is the hydrodynamic diameter, k is Boltzmann's constant, T is absolute temperature, η is viscosity, and D is the

translational diffusion coefficient. These measurements were done by placing 5 mL of a dispersion of nanoparticles in ethanol into a disposable plastic cuvette with a path length of 1 cm. The refractive index of Cu_2O (2.94) was used as an approximation of the refractive index of $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, which has not been determined in the literature.¹⁹

Mott–Schottky Measurements. Electrochemical impedance spectroscopy was used to measure the flat-band potentials of nanoparticles of $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, using a frequency of 30 kHz and an ac amplitude of 5 mV. Measurements were carried out using a Parstat-2263 potentiostat from Princeton Applied Research. A three-neck flask filled with 0.5 M Na_2SO_4 solution (pH 6.5) was purged with N_2 gas 30 min prior to the experiment. A flow of N_2 gas was kept over the headspace to purge any oxygen during the experiment. A film of NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ deposited on fluorine-doped tin oxide (FTO, Pilkington TEC-15) served as the working electrode, Pt foil as a counter electrode, and a saturated calomel electrode (SCE sat. KCl) as the reference electrode. The working electrode was made by depositing an ethanol solution of the nanoparticles onto the FTO slides at 70 °C in air.

Current–Voltage Measurements (*i*–*v* Curves). $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ nanoparticle films were deposited on fluorine-doped tin oxide (FTO) slides by a drop-cast method and annealed under vacuum at 200 °C for 2 h. The films were then immersed in a 0.1 mM solution of D1 (methanol) or D2 (1% methanol in water) overnight, rinsed with ethanol, and dried in air. Pt counter electrodes were fabricated by applying a 6 mM solution of H_2PtCl_6 in ethanol to FTO on a glass substrate (1 drop/ cm^2) and heating to 350 °C in air for 30 min. The working and counter electrodes were sandwiched together with a Parafilm gasket, and the redox electrolyte (0.2 M KI and 0.02 M I_2 in ethylene glycol) was introduced by capillary diffusion. Current–voltage experiments were performed using a CH-Instruments CH620a potentiostat under simulated AM 1.5 G irradiation at 100 mW/cm^2 (Oriel) using a scan rate of 10 mV s^{-1} . Scans were started negative of the open-circuit voltage (V_{oc}) and scanned toward the short-circuit condition (I_{sc} , $V = 0$). The sensitized film served as the working electrode, and platinized FTO served as counter and reference electrodes.

Steady-State Absorption and Fluorescence. Spectra were recorded in 1 cm path length cuvettes with the following spectrophotometers: diode array HP 8452, Shimadzu - UV-IR (2041PC), and Hitachi double beam UV/vis spectrophotometer (U-2800). Steady-state fluorescence spectra were measured using a Photon Technology International MP-1 spectrometer and corrected for detection system response and excitation source intensity as a function of wavelength. Excitation was provided by a 75 W xenon-arc lamp and single-grating monochromator. Fluorescence was detected at 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.

Electrochemical and Spectroelectrochemical Experiments. The voltammetric characterization of the redox processes was performed with an Autolab potentiostat-galvanostat (Electrochemical Instruments) in a conventional three-electrode cell. Electrochemical and spectroelectrochemical studies of porphyrins were carried out in anhydrous *N,N*-dimethylformamide (DMF) deoxygenated solution (argon bubbling), with 0.10 M tetra-*n*-butylammonium perchlorate (TBAClO_4) as supporting electrolyte. For cyclic voltammetry, a Pt working electrode, a Pt counter electrode, and a silver wire

quasi-reference electrode were used, whereas, for spectroelectrochemistry, a Pt mesh was used as working electrode. Absorption spectra of the dyes in the reduced state were obtained by applying a fixed potential at the redox potential of the first cathodic wave. After each voltammetric experiment, ferrocene was added as an internal standard ($\text{Fc}/\text{Fc}^+ = 0.72$ V vs normal hydrogen electrode), and the potential axis was calibrated against the formal potential for the NHE. The Pt working electrode was cleaned between experiments by polishing with 0.3 μm alumina paste, followed by solvent rinses.

Time-Resolved Absorption. Transient absorption measurements in the femtosecond to nanosecond window were acquired with a kilohertz pulsed laser source and a pump–probe optical setup. Laser pulses of ca. 100 fs at 800 nm were generated from an amplified, mode-locked titanium sapphire kilohertz laser system (Millennia/Tsunami/Spitfire, Spectra Physics). The laser pulse was divided and a part was sent through an optical delay line and focused onto a 3 mm sapphire plate to generate a white light continuum for the probe beam. The rest of the pulse was used to pump an optical parametric amplifier to generate excitation pulses selected using a mechanical chopper. Polarization of the pump beam was set to the magic angle (54.7°) relative to the probe beam, and its intensity was adjusted using a continuously variable neutral density filter. White light generated was compressed by prism pairs (CVI) before passing through the sample. The white light probe was dispersed by a spectrograph (300 line grating) onto a charge-coupled device (CCD) camera (DU420, Andor Tech.). The final spectral resolution was about 2.3 nm for over a nearly 300 nm spectral region. Decay-associated spectra (DAS) were obtained by globally fitting the transient absorption kinetic traces over a selected wavelength region using a parallel kinetic model (eq 2)²⁰

$$\Delta A(\lambda, t) = \sum_{i=1}^n A_i(\lambda) \exp(-t/\tau_i) \quad (2)$$

where $\Delta A(\lambda, t)$ is the observed absorption 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 DAS and represents the amplitude spectrum of the i th kinetic component, which has a lifetime of τ_i .

RESULTS AND DISCUSSION

Synthesis and Characterization of NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$. Nanoparticulate (NP)- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ was prepared by a flux-mediated synthesis using Cu_2O nanoparticles, Ta_2O_5 nanoparticles, and CuCl, following procedures similar to those used for nanoparticles of the Cu(I)-niobate phases such as $\text{Cu}_2\text{Nb}_8\text{O}_{21}$.²¹ The Cu_2O and Ta_2O_5 nanoparticles were synthesized following methods reported elsewhere.^{22,23} Both Cu_2O nanoparticles (0.109 g) and Ta_2O_5 nanoparticles (0.390 g) were ground together with a mortar and pestle inside a glovebox, along with 0.250 g of CuCl as the flux.²⁴ In flux synthesis, the inorganic salt is heated to above its melting point and functions as a relatively low-temperature reaction medium for the dissolution of the reactant metal oxides and the formation of high-quality crystals of the product phase. The metal oxide nanoparticles were allowed to react within the molten CuCl flux at this temperature, yielding a better dispersion of the nanoparticles during the reaction. This mixture was placed under vacuum in a fused-silica reaction

vessel and then heated at 900 °C for 24 h. Afterward, the powder obtained, which is a mixture of bulk and NP-Cu₅Ta₁₁O₃₀, was sonicated in absolute ethanol for 30 min, and the larger particles were removed from the nanoparticle solution by centrifugation via sedimentation at 3000 rpm for 20 min. The yellow supernatant, consisting of the nanoparticles suspended in ethanol, was decanted to produce a yield on the order of ~1% in mass.

The NP-Cu₅Ta₁₁O₃₀ product was characterized by UV–vis, DLS, and HR-TEM. Figure 1 shows a representative HR-TEM

Figure 1. Representative HR-TEM of NP-Cu₅Ta₁₁O₃₀ where a quasi-spherical distribution of particles with sizes of 15 ± 5 nm can be observed. Inset: Size distribution obtained by DLS of NP-Cu₅Ta₁₁O₃₀ dispersed in an ethanol solution.

micrograph of NP-Cu₅Ta₁₁O₃₀ with a narrow size distribution (15 ± 5 nm) having quasi-spherical morphologies, as measured from 50 nanoparticles (Supporting Information, Figure S1). It is noteworthy that the NP-Cu₅Ta₁₁O₃₀ product does not exhibit crystallinity detectable by powder XRD, suggesting either very small crystalline domains or a high amount of amorphous content. Although the nanoparticles show a slight tendency for agglomeration when they are dried, they are stable and remain dispersed for months in an ethanol solution. In order to gain insight into their behavior in ethanol solution, DLS measurements were performed.^{25,26} A size distribution centered on 12 nm (Figure 1, inset) was observed. Within the experimental error, the size and distribution of NP-Cu₅Ta₁₁O₃₀ measured by DLS is in good agreement with the HR-TEM images.

The UV–vis absorption spectrum was recorded in order to compare the absorption of NP-Cu₅Ta₁₁O₃₀ to that of bulk Cu₅Ta₁₁O₃₀. Figure 2a shows the UV–vis absorption spectrum of Cu₅Ta₁₁O₃₀ at a concentration of 0.75 mg/mL in ethanol. The energy gap for NP-Cu₅Ta₁₁O₃₀ was determined using a Tauc plot, (eq 3²⁷ and inset in Figure 2a), where α is the absorption coefficient, h is Planck's constant, ν represents the frequency of incident light, k is a proportionality constant, and E_g is the energy gap.

$$(\alpha h\nu)^2 = k(h\nu - E_g) \quad (3)$$

The energy gap obtained for these NP-Cu₅Ta₁₁O₃₀ is 3.1 ± 0.2 eV, which is significantly larger than the Cu₅Ta₁₁O₃₀ bulk band gap situated at 2.6 eV.²⁸ This result suggests that, in NP-Cu₅Ta₁₁O₃₀, the Bohr radius is larger than 7.5 nm. Hence, our sample is in the quantum confinement regime and the

Figure 2. (a) Absorption spectrum of NP-Cu₅Ta₁₁O₃₀ in ethanol at a concentration of 0.75 mg/mL. Inset: Absorption onset value of the first direct allowed transition for NP-Cu₅Ta₁₁O₃₀ (red line) and 99% confident bands (blue line). (b) Mott–Schottky plot of NP-Cu₅Ta₁₁O₃₀.

potentials of the conduction and valence bands are shifted from the bulk potentials. In order to determine the new positions of the semiconductor energy levels, Mott–Schottky analyses were performed. In this case, for p-type semiconductors, the capacitance is related to the flat-band potential (V_{fb}) as given in eq 4²⁹

$$\frac{1}{c^2} = \left(\frac{2}{\epsilon \epsilon_r \epsilon_0 N_A A^2} \right) \cdot \left(-V_0 + V_{fb} - \frac{KT}{e} \right) \quad (4)$$

where c is the capacitance, e is the charge of the electron, ϵ_r is the dielectric constant of the material, ϵ_0 is the permittivity of free space, N_A is the acceptor density, A is the geometrical area of the working electrode, K is Boltzmann's constant, and T is temperature in Kelvin. Plotting the inverse square of capacitance against applied bias yields a straight line, which can be extrapolated to the x-ordinate (V_0) for use in eq 5.

$$V_0 = V_{fb} - \frac{KT}{e} \quad (5)$$

These data are plotted in Figure 2b; the negative slope indicates that the semiconductor is p-type. The value obtained for V_0 is 0.625 V, and hence, V_{fb} is 0.652 V vs SCE. Converting from SCE to NHE, the V_{fb} is 0.896 V vs NHE. The valence band energy, E_v , can be obtained from eq 6

$$E_v = V_{fb} - KT \cdot \ln \left(\frac{N_A}{N_V} \right) \quad (6)$$

where N_A and N_V are the acceptor level and the densities of states, respectively. The acceptor level, N_A , can be calculated using the second term of the Mott–Schottky equation where

Figure 3. Molecular structures of the dyes **D1** and **D2** in their acid forms. Molecular structures of dyes **D1E** and **D2E**, in their ester forms, are shown in the [Supporting Information](#).

$$\text{Slope} = \frac{-2}{eE_0\epsilon N_A A^2} \quad (7)$$

Using an N_A of $\sim 10^{16}$ and densities of states of $\sim 10^{19}$, E_v is calculated to be 1.07 V vs NHE. Thus, the valence band is ~ 200 mV more positive than the oxidation potential of water at pH of 6.5.^{15,28,29}

Synthesis of Dyes. The structures of the dyes used for these studies are shown in [Figure 3](#). They were prepared using variations of methods reported in the literature and characterized using NMR, mass spectrometry, and UV–visible spectroscopy. Details are given in the [Experimental Section](#).

Electrochemical Experiments. Cyclic voltammograms for **D1E** and **D2E** were obtained in dimethylformamide containing tetrabutylammonium perchlorate (DMF/ ClO_4TBA) as the supporting electrolyte with a Pt working electrode, a Pt counter electrode, and Ag wire as a reference electrode. Both dyes were expected to have the reduction potential of their first singlet excited state more positive than the valence band of NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$.^{30,31} [Figure 4](#) shows the CV for (a) **D1E** where a reversible porphyrin reduction is observed at -0.41 V vs NHE and (b) **D2E** having a quasi-reversible porphyrin reduction at -0.23 V vs NHE. The porphyrin reduction potential of **D2E** is less negative than that of **D1E** due to the presence of the electron-withdrawing alkylated pyridyl groups.

Based on the reduction potentials obtained for the nanoparticles and the dyes, [Figure 5](#) depicts the relative energetics of the ground and excited states of the dyes and the conduction band edge (CB) and valence band edge (VB) of NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$. The potential for the first reduction ($D/D^{\bullet-}$) of the dye was measured electrochemically, as discussed above, and the potential for the reduction of the excited state ($D^*/D^{\bullet-}$) was calculated using the zero–zero optical excitation energy estimated from the absorption spectra for porphyrin **D1** and **D2** attached to nanoparticles, where E_{00} is ~ 2.0 eV for both, within the experimental error (see [Figure S2](#)). As depicted in [Figure 5](#), the excited singlets of **D1** and **D2** are thermodynamically capable of photoinjecting a hole into the VB because the position of the VB of NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ is at less positive potentials than the porphyrin dye $D^*/D^{\bullet-}$ levels. In contrast, the conduction band potential of NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ is more negative than the oxidation potential of the excited states of the porphyrins by >1.12 V and >1.30 V for **D1** and **D2**, respectively, and thus electron injection from the excited dye into the conduction band of the semiconductor is not thermodynamically possible.

Figure 4. Cyclic voltammogram of (a) **D1E** and (b) **D2E** in DMF/ ClO_4TBA with a Pt working electrode, a Pt counter electrode, and a Ag wire as the reference electrode.

In order to study the photophysical behavior of the systems **D1**–NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and **D2**–NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, the dyes were attached to the nanoparticles as follows. The dye (**D1** or **D2** in acid form) dissolved in methanol ($[\text{dye}] \sim 10^{-3}$ M) was added dropwise into an ethanol suspension of $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ until the mixture reached an absorbance of 0.4 at 560 nm ($[\text{dye}] \sim 10^{-5}$ M). The suspension was stirred for 24 h at 40°C to reach equilibrium conditions. The system **D1E**–NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, where **D1** is in ester form, was studied as well; results obtained are similar to the **D1**–NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ (see the [Supporting Information](#)).

Absorption and Steady-State Fluorescence Experiments. UV–vis absorption spectra of **D1**, **D1**–NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, **D2**, and **D2**–NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ in ethanol were recorded ([Figure 6](#)). After the dyes were attached to the nanoparticles, a broadening and shifting to longer wavelengths of the Soret and Q-bands was observed for both dyes. This phenomenon is more significant for **D2** than **D1**. Since the

Figure 5. Diagram depicting the reduction potentials for the ground state and the lowest excited singlet states of **D1** and **D2**, the NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ conduction band energy (CB), and the NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ valence band energy (VB).

Figure 6. Absorption (solid lines) and emission (dashed lines) spectra of **D1** (panel a) and **D2** (panel b) before (red line) and after (black line) attachment to the NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ nanoparticles. Emission spectra were taken with excitation at 540 nm.

experimental conditions are the same, this may be explained by taking into account that **D2** has three positive charges on the methylpyridinium groups and it is possible that (instead of, or in addition to, attaching to the nanoparticles through the phosphonic moiety) **D2** associates with the nanoparticles in a different way. Emission spectra of **D1**, **D1**-NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, **D2**, and **D2**-NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ in ethanol were taken with excitation at 540 nm. Figure 6a,b shows a complete quenching of fluorescence for both dyes when they are attached to NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$. This fluorescence quenching is consistent with the first excited singlet state of the porphyrins being deactivated by means of electron transfer from the NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ VB to the excited dye (hole injection into the VB).

Transient Absorption Measurements. Transient absorption measurements were done in both systems to investigate the hole injection into the VB of NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ by the excited dyes and to determine the injection and recombination rates. The absorption signatures of the reduced dyes **D1** $^{\bullet-}$ and **D2** $^{\bullet-}$ were obtained by spectroelectrochemistry, as is shown in Figure 7a,c, respectively. The difference absorption spectrum for **D1** $^{\bullet-}$ shows ground-state bleaching of the Q-bands at 560 and 610 nm. There is also a broad absorption band at 620–760 nm. The difference absorption spectrum for **D2** $^{\bullet-}$ presents a well-defined ground-state bleaching of Q-bands at 560 and 610 nm and a broad band at ~620–770 nm.

The decay-associated spectra (DAS) for **D1**-NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and **D2**-NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ in ethanol solution measured by fs transient absorption after excitation at 428 nm are shown in Figure 7b,d, respectively. For **D1**-NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, global analysis of the transient absorption gives a satisfactory fit with three decay lifetimes of 0.7, 8, and 190 ps (Figure 7b). The 0.7 ps DAS shows a characteristic induced absorption at ~640–740 nm, which corresponds to the **D1** radical anion and, therefore, can be associated with the decay of the **D1** $^{\bullet-}$ -NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}(+)$ transient. The 8 ps DAS can be attributed to the formation of the **D1** $^{\bullet-}$ -NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}(+)$ state since it shows ground-state bleaching of Q-bands and stimulated emission at ~670 nm. The bleaching maxima of the Q-bands are red shifted, probably due to the attachment of **D1** to the nanoparticles. The 190 ps DAS features ground-state bleaching of the Q-band maxima that is blue shifted compared to the 0.7 ps DAS and 8 ps DAS and, therefore, can be associated with **D1** molecules that are aggregated and/or not directly attached to the nanoparticles. Because of the high heterogeneity of the system the obtained lifetimes do not correspond to single species. These lifetimes represent an average of the decay of several slightly different species. For **D1**-NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, there is likely some population with very fast formation of a charge separated state (<100 fs). This would explain the high amplitude of 0.7 ps DAS in such an inverted kinetics case, but overall, the rate of decay of the charge-separated species is greater than the average effective rate of formation.

For the system **D2**-NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$, the global analysis of the transient absorption gives a satisfactory fit with four decay lifetimes of 2.8 ps, 19.6 ps, 277 ps, and a nondecaying lifetime on a 1 ns time scale (Figure 7d). The 2.8 ps DAS does not show stimulated emission and instead shows **D2** radical-anion-induced absorption at ~580–700 nm and can, therefore, be associated with the decay of the species **D2** $^{\bullet-}$ -NP- $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}(+)$. The charge separated species is formed in <100 fs, and its rise time is too fast to observe. The other three DAS show ground-state bleaching of Q-band maxima that is blue shifted compared to the 2.8 ps DAS and which, therefore, can be attributed to **D2** that is aggregated and/or not directly attached to the semiconductor surface.

In thermodynamic terms, the more rapid hole injection observed for the **D2** system (as compared to the **D1** case) may be ascribed to the larger energetic driving force for the process, i.e., as shown in Figure 5. Alternatively, the driving force for charge recombination is greater for the **D1** system, and thus this rate constant is larger than that for the **D2** case.

DSSC Measurements. The $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ nanoparticles were deposited onto fluorine-doped tin oxide (FTO) slides. Characterization of annealed films by X-ray diffraction (XRD) indicates a phase pure material. Energy-dispersive spectroscopy

Figure 7. Difference absorption spectra (a) ($D1^* - D1$) and (c) ($D2^* - D2$) obtained by spectroelectrochemistry. Decay-associated spectra in ethanol solution measured by fs transient absorption after excitation at 428 nm for (b) $D1-NP-Cu_5Ta_{11}O_{30}$ and (d) $D2-NP-Cu_5Ta_{11}O_{30}$.

(EDS) as well as elemental mapping both confirm the presence of Cu and Ta in appropriate ratios (see the [Supporting Information](#)). Current–potential scans were performed in the dark and under AM 1.5 G irradiation at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$, starting from negative applied potentials and continuing to the I_{sc} condition. The results are shown in [Figure 8](#).

Figure 8. Linear sweep voltammograms of **D1** (black lines) and **D2** (red lines) in the dark (dotted lines) and under AM 1.5 G irradiation (solid lines) with a sweep rate of $10 \text{ mV} \cdot \text{s}^{-1}$.

In [Figure 8](#), positive current indicates hole injection into the photocathode. In the dark, both dye–nanoparticle systems show negligible current as no hole injection occurs. At suitably negative applied potentials, somewhat larger currents in the opposite direction are observed. These are likely due to reduction of the redox mediator by the semiconductor. In fact, when no dye is present, much larger currents of this type are observed and are similar under both dark and light conditions (see the [Supporting Information](#)). When light is applied to the

electrodes bearing the dye–nanoparticle composites, photo-injection of holes from the dye molecules into the nanoparticles and thence into the circuit is observed ([Figure 8](#)). As summarized in [Table 1](#), open-circuit voltages (V_{oc}) of 110

Table 1. Short-Circuit Current, Open-Circuit Voltage, Fill Factor, and Light Conversion Efficiency for **D1** and **D2**

dye	I_{sc} ($\mu\text{A}/\text{cm}^2$)	V_{oc} (mV)	ff	η (%)
D1	5.28	200	0.260	2.75×10^{-4}
D2	2.85	110	0.265	8.31×10^{-5}

and 200 mV were observed for nanoparticles bearing **D2** and **D1**, respectively. Such V_{oc} values are comparable to those observed for NiO ($\sim 100 \text{ mV}$)¹⁶ and other Cu(I)-based p-DSSCs (~ 150 – 300 mV)^{32,33} using the I^-/I_3^- redox mediator. Short-circuit currents (I_{sc}) were on the order of a few μA per cm^2 . [Table 1](#) also reports the fill factors (ff) and light conversion efficiencies (η), calculated as discussed in the [Supporting Information](#). These results indicate that the dye–nanoparticle composites are indeed capable of light-driven hole injection into an external circuit. SEM images of annealed films indicate growth of the nanoparticles to micron sizes, disrupting the homogeneity of the film; this, along with the lack of a suitable blocking layer³⁴ to slow charge recombination, leads to the low overall efficiency of the cell and differences in current densities. While efficiency in the DSSC is low, further investigations into optimization of the film preparation conditions will be necessary to increase its overall efficiency.

CONCLUSIONS

The preparation of p-type semiconductor $Cu_5Ta_{11}O_{30}$ nanoparticles (NP- $Cu_5Ta_{11}O_{30}$) with a valence band edge suitable for water oxidation has been described. Two sensitizers, zinc 4-(10,15,20-tris(4-pyridinyl)-porphin-5-yl)phenylphosphonic acid (**D1**) and its analogue, in which the pyridine groups are

methyated (D2), were shown to have excited-state reduction potentials that were thermodynamically capable of photo-injecting a hole into the VB of the NP-Cu₅Ta₁₁O₃₀. These sensitizers are not thermodynamically capable of photoinjecting electrons into the CB of the NP-Cu₅Ta₁₁O₃₀. Transient absorption measurements of the D1–NP-Cu₅Ta₁₁O₃₀ system show hole injection in 8 ps and very fast recombination in ~700 fs. The D2–NP-Cu₅Ta₁₁O₃₀ system shows very fast injection, <100 fs, and slower recombination on the 2.8 ps time scale. DSSC measurements on the NP-Cu₅Ta₁₁O₃₀ sensitized with D1 and D2 show significant photocurrent responses under simulated solar irradiance. Taken together, the thermodynamic, spectroscopic, and cathodic *i*–*v* measurements lead us to conclude that these systems function by a photoinduced hole injection mechanism. Investigating the use of NP-Cu₅Ta₁₁O₃₀ as a new p-type semiconductor with a VB more positive than the water oxidation potential and extremely negative CB (< –2.0 V vs NHE) is a step in the development of new materials for p-DSSCs, which could lead to more efficient ways to carry out solar water splitting.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b02174.

HR-TEM and SEM images, EDS and elemental mapping, XRD, DLS, UV–vis, schematic and details of dye synthesis, ¹H NMR results, absorption and transient absorption spectra, power–voltage curves and control experiments, and fill factor and efficiency calculations (PDF)

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Notes

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