Bioinspired High-Potential Porphyrin Photoanodes

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ABSTRACT: We report a selection of high-potential porphyrin photoanodes (HPPPs) for use in photocathodic electrochemical cells (PECs). The anodes consist of bispentafluorophenyl free-base and metallo-porphyrin sensitizers bearing anchoring groups for attachment to metal-oxide surfaces including TiO₂ and SnO₂ nanoparticles. The term ‘high potential’ refers to the relatively large and positive value of the electrochemical reduction potential for the bispentafluorophenyl porphyrin radical cation (P⁺ + e⁻ → P) as compared with more conventional nonfluorinated analogues. Photoelectrochemical measurements demonstrate the sensitizers used in these HPPPs extend the absorption of the bare anode well into the visible region. Terahertz spectroscopic studies show the photoexcited dyes are capable of injecting electrons into the conduction band of an underlying metal-oxide with appropriate energetics. The reduction potentials of the resulting photogenerated porphyrin radical cations are relatively high (ranging from ∼1.35 to 1.65 V vs NHE depending on the sensitizer). This is demonstrated by the ability of dye-sensitized solar cells, containing our HPPPs, to use the Br⁻/Br²⁻ redox couple as a regenerative electron mediator with superior performance in comparison to results obtained using the lower-potential I⁻/I²⁻ relay. Computational modeling of the structures and equivalent circuits assists in a molecular-based understanding of these systems. Further, the oxidation power of the porphyrin radical cations generated in these bioinspired constructs is similar to that found in the reaction centers of their natural counterpart (photosystem II); thus, HPPPs are promising as components in artificial systems for photochemical water spitting applications.

INTRODUCTION

The development of cost-effective alternative energy sources to meet global human energy demands (∼16 TW) in an environmentally and socially responsible manner is critical to mitigating anthropogenic climate change and achieving energy security.1–3 Of the available carbon-neutral energy sources, solar energy is abundant (striking the Earth’s surface at a rate of ∼120 000 TW), yet diffuse (∼100 mW/cm²) and intermittent.4,5 Thus, devising low-cost methods for its capture, conversion, and storage is among the grand challenges of science.6,7 Biological photosynthetic energy conversion offers many useful clues8–10 that have prompted advances in the field of artificial photosynthesis.8,11–18 In addition, sensitization of metal-oxide wide band gap semiconductor surfaces with inorganic transition-metal complexes or organic dyes has been actively pursued in developing methods for converting solar energy to electricity by dye-sensitized solar cells (DSSCs).19–26 Such approaches typically rely on the use of relatively low potential regenerative mediators, (the I⁻/I²⁻ redox couple occurs at ∼ +0.53 V vs NHE)30 and in most cases do not adequately address the energetic requirements of water oxidation.

The first photoassisted water oxidation by Fujishima and Honda31 produced hydrogen and oxygen from UV irradiation of n-type TiO₂. However, low quantum yields and limited use of the available solar energy spectrum are features not suitable for large-scale deployment. Examples of photoassisted and photoinduced water splitting have been reported using visible and visible coupled with ultraviolet light, respectively.32–34 These systems incorporate a hybrid Ru–polypyridyl dye-sensitized Fujishima–Honda cell interfaced with a water-oxidation catalyst. In general, slow electron-transfer kinetics between the catalyst and photooxidized sensitizer, as well as fast back electron transfer from TiO₂, limit the quantum and energy storage efficiencies of these cells, detracting from their practicality. However, an increase of the driving force for electron transfer between the catalyst and photooxidized sensitizer might mitigate these overall unfavorable electron-transfer kinetics.35

In biological photosynthesis, the evolution of what became the water-oxidizing enzyme photosystem II (PSII) most likely...
occurred via intermediate stages. Early forms presumably operated on substrates that are easier to oxidize, and later forms, having more oxidizing reaction centers, became capable of water oxidation. Similar strategies may prove useful in developing artificial photosynthetic systems, most notably the development of light absorbers with potentials suitable for efficient water-oxidation chemistry. Porphyrins are a promising class of compounds in this regard as their electronic and optical properties are readily controlled via synthetic manipulation. This class of compounds has also shown recent promise as sensitizers in solar-to-electric application.

We have previously reported a co-deposited TiO2 photoanode for visible light splitting that utilizes a zinc porphyrin and an iridium water-oxidation catalyst. Here, we report the optical and electronic properties for a selection of anodes sensitized with electron-deficient chromophores including the free base (1), zinc (2), and palladium (3) derivatives of a bispentafluorophenyl porphyrin bearing a carboxylate group for functionalization of metal-oxide surfaces including TiO2 and SnO2 nanoparticles (Chart 1). Investigation of these constructs via terahertz spectroscopy and photoelectrochemical measurements demonstrates the need for appropriately balancing the electronic and optical properties of the high potential dye and metal oxide.

In this report, we aim to exploit the relative ease of assembly and testing of DSSCs as a platform for evaluating the energetics of dye/metal oxide interfaces, while screening for systems capable of oxidizing relatively high-potential sources of electrons and are, thus, promising candidates for developing water-oxidizing photoanodes. The Br3−/Br− relay is ~500 mV more positive than the I3−/I− couple, thus, most sensitizers are insufficiently oxidizing to accept electrons from Br−. Likewise, PECs that benefit from an increase in open-circuit voltage (VOC) upon replacement of I3−/I− by Br3−/Br− are typically offset by a decrease in the short-circuit current (JSC).

**EXPERIMENTAL SECTION**

**Sample Preparation and Characterization.** All compounds were synthesized from commercially available starting materials (see Supporting Information, Synthesis and Structural Characterization). All chemicals were purchased from Aldrich or Alfa Aesar. Solvents were obtained from Aldrich or Mallinckrodt. Dichloromethane was purified with a solvent purification system (Innovative Technologies, Inc.) using a 1 m column containing activated alumina. All solvents were stored over the appropriate molecular sieves prior to use. Thin-layer chromatography (TLC) was performed with silica gel coated glass plates from EMD Chemicals. Column chromatography was carried out using silica gel 60, 230–400 mesh from EMD Chemicals. NMR spectra were recorded on Bruker spectrometers operating at 400 or 500 MHz. NMR samples were prepared in deuteriochloroform or 1% deuteriopyridine in deuterochloroform with tetramethylsilane as an internal reference for 1H NMR and trichlorofluoromethane as an external reference for 19F NMR. Mass spectra were obtained with a matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrometer. Steady-state absorbance spectra were measured on a Varian Cary 300 UV–visible spectrophotometer. Films of TiO2 and SnO2 nanoparticles were highly scattering so spectra were obtained in diffuse reflectance geometry using an integrating sphere. Steady-state fluorescence spectra were measured using a Shimadzu RF-5301PC spectrometer.

**Solar Cell Fabrication and Characterization.** DSSCs were prepared in a manner similar to that reported previously. Commercially available P25 TiO2 and SnO2 nanoparticles were used as received from Degussa (now Evonik) and Alfa Aesar, respectively. Fluorine-doped tin oxide (FTO) conductive glasses (Tec 8, visible light transmittance 77%, Hartford Inc., USA) were rinsed with ethanol before use. Pastes composed of 1.0 g of TiO2 or 1.1 g of SnO2 in 2 mL of Milli-Q water were stirred overnight to obtain a homogeneous dispersion and then coated by the doctor-blade method onto the FTO glasses with an area of 0.15 cm2 and thickness ~10 μm. The electrodes were dried at room temperature and sintered in air at 450 °C for 2 h with a ramp rate of 5 °C/min. The TiO2 and SnO2 electrodes were sensitized by soaking in a 0.3 mM solution of N719 dye in ethanol or 0.1 mM solution of porphyrin compounds 1–3 in 10% ethanol in dichloromethane overnight at room temperature. Following sensitization, the photoanodes were rinsed with 10% ethanol in dichloromethane solution and dried at room temperature.

Counter electrodes were prepared by coating an FTO glass slide with two drops of 0.01 M hexachloroplatinic acid (H2PtCl6) in ethanol and heating at 400 °C for 15 min. An electrolyte (A) consists of 0.6 M tert-butylammonium iodide, 0.05 M iodine, 0.1 M lithium iodide, and 0.5 M tert-butyl pyridine in a 50/50 (v/v) mixture of valeronitrile and acetonitrile. An electrolyte (B) is 0.6 M tert-butylammonium bromide, 0.05 M bromine, 0.1 M lithium bromide, and 0.5 M tert-butyl pyridine in a 50/50 (v/v) mixture of valeronitrile and acetonitrile. To assemble a DSSC, a dye-sensitized TiO2 or SnO2 photoanode and a counter electrode were sealed to make a sandwich-type cell by heating with 60 μm thick Thermoplast hot-melt sealing material (SX1170-60, Solaronix SA, Switzerland) as a spacer between the electrodes. The electrolyte solution was injected into the cell through one of two predrilled holes in the counter electrode, and then the holes were sealed with a piece of the Thermoplast material covered by a piece of aluminum foil. The DSSCs were kept at room temperature for 2 h before photocurrent–voltage (I–V) and incident photon-to-current efficiency (IPCE) measurements. The irradiation source for the I–V measurement was a 300 W ozone-free xenon lamp equipped...
with a 50% IR blocking filter (Newport, USA) to simulate solar light. The light intensity was 100 mW/cm². The current–voltage curves were obtained by measuring the photocurrent of the cells using a Keithley model 2400 digital source meter under an applied external potential scan. Measurement of the IPCE of all cells was performed using a PV Measurements Inc. Solar Cell Spectral Response Measurement System Model QEXY utilizing monochromatic light from a xenon arc lamp filtered by a dual-grating monochromator and individual filters to test the device. Calibration of the instrument was performed prior to use by using a silicon photodiode for the whole calibration range, between 300 and 1000 nm. Due to the relatively slow response times of dye-sensitized solar cells, calibration of the instrument and all subsequent measurements were performed with a chopping speed of 5 Hz.

Reflectance Measurements. UV–visible spectra were taken on a Varian Cary 3 spectrophotometer with an integrating sphere attachment. Thin films of different TiO₂ or SnO₂ samples were prepared by the doctor-blade method on microscope slides and subjected to thermal treatment at 450 °C for 2 h with a ramp rate of 5 °C/min. The thin films were then sensitized with N719 dye or porphyrin dyes by soaking in an ethanol solution overnight and dried at room temperature before collecting spectra. The same sensitized films were also used in terahertz studies.

Electrochemical Measurements. Cyclic voltammetry was performed with an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat using a glassy carbon (3 mm diameter) or platinum disk (1.6 mm diameter) working electrode, a platinum counter electrode, and a silver wire pseudoreference electrode in a conventional three-electrode cell. Anhydrous dichloromethane was used as the solvent for electrochemical measurements. The supporting electrolyte was tetrabutylammonium hexafluorophosphate in dichloromethane, and the solution was deoxygenated by bubbling with nitrogen. The working electrode was cleaned between experiments by polishing with an alumina slurry, followed by solvent rinses. The concentration of the electroactive compound was ∼3 × 10⁻³ M. The potential of the pseudoreference electrode was determined using the ferrocenium/ferrocene redox couple as an internal standard (with E1/2 taken as 0.690 V vs NHE in dichloromethane). The voltammograms were recorded at a 100 mV s⁻¹ scan rate. All potentials listed in this manuscript are referenced to the normal hydrogen electrode (NHE).

Time-Resolved Terahertz Spectroscopy Measurements. An amplified Ti:sapphire laser (Tsunami/Spitfire from Spectra Physics) generated 800 mW of pulsed near-IR light at a 1 kHz repetition rate. The pulse width was 100 fs, and the center wavelength was 800 nm. Roughly two-thirds of the power was frequency doubled and then filtered to produce 40 mW of 400 nm (3.10 eV) light for the pump beam. The remainder of the near-IR light was used to generate and detect terahertz radiation. Terahertz radiation was generated using optical rectification in a ZnTe(110) crystal and detected using free space electro-optic sampling in a second ZnTe(110) crystal. Terahertz data were taken at room temperature, and the average of two samples was taken for each data set. To analyze electron injection dynamics, the change in terahertz transmission was monitored as the time delay between the 400 nm pump pulse and the terahertz probe pulse was varied. Further information on the spectrometer and techniques can be found in the literature.⁴⁶–⁴⁸

Computational Structural Modeling. Binding of Br⁻ and I⁻ anions to bispentafuorophenyl free-base and metallo-porphyrin sensitizers, bearing linkers for attachment to metal-oxide surfaces, has been analyzed for minimum energy configurations obtained at the B3LYP/6-31G(d,p) level for H, C, O, N, F, Br, and LanL2DZ for Zn, Pd, and I. All calculations done were done in solvent (dichloromethane), using the PCM solvent model as implemented in the program Gaussian 09.⁵⁹ The electrostatic potential for sensitizers 1–3 was computed using the Merz–Singh–Kollman scheme.⁶⁰,⁶¹

Modeling Current–Voltage Characteristic Curves. Scheme 1 shows a schematic energy level diagram for the

![Scheme 1](image)

**Scheme 1. Charge Transfer Kinetics Diagram (Top) and Equivalent Circuit (Bottom) Used to Model the Solar Cell Current–Voltage Characteristics (M = Ti, Sn; X = Br, I)⁶²⁶⁶³**

"The dominant mechanisms are shown including the current density J_L induced upon photoexcitation and electron injection into the conduction band of the semiconductor surface (green), recombination processes that behave as a diode (red) and a resistor (blue) in series with the current source, and a series resistance R_S that takes into account the resistances of the photoanode and electrolyte in solution. kinetic of interfacial electron transfer induced by illumination of the photoanode and competing back transfer mechanisms as well as an equivalent circuit used to model the photocurrent–voltage characteristics of the photoelectrochemical cells under DC conditions.⁵²,⁵³ The output current density as a function of applied bias voltage V was computed as follows

\[
J = J_L - J_D - J_{SH}
\]

\[
J = J_L - J_D \left\{ \exp \left( \frac{q(V + JAR_S)}{f kT} \right) - 1 \right\} - \frac{V + JAR_S}{AR_{SH}}
\]

where J_L is the illumination current density induced upon photoexcitation and interfacial electron injection into the conduction band of the semiconductor surface; J_{SH} and R_{SH} are the shunt current density and resistance due to surface leakage caused by the direct recombination of the photoinjected carrier with redox species in the electrolyte solution and the dark current along the edges of the cell; and J_D = J_D\{q(V + JAR_S)/(kT) - 1\} is the current

dx.doi.org/10.1021/jp210096m J. Phys. Chem. C 2012, 116, 4892–4902
density of the interfacial diode junction leading to recombination into the photooxidized dye. The latter contribution to the current density is modeled by the Shockley ideal diode equation for the net current flowing through the diode where \( J_0 \) is the saturation current which is the diode leakage current density in the absence of light; \( k \) is the Boltzmann’s constant; \( T \) is the absolute temperature with \( kT/q = 0.0259 \) V; \( A \) is the device area; \( f \) is the ideality factor; and \( R_S \) is the cell series resistance including the bulk resistivity of the semiconductor and the resistance of the electrolyte. Equation 2 gives an estimate of the open circuit voltage of the cell with high shunt resistance

\[
V_{OC} \approx \frac{f kT}{q} \ln \left( \frac{J_L}{J_0} + 1 \right)
\]

(2)

The sets of parameters that reproduce the experimental photocurrent–voltage characteristics via eq 1 for all devices studied are reported in Table 1.

### RESULTS

**Steady-State Optical Studies.** To estimate the \( E^{0 \rightarrow 0} \) transition energy of compounds 1–3, we measured the steady-state absorption and emission spectra of methyl esters of these compounds (Figure 1). In dichloromethane, the absorption spectrum of the free base exhibits visible absorption peaks (Q bands) at 510, 543, 587, and 641 nm. In addition, an intense Soret band is present at 416 nm (see Supporting Information, Figures S1 and S2). Consistent with the rigid ring structure of the porphyrin, the emission spectrum of methyl ester of the free base (1) reveals a modest Stokes shift of 5 nm, with the shortest wavelength emission band at 646 nm. The intersection of the normalized absorption and emission spectra yields an estimated \( E^{0 \rightarrow 0} \) transition energy of \( \sim 1.93 \) eV (see Supporting Information, Figure S3). In comparison, the longest-wavelength absorption and shortest-wavelength emission bands of the methyl ester of the zinc species (2) (\( \lambda_{\text{max}} = 578 \) and 590 nm, respectively) are of significantly higher energy relative to the associated free base analogue, yielding an estimated \( E^{0 \rightarrow 0} \) transition energy of \( \sim 2.12 \) eV. For the methyl ester of the palladium species (3), the longest-wavelength absorption and shortest-wavelength emission bands are further blue-shifted (\( \lambda_{\text{max}} = 554 \) and 560 nm, respectively) in comparison with the related zinc analogue, yielding an estimated \( E^{0 \rightarrow 0} \) transition energy of \( \sim 2.12 \) eV.

![Figure 1. Absorption (solid lines) and emission (dashed lines) spectra of the methyl esters of (a) 1, (b) 2, and (c) 3 in dichloromethane.](image)

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<th>dye</th>
<th>oxide</th>
<th>electrolyte</th>
<th>( J_L ) (mA/cm(^2))</th>
<th>( J_0 ) (mA/cm(^2))</th>
<th>( R_S ) (( \Omega ))</th>
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*Table 1. Performance of Solar Cells Based on 1, 2, 3, and N719 with Either I\(_3^-\)/I\(^+\) or Br\(_3^-\)/Br\(^+\) Redox Couples As Regenerative Electron Mediators and TiO\(_2\) or SnO\(_2\) Nanocrystalline Substrates Modeled by the Equivalent Circuit Shown in Scheme 1a*
estimated $E^{0-0}$ transition energy of $\sim 2.23$ eV. Although films of P25 TiO$_2$ nanoparticles sensitized with compounds 1–3 were highly scattering, spectra obtained in diffuse-reflectance geometry with an integrating sphere give the spectral profile of the sensitizing dye (see Supporting Information, Figure S4).

**Electrochemical Studies.** The 10,20-bis(pentafluorophenyl) groups have a strong influence on the electrochemical properties of the porphyrin ring system as the electron-withdrawing nature of these functional groups destabilizes the formation of the radical-cation species. For the methyl ester derivative of the free base (1) in dichloromethane, two quasi-reversible one-electron redox processes are observed with midpoint potentials ($E_{1/2}$) of 1.57 and 1.78 V vs NHE (Figure 2).

Figure 2. Cyclic voltammograms recorded at a glassy carbon electrode for the methyl-ester derivatives of (a) 1, (b) 2, and (c) 3 in dichloromethane.

These redox processes are significantly shifted in the anodic direction compared to the nonfluorinated analogue, 5,15-bis(4-carbomethoxyphenyl)-10,20-bis(2,4,5-trimethylphenyl)porphyrin, where the porphyrin radical cation/porphyrin redox couple occurs with an $E_{1/2}$ of 1.29 V vs NHE. For the methyl ester of the zinc species (2), the first and second oxidations of the porphyrin occur with an $E_{1/2}$ of 1.35 and 1.59 V vs NHE, respectively, and are, thus, cathodically shifted versus the free base analogue. The electrochemical behavior of the methyl ester of the palladium species (3) differs from the zinc species. In this compound, the first oxidation is anodically shifted in comparison with the free base to an $E_{1/2}$ of 1.65 V vs NHE, but the second oxidation is obscured by limitations of the electrochemical window.

In accordance with the Rhem Weller approximation, excited-state redox potentials for compounds 1–3 were estimated from the corresponding ground-state potentials and $E^{0-0}$ transition energies as expressed in eq 3:

$$E^o(\text{P}^+/\text{P}) \approx E^o(\text{P}^*+/\text{P}) - \frac{E^{0-0}(\text{P} \rightarrow \text{1P})}{e}$$

(3)

where $E^o(\text{P}^*/\text{P})$ is the excited-state potential for the porphyrin-radical cation/excited-singlet state porphyrin couple; $E^o(\text{P}^*/\text{P})$ is the ground-state potential for the porphyrin-radical cation/porphyrin couple, $E^{0-0}(\text{P} \rightarrow \text{1P})$ is the estimated $E^{0-0}$ porphyrin ground state to porphyrin excited-singlet state transition energy, and $e$ is the elementary charge of an electron. The values of these excited-state potentials are pertinent, as they determine the thermodynamic feasibility of photoinduced electron transfer to the bound metal oxide, as expressed in eq 4:

$$\Delta G^o_{\text{ET}} = eE^o(\text{P}^*/\text{P}) - eE^o_{\text{CB}}$$

(4)

where $\Delta G^o_{\text{ET}}$ is the free energy of excited-state electron transfer and $E^o_{\text{CB}}$ denotes the metal-oxide conduction-band potential. Conversely, ground-state potentials allow for an estimation of the potential photogenerated at the anode surface, which in turn determines the driving force for hole transfer to a given electron donor, in this study I$^-$/Br$_3^-$, as expressed in eq 5:

$$\Delta G^o_{\text{HT}} = eE^o(\text{X}_2^+/\text{X}^-) - eE^o(\text{1P}^*/\text{P})$$

(5)

where $\Delta G^o_{\text{HT}}$ is the free energy of ground-state hole transfer, and $E^o(\text{X}_2^+/\text{X}^-)$ denotes the potential for the one electron dihalide radical anion/halide couple. Ultimately, the ground and excited state potentials are pinned together by the $E^{0-0}$ transition energy of the material (Scheme 2). In a photoelectrochemical cell, a fraction of this energy can be converted to electrical potential, where the maximum obtainable $V_{OC}$ depends on the quasi-Fermi level of the metal oxide conduction band and the redox potential of the solution. To facilitate comparison, estimated potentials, taken from the literature, for the TiO$_2$, SnO$_2$, and I$_3^-$/$I^-$ and Br$_5^-$/Br$_3^-$/Br$_4^-$/redox couples, are included in Scheme 2 along with the estimated ground state and excited state potentials for compounds 1–3. The precise values of these potentials are sensitive to the specific sensitizer and electrolyte conditions used. Likewise, experimental values obtained in the absence of some components of an operational cell may not reflect actual values. Because the Fermi level depends on the electron concentration in the metal oxide, changes in $V_{OC}$ can be related to recombination processes as expressed in eq 6:

$$V_{OC} = \frac{kT}{e} \ln \left( \frac{J_{\text{inj}}}{k_{\text{rec}}n_c \mu \left[ I_{3^-} \right]} \right)$$

(6)

where $J_{\text{inj}}$ is the flux of injected electrons; $k_{\text{rec}}$ is the rate constant for $I_{3^-}$ reduction; and $n_c$, $\mu$ is the conduction band electron density in the dark.

**Time-Resolved Terahertz Studies.** Interfacial electron transfer dynamics of functionalized metal-oxide nanoparticle thin films were studied, with subpicosecond temporal resolution, using time-resolved terahertz spectroscopy. In these experiments, terahertz radiation is absorbed by mobile electrons in the metal-oxide conduction band, and the change in terahertz amplitude is a product of the carrier density and mobility. Photoexcitation and subsequent electron injection...
result in an increase of the metal-oxide free-carrier population, decreasing the terahertz transmission amplitude. Thus, such measurements allow for a direct comparison of the time scale and efficiency of photoinduced charge injection and recombination or trapping.

Results obtained for the 400 nm optical pump/terahertz probe of TiO$_2$ and SnO$_2$ nanoparticle thin films, including bare films and films functionalized with compounds 1–3 and N719, are illustrated in Figure 3. Indeed, there is a negligible change in the terahertz transmittance of the bare TiO$_2$ and SnO$_2$ samples, consistent with the negligible absorbance at 400 nm for these metal oxides. Results, obtained using N719 as the sensitizing dye, indicate effective photoinduced charge injection on both TiO$_2$ and SnO$_2$ films. By contrast, only the zinc derivative (2) of compounds 1–3 gives rise to any significant terahertz absorption on both TiO$_2$ and SnO$_2$ films. For the more highly oxidizing free base and palladium derivatives, only the SnO$_2$ films give rise to effective charge injection. These results are consistent with the excited-state potentials listed in Scheme 2 and the more positive potential of the SnO$_2$ conduction band in comparison with TiO$_2$.

Although the excited-state potential of the Pd derivative (3) is estimated to be slightly negative of the TiO$_2$ conduction band, no appreciable change in terahertz amplitude is detected in these systems, suggesting that deactivation pathways other than interfacial charge transfer dominate. For Pd porphyrins, rapid intersystem crossing (ISC) to the triplet state due to increased spin orbit coupling induced by the heavy atom effect of palladium may be involved. The potential of the triplet state is most likely poised positive of the TiO$_2$ conduction band. However, no attempts were made in this study to elucidate the mechanism of possible competing deactivation pathways.

Also evident in Figure 3 are the differing time scales of electron injection for all of the sensitizing dyes attached to SnO$_2$ versus TiO$_2$. These distinctions have been reported in the literature for Ru polypyridyl sensitizing dyes, and our observations are consistent with those studies. 62–65 For TiO$_2$, electron injection is completed within the instrument response-limited time of approximately 300 fs after photoexcitation for all of the dyes studied. Injection into SnO$_2$ is slower and is biphasic with an injection component which is completed within the instrument response-limited time and a slower component which continues for 10–80 ps.

**Photocurrent–Voltage Characteristics of Nanocrystalline Photoelectrochemical Cells.** DSSC photoanodes composed of either TiO$_2$ or SnO$_2$ nanoparticles sensitized with compounds 1–3, as well as N719, were prepared using the I$_{2}/$I$^{-}$/Br$_3$/Br$^{-}$ couple as a regenerative electron mediator and a Pt counter electrode as the cathode (see Experimental Section for details). In these constructs, the maximum obtainable $V_{OC}$ depends on the quasi-Fermi level of the metal oxide conduction band and the redox potential of the solution. To allow for a fairer comparison of performance between cells made with TiO$_2$ versus SnO$_2$, no attempts were made to improve the overall cell efficiency by adopting techniques such as surface treatment of TiO$_2$ films with TiCl$_4$. For DSSCs, the overall energy conversion efficiency ($\eta$), is a product of the short-circuit current density ($J_{SC}$), the open-circuit voltage ($V_{OC}$), and the fill factor (FF) according to eq 7

$$\eta = \frac{\text{power out}}{\text{power in}} = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}}$$

where $P_{in}$ is the total solar incident on the cell (100 mW/cm$^2$ for AM 1.5). The measured photovoltaic parameters are summarized in Table 2.
Table 2. Photovoltaic Parameters, Including the Open Circuit Voltage $V_{OC}$, Short-Circuit Current Density $J_{SC}$, Fill Factor FF, and Efficiency $\eta$ Measured at 100 mW/cm$^2$ Illumination

<table>
<thead>
<tr>
<th>dye</th>
<th>oxide</th>
<th>electrolyte</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>0.14</td>
<td>0.37</td>
<td>0.31</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>0.13</td>
<td>0.62</td>
<td>0.26</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>SnO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>1.01</td>
<td>0.31</td>
<td>0.32</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>2.53</td>
<td>0.64</td>
<td>0.47</td>
<td>0.76</td>
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<tr>
<td>2</td>
<td>TiO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>0.90</td>
<td>0.55</td>
<td>0.51</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>0.21</td>
<td>0.69</td>
<td>0.42</td>
<td>0.06</td>
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<tr>
<td></td>
<td>SnO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>2.51</td>
<td>0.37</td>
<td>0.41</td>
<td>0.39</td>
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<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>1.32</td>
<td>0.59</td>
<td>0.51</td>
<td>0.40</td>
</tr>
<tr>
<td>3</td>
<td>TiO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>0.25</td>
<td>0.37</td>
<td>0.26</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>0.16</td>
<td>0.62</td>
<td>0.3</td>
<td>0.03</td>
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<tr>
<td></td>
<td>SnO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>0.81</td>
<td>0.31</td>
<td>0.37</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>3.37</td>
<td>0.66</td>
<td>0.45</td>
<td>1.00</td>
</tr>
<tr>
<td>N719</td>
<td>TiO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>9.59</td>
<td>0.77</td>
<td>0.61</td>
<td>4.48</td>
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<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>0.15</td>
<td>0.67</td>
<td>0.45</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>SnO$_2$</td>
<td>A (I$_3^−$/I$^−$)</td>
<td>10.33</td>
<td>0.46</td>
<td>0.38</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B (Br$_3^−$/Br$^−$)</td>
<td>0.04</td>
<td>0.08</td>
<td>0.71</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**TiO$_2$ Anodes Using the I$_3^−$/I$^−$ Mediator.** For anodes composed of TiO$_2$ using the I$_3^−$/I$^−$ mediator—conditions employed in a typical Grätzel-type DSSC—only a negligible photocurrent is obtained with compounds 1 and 3 as sensitizer (Figure 4(a) and Table 2). These results, obtained in complete photoelectrochemical cells, are consistent with terahertz data performed on isolated dye-sensitized thin films. Thus, such poor performance is most likely due to unfavorable energetic positioning of the excited state of these relatively highly oxidizing dyes in comparison with the more negative conduction band of TiO$_2$ versus SnO$_2$ (Scheme 2). For similar cells, sensitized with compound 2, a modest photocurrent (0.9 mA/cm$^2$) is obtained at short circuit, consistent with the conclusion that the excited state relay of 2 is poised negative of the TiO$_2$ conduction band. For comparison, results obtained using a similar cell configuration but with TiO$_2$, I$_3^−$/I$^−$, and N719 are illustrated in Figure 5(a) and Table 2. It is clear that cells with N719 are far superior in overall performance versus cells employing porphyrin dyes (1–3) studied here on TiO$_2$ with I$_3^−$/I$^−$ (Table 2).

**Figure 4.** (a) Photocurrent—voltage characteristics of TiO$_2$ nanocrystalline photoelectrochemical cells sensitized with (a) 1, (b) 2, and (c) 3 using either the I$_3^−$/I$^−$ (solid lines) or Br$_3^−$/Br$^−$ (dashed lines) redox couple as a regenerative electron mediator. (b) Photocurrent—voltage characteristics of SnO$_2$ nanocrystalline photoelectrochemical cells sensitized with (a) 1, (b) 2, and (c) 3 using either the I$_3^−$/I$^−$ (solid lines) or Br$_3^−$/Br$^−$ (dashed lines) redox couple as a regenerative electron mediator.
diminished upon replacing the $I_3^-/I^-$ mediator with $Br_3^-/Br^-$ (a 99% decrease in $\eta$), reflecting the inability of this dye (N719) to effectively utilize the higher-potential $Br_3^-/Br^-$ couple.

_SnO$_2$ Anodes Using the $I_3^-/I^-$ Mediator._ Moving from TiO$_2$ to the more positively poised SnO$_2$ has a significant effect on cell performance with sensitizers 1–3. This change results in a 400%, 56%, and 350% increase in $\eta$, respectively, in comparison with the $I_3^-/I^-$ mediator and TiO$_2$ as the metal oxide (Figure 4(b) and Table 2). Although all the porphyrin-based anodes show an increase in $J_{SC}$ upon replacing Sn for Ti with $I_3^-/I^-$ as the redox mediator, the $V_{OC}$ is limited by the positive energetic displacement of the SnO$_2$ conduction band with respect to TiO$_2$. These are, however, the same energetic conditions which favor initial photoinduced charge separation in these HPPPs. By comparison, cells with N719 show a $V_{OC}$ comparable to those obtained in the porphyrin systems under similar conditions (Figure 5(b) and Table 2). However, for cells sensitized with N719, the overall energy conversion efficiency is decreased upon replacing TiO$_2$ with SnO$_2$ as semiconductor. We see a 59% decrease in $\eta$ in comparison with the $I_3^-/I^-$ mediator and TiO$_2$ as the metal oxide. This decrease in $\eta$ is due to the decreased $V_{OC}$ and the relatively poor fill factor (FF) associated with SnO$_2$. This represents a 40% and 38% decrease in $V_{OC}$ and FF, respectively, in comparison with measurements obtained using the $I_3^-/I^-$ mediator and TiO$_2$ as the metal oxide.

_SnO$_2$ Anodes Using the $Br_3^-/Br^-$ Mediator._ The overall lower $V_{OC}$ obtained with SnO$_2$ versus TiO$_2$ could be improved if the photooxidized dye was capable of efficiently turning over a higher-potential redox mediator such as the $Br_3^-/Br^-$ couple. This is indeed the case for cells using compounds 1 and 3 as sensitizer where there is an overall increase in both $V_{OC}$ and $J_{SC}$ resulting in a 660% and 1011% increase in $\eta$, respectively, in comparison with the measurements obtained with $I_3^-/I^-$ and SnO$_2$ (Figure 4(b) and Table 2). For the lower-potential species 2, the increase in $V_{OC}$ obtained with $Br_3^-/Br^-$ comes at the expense of a decrease of $J_{SC}$ resulting in a 3% increase in $\eta$ compared with using $I_3^-/I^-$ as mediator and SnO$_2$ as the metal oxide. For cells sensitized with N719, the inability of this dye to effectively utilize the higher-potential $Br_3^-/Br^-$ couple as redox mediator results in zero photocurrent under these cell conditions (Figure 5(b) and Table 2). Thus, the high-potential dyes 1 and 3 are most efficient under the same conditions in which the lower-potential N719 is most inefficient, i.e., with SnO$_2$ as the metal oxide and $Br_3^-/Br^-$ as the mediator. Conversely, the high-potential dyes 1 and 3 are most inefficient under the same conditions in which the lower-potential N719 is most efficient, i.e., with TiO$_2$ as the metal oxide and $I_3^-/I^-$ as the mediator. These results illustrate the critical interplay between the various components of these molecular photoelectrochemical devices and the need to appropriately balance their electronic and optical properties upon displacing the energetics of the overall system to more oxidizing conditions.

**Photocurrent Action Spectra Obtained with Nano-crystalline Photoelectrochemical Cells.** For DSSCs, external quantum efficiency of a given system is typically reported in terms of incident photon to current efficiency (IPCE). As expressed in eq 8

$$\text{IPCE} = \text{LHE} \times \Phi_{\text{inj}} \times \eta_C$$

IPCE is the product of the light harvesting efficiency (LHE) of the dye at a given wavelength, the electron injection efficiency ($\Phi_{\text{inj}}$), and the charge collection efficiency ($\eta_C$). Thus, IPCE action spectra offer insight into the efficiency of photoelectric conversion as a function of excitation wavelength. Likewise, the IPCE should reflect the spectral profile of the sensitizing dye (Figure 6). However, the immobilized species are red-shifted in comparison with solution absorption measurements of the model methyl ester compounds, indicating a coupling of the transition moments of the dyes with the surface.

**Analysis of Current Voltage Curves.** The performance of solar cells based on sensitizers 1, 2, 3, and N719, using either $I_3^-/I^-$ or $Br_3^-/Br^-$ redox couples as regenerative electron mediators and TiO$_2$ or SnO$_2$ nanocrystalline substrates, is reported in Tables 1 and 2. These results show an increase in the series resistance by a factor of between 1 and 4 when the TiO$_2$ photoanode is replaced by SnO$_2$ for a given dye and electrolyte reflecting a higher conductivity in the TiO$_2$ photoanodes. $R_s$ increases by a factor of between 4 and 17 for bromide relative to iodide for dyes 1–3, consistent with higher conductivities reported for iodide over bromide at low concentrations. A more significant impact of the substitution of $I^-$ by $Br^-$ on the current–voltage characteristics for solar cells based on sensitizers 1–3 is the systematic reduction of the saturation recombination current $J_0$ and increase in the open circuit voltage $V_{OC}$. This trend can be understood based on electrostatic potential calculations that show tighter binding of bromide to the porphyrins.

The computed electrostatic potential (see Supporting Information) shows evidence of stabilization of the $Br^-$ redox species by polarization and electrostatic contributions, including interaction of the anions with the permanent quadrupole moments of the aromatic rings.$^{66,67}$ With its
smaller ionic radius (Br\(^-\): 1.82 Å, I\(^-\): 2.06 Å), Br\(^-\) interacts more strongly and binds more closely to the aromatic rings than I\(^-\) by anion-\(\pi\) stabilization. Up to four Br\(^-\) anions per porphyrin are predicted to bind to 1 and 3 with a stabilization energy between \(-5\) and \(-13\) kcal/mol, including two Br\(^-\) ions bound to the pentafluorophenyl groups and two additional Br\(^-\) ions bound to the carbomethoxyphenyl groups (see Figure 7 and Table 3). We also find that one additional Br\(^-\) binds to the Zn center of 2 with the substantial stabilization energy of \(-12.5\) kcal/mol. This is a much stronger metal–anion interaction than seen for Zn–I\(^-\) and Pd–Br\(^-\) where the corresponding stabilization energies are very low: less negative than \(-1.0\) kcal/mol. This can be attributed to both the relative size of studied anions and a more favorable charge distribution for anion binding in 2 than the other compounds (see Supporting Information). In contrast to the studies with bromide, calculations of the interactions between 1–3 and the larger iodide ions show negligible or no stabilization due to ion binding.

The electrostatic field of anions in the solution shifts the electron donor and acceptor states, as well as the edge of the conduction band, to more negative potentials and reduces the concentration of electrons at the surface. The larger stabilization energy of the closely bound bromide ions leads to a larger shift toward negative potentials in the donor state relative to the bottom of the semiconductor conduction band, which results in a larger barrier for back transfer of electrons from the semiconductor to the donor state and a favorable reduction in \(J_0\) (see Scheme 3). The resulting reduction of the recombination current density \(J_0\) reduces the slope of the characteristic curve at \(V \rightarrow 0\) and increases the open circuit voltage \(V_{OC}\) (see Figures 4 and 5). The illumination current density increases (or decreases) when the donor state is displaced to a range of the conduction band with larger (or smaller) density of states relative to I\(^3\)/I\(^-\) depending on the energy level alignment of the donor state with the metal-oxide density of states.

**DISCUSSION**

Natural photosynthesis offers many desirable features; yet, not every facet should be a target for chemical mimicry. Biological photosynthetic machinery appears to be limited by the inherited “legacy” biochemistry of the quinone/quinol redox couple and key energy carriers such as NAD(P)H and ATP. The ability to alter the energetics of the primary electron acceptor, and other components, is a promising feature of artificial systems. Using anode materials with conduction-band energies poised more positive of TiO\(_2\) (illustrated in this work by replacing TiO\(_2\) with SnO\(_2\)) allows the energetics of a sensitizer dye to be tuned to higher potentials without adversely affecting the excited-state electron-transfer chemistry. Using this strategy, absorption of photons over a larger spectral range could be accomplished if photosystems were stacked in optical, in addition to electrical, series.\(^6\) Unlike the natural photosynthetic apparatus, such an artificial Z-scheme (tandem cell)
Table 3. Ion–Ring Distances, Nearest Pyrrole H Distances, and Stabilization Energy $E_s$ for One or Two Br$^-$ Ions Bound to the Pentafluorophenyl or Carbomethoxyphenyl Rings of Sensitizers 1–3 Based on B3LYP/6-31G(d,p) Calculations$^a$

| dye | number of ions | pentafluorophenyl rings | | | | | | | | carbomethoxyphenyl rings | | | |
|-----|----------------|-------------------------|---|---|---|---|---|---|---|---|---|---|---|---|
| 1   | 1              | 3.8                     | 2.7 | -4.5 |
| 2   | 2              | 4.3                     | 2.9 | -7.9 |
| 3   | 1              | 4.2                     | 2.9 | -2.3 |
| 2   | 2              | 4.2                     | 2.9 | -7.9 |
| 3   | 1              | 4.2                     | 2.9 | -2.3 |
| 2   | 2              | 4.2                     | 2.9 | -7.9 |

$^a$“Two ions are bound to opposing rings as in Figure 7.

### ASSOCIATED CONTENT

#### Supporting Information

Synthesis and Structural Characterization, Optical Data, Electrochemical Data, Computational Data, and complete reference 49. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-07ER15909) and the Camille & Henry Dreyfus Foundation.

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