Electron Injection Dynamics from Photoexcited Porphyrin Dyes into SnO₂ and TiO₂ Nanoparticles

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ABSTRACT: The photoexcited electron injection dynamics of free-base and metallo-derivatives of tris(pentafluorophenyl)porphyrins bound to TiO₂ and SnO₂ nanoparticle surfaces have been investigated using time-resolved terahertz spectroscopy (TRTS). The metallo-derivatives include Zn(II), Cu(II), Ni(II), and Pd(II). For the TiO₂–porphyrin assemblies, electron injection from the photoexcited dye to the semiconductor occurs only when using the zinc derivative as the sensitizer because it is the only dye studied in this report with long-lived excited states higher in energy than the TiO₂ conduction band edge. All of the dyes, however, have excited-state energies above the SnO₂ conduction band edge, and the electron injection rates vary widely from 0.4 to 200 ps depending on the sensitizer. For the SnO₂–porphyrin assemblies, electron injection is strongly influenced by competition with alternate deactivation routes that are accessible following Soret band excitation. These results offer thermodynamic and kinetic considerations for designing improved high-potential porphyrin photoanodes with applications to solar-powered water oxidation.

INTRODUCTION

Solar energy has been widely investigated as a renewable alternative to fossil fuels, and significant progress has been made in the area of solar-to-electric transduction using traditional photovoltaic solar cells as well as dye-sensitized solar cells (DSSCs).¹,² Solar electric cells, however, cannot store energy for future use (i.e., when the sun sets) without utilizing additional components such as batteries or electrolyzers. Biology offers inspiration for achieving integrated solar-to-fuel devices that, like their photosynthetic counterparts, use sunlight to directly oxidize water into oxygen, protons, and electrons (necessary components of fuel production).³⁻⁵ To this aim, researchers have incorporated aspects of DSSCs to construct hybrid water oxidation systems.⁶⁻¹¹ Although their specific design details differ, most of these systems incorporate thin-film dye-sensitized nanoparticle photoanodes to convert visible light to oxidizing power and catalysts to facilitate water oxidation. In general, these systems have relatively low efficiencies and in some cases require the assistance of an external bias voltage or UV illumination.¹⁰

One approach to improving the efficiency of such devices is identifying the physical processes involved and understanding how they affect each other and the overall performance. In dye-sensitized cells designed for either water oxidation or electricity production, these processes include light harvesting by the sensitizer, electron injection from the sensitizer to the semiconductor, and electron transport through the semiconductor.¹⁰,¹² Electron injection plays a particularly important role because it is the step that initiates charge movement. Often, electron injection efficiency can be directly correlated with device performance.¹³⁻¹⁸ With femtosecond to picosecond time scales, electron injection has been studied using several ultrafast pump/probe techniques including infrared transient absorption,¹⁹⁻²¹ visible transient absorption,²²,²³ and THz spectroscopy.²⁴⁻²⁸

The photophysical properties and photoinduced electron-transfer dynamics of porphyrins have been widely studied,²⁹⁻³² and porphyrins have also shown success as sensitizers in high efficiency DSSCs.²,³⁰,³³ Accordingly, a series of bis(pentafluorophenyl) sensitizers was recently investigated in the design of photoanodes for DSSCs and photoelectrochemical cells.⁶,³⁴ Due to the relatively large potential generated by the porphyrin radical cation/porphyrin redox couple (P⁺⁺/P), these photoanodes are promising components for water-oxidation systems. This study, which features a selection of analogous 5-(4-carboxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrins (Figure 1A) bound to TiO₂ and SnO₂ nanoparticles, analyzes the electron injection from the excited states of the dye molecules to the semiconductor conduction band.

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Figure 1. (A) 5-(4-Carboxyphenyl)-10,15,20-tris(pentafluorophenyl)-porphyrin: the porphyrin base (PF15) for the compounds investigated. In this work, M = H2, Zn(II), Cu(II), Ni(II), or Pd(II). The carboxylic acid functional group serves as an anchor to metal oxide surfaces. (B) Jablonski diagram of a typical porphyrin. Solid lines indicate excitation, dashed lines denote emission, and curvy lines are non-radiative processes. Ranges of typical time scales for internal conversion (IC), intersystem crossing (ISC), fluorescence (Fluor), and phosphorescence (Phos) are indicated.

■ EXPERIMENTAL METHODS

Synthesis and Characterization. All compounds were synthesized from commercially available starting materials. All chemicals were purchased from Aldrich or Alfa Aesar, and solvents were obtained from Aldrich or Mallinckrodt. Dichloromethane was purified on a 1 m alumina column prior to use (Innovative Technologies, Inc.). All solvents were stored over the appropriate molecular sieves prior to use. The free-base, 5-(4-carboxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (H2PF15), was prepared using a modified version of a previous report.35 (See the Supporting Information for synthetic details and characterization.) Zinc, copper, nickel, and palladium ions were inserted into H2PF15 or its methyl ester analogue with metal(II) acetate or chloride salts by standard methods.36 Thin layer chromatography (TLC) was performed with silica gel 22 to 43 nm. Thin films of TiO2 and SnO2 were prepared from TiO2 nanoparticles (Aeroxide P25) were purchased from Alfa Aesar and ranged in size from 22 to 43 nm. Thin films of TiO2 and SnO2 were prepared from aqueous suspensions. Pastes composed of 1.0 g of TiO2, or 1.1 g of SnO2, in 2.00 mL of water (Milli-Q) were stirred overnight to obtain a homogeneous dispersion and doctor-bladed onto 1 mm thick fused quartz microscope slides (GM Associates). The resulting films were approximately 10 μm thick. The slides 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 0.1 mM solution of the appropriate porphyrin compound 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. Films of TiO2 and SnO2 nanoparticles were highly scattering so spectra were obtained in diffuse reflectance geometry using an integrating sphere. The same samples were used for both the THz and UV−vis measurements.

Electrochemistry. Cyclic voltammetry was performed with an EG&G Princeton Applied Research model 273 potentiostat/galvanostat using a glassy carbon (3 mm diameter) or platinum disc (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 voltammograms of the porphyrin solutions were recorded as the methyl ester analogues for the free-base, zinc, and palladium compounds. The potential of the pseudoreference electrode was determined using the ferrocenium/ferrocene couple as an internal standard (with E1/2 taken as 0.690 V vs NHE in dichloromethane).38 The voltammograms were recorded at a scan rate of 100 mV/s. All potentials listed in this manuscript are referenced to the normal hydrogen electrode (NHE).

Time-Resolved THz Spectroscopy. An amplified Tisapphire laser (Tsunami/Spitfire from Spectra Physics) produced 800 nm of pulsed near-IR light at a 1 kHz repetition rate with a ∼120 fs pulse width and 800 nm center wavelength. Roughly two-thirds of the power was frequency doubled and filtered to produce 40 mW of 400 nm (3.10 eV) light for the pump (photoexcitation) beam. The remaining third of the near-IR light was used to generate and detect THz radiation. THz 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. Data were taken at room temperature, and the average of two samples was determined for each data set. To analyze electron injection dynamics, the change in peak time-domain THz transmission was monitored as the time delay between the 400 nm pump pulse and the THz probe pulse was varied. More detailed information on the spectrometer and technique has been reported in the literature.34,35,39,40

■ RESULTS AND DISCUSSION

Steady-State Optical Studies. Porphyrins generally have two main absorption bands in the visible region. A Jablonski diagram showing the relevant transitions is shown in Figure 1B. Excitations from the ground state (S0) to the first singlet-excited state (S1) comprise the Q-band. The higher energy Soret band, or B-band, results from excitations from S0 to S2. Both of these transitions are π−π* transitions that involve electron redistribution within the conjugated π systems of the porphyrin rings.

UV−vis spectra of the H2PF15 and H2PF13 ethyl ester in dichloromethane and of the H2PF15 acid on TiO2 as well as SnO2 surfaces are shown in Figure 2. Peak positions for all of the porphyrins are listed in Table 1, and additional spectra can be found in Figure S1 (Supporting Information). The two peaks (four for H2PF13) observed between 500 and 600 nm form the Q-band. The Soret bands, or B-bands, are observed in the 400−420 nm range.
Q-band peaks for the porphyrins bound to TiO₂ and SnO₂ are broadened in relation to the peaks in dichloromethane but are not significantly red-shifted, which suggests little to no surface aggregation.41

All porphyrins studied in this report except for NiPF₁₅ exhibit visible emission upon illumination. The emission spectrum of H₂PF₁₅ is shown in Figure 2A, emission maxima for all of the visible emission upon illumination. The emission spectrum of aggregation.41 not significantly broadened in relation to the peaks in dichloromethane but are included in Figure S1. As proposed by Gouterman, porphyrins can be classified as fluorescent, phosphorescent, luminescent, or radiationless based on their emission properties.31 Furthermore, the best predictor of emission properties is the identity of the central substituent (metal ion) of the porphyrin ring. Figure 1B shows schematically the various radiative and non-radiative processes that can occur in porphyrins after either Soret or Q-band excitation.

Porphyrins that show emission primarily from the S₁ state are classified as fluorescent. The emission spectra of H₂PF₁₅ and ZnPF₁₅ are characteristic of fluorescence (Figures 1A and S1) and exhibit two strong peaks, Q(0,0) and Q(0,1).

Phosphorescent porphyrins undergo rapid intersystem crossing from the S₁ state to the lowest-lying triplet state T₁, from which emission occurs. Fluorescence may still occur from the S₁ state but with decreased quantum yield relative to fluorescent porphyrins.31 Palladium porphyrins are typically phosphorescent because the heavy Pd(II) cation increases spin–orbit coupling, which increases the rate of intersystem crossing from S₁ to T₁. The weak fluorescence observed for PdPF₁₅ versus H₂PF₁₅ and ZnPF₁₅ (Figure S2) is characteristic of phosphorescent porphyrins.

The emission from luminescent porphyrins is neither purely fluorescent nor phosphorescent due to mixing of triplet and singlet states. In 1968, Gouterman coined the terms “triplet” and “triplet” to describe the mixed states that arise when a paramagnetic metal with one unpaired electron, such as Cu(II), is coordinated by a porphyrin.42 This terminology has been extended to “singlهد dublets” as well. Since the coupling is fairly weak, the terminology retains the triplet or singlet identity of the underlying porphyrin state. However, it is necessary to acknowledge mixing of the unpaired electron from Cu(II), thereby resulting in triplet states becoming tripdoublets (^2T) or triquartets (^4T), while singlet states become singdublets (^2S). The emission of CuPF₁₅, which has one broad peak with a maximum value of 706 nm, is consistent with the luminescence reported in the literature for similar Cu porphyrins.43,44

Porphyrins that yield no detectable photoluminescence upon excitation, due to the availability of rapid relaxation pathways, are termed radiationless. In the well-documented case of Ni porphyrins, these relaxation pathways involve metal centered (d, d) states, which are accessible because of unoccupied d-orbitals on the Ni(II) cation.29 Accordingly, essentially no emission is observed from NiPF₁₅.

**Electrochemistry.** The pentafluorophenyl groups have a strong influence on the electrochemical properties of the porphyrin ring system, since their electron withdrawing nature destabilizes formation of the radical cation species.35 For the methyl ester derivative of H₂PF₁₅ in dichloromethane, two quasi-reversible one-electron redox processes are observed with midpoint potentials (E_{1/2}) of 1.68 and 1.93 V vs NHE. These potentials are significantly shifted in the anodic direction (more

### Table 1. Steady-State Optical Properties of PF₁₅ Methyl Esters in Dichloromethane

<table>
<thead>
<tr>
<th>porphyrin</th>
<th>B(0,0) (nm)</th>
<th>Q(1,0) (nm)</th>
<th>Q(0,0) (nm)</th>
<th>Q(0,1) (nm)</th>
<th>Q(0,1) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂PF₁₅</td>
<td>413, 3.01</td>
<td>507, 2.45b</td>
<td>536, 2.31b</td>
<td>641, 1.93</td>
<td>706, 1.76</td>
</tr>
<tr>
<td>ZnPF₁₅</td>
<td>415, 2.99</td>
<td>544, 2.28</td>
<td>578, 2.15</td>
<td>585, 2.12</td>
<td>637, 1.95</td>
</tr>
<tr>
<td>CuPF₁₅</td>
<td>409, 3.03</td>
<td>535, 2.22</td>
<td>570, 2.18</td>
<td>580, 2.16</td>
<td>637, 1.76</td>
</tr>
<tr>
<td>NiPF₁₅</td>
<td>406, 3.05</td>
<td>524, 2.37</td>
<td>557, 2.22</td>
<td>561, 2.21</td>
<td>604, 2.05</td>
</tr>
<tr>
<td>PdPF₁₅</td>
<td>410, 3.02</td>
<td>520, 2.38</td>
<td>553, 2.24</td>
<td>561, 2.21</td>
<td>604, 2.05</td>
</tr>
</tbody>
</table>

*In this notation, the numbers in parentheses are the number of vibrational quanta in the excited and ground electronic states, respectively. Due to the reduced symmetry of H₂PF₁₅ relative to its metalated counterparts, the Q(0,0) peak is split into Q(0,0) and Q(0,0) peaks and Q(1,0) is split into Q(1,0) and Q(1,0). The Q peaks are observed at shorter wavelengths (higher energies). The emission peak observed for CuPF₁₅ is better classified as a T(0,0) peak because it represents emission from the tripdoublet–quartet manifold.*

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positive potentials) compared to the bis(pentafluorophenyl)-porphyrin analogue [5,15-bis(4-carbomethoxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin], where the porphyrin radical cation/porphyrin couple (P°+/P) occurs with an E1/2 value of 1.57 \text{ V} vs \text{ NHE} \text{6,34} and the nonfluorinated analogue [5,15-bis(4-carbomethoxyphenyl)-10,20-bis(2,4,5-trimethylphenyl)-porphyrin], where the P°+/P couple occurs with an E1/2 value of 1.29 \text{ V} vs \text{ NHE}. \text{46} For the metallo complexes, the P°+/P couple can be further perturbed anodically or cathodically. The observed potentials for the Zn, Ni, Cu, and Pd species are provided in Table 2.

Table 2. Ground State Reduction Potentials (V vs \text{ NHE}) of PF15 Methyl Esters Determined by Cyclic Voltammetry

<table>
<thead>
<tr>
<th>porphyrin</th>
<th>E1/2 (V)</th>
<th>ΔE° (mV)</th>
<th>E1/2 (V)</th>
<th>ΔE° (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2PF15</td>
<td>+1.68</td>
<td>99</td>
<td>+1.93</td>
<td>104</td>
</tr>
<tr>
<td>ZnPF15</td>
<td>+1.47</td>
<td>131</td>
<td>+1.72</td>
<td>132</td>
</tr>
<tr>
<td>CuPF15</td>
<td>+1.63</td>
<td>196</td>
<td>+1.96</td>
<td>234</td>
</tr>
<tr>
<td>NiPF15</td>
<td>+1.68</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdPF15</td>
<td>+1.73</td>
<td>136</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The cyclic voltammograms are shown in Figure S3 (Supporting Information). \text{5} Peak-to-peak separations of the observed couples.

In accordance with the Rehm–Weller approximation, \text{47,48} excited-state reduction potentials for the S1 state are estimated by adding the E° transition energies to the corresponding ground state potentials as follows:

\[
E°(P°+/P) \approx E°(P°+/P) - \frac{E°(P \rightarrow P°)}{\epsilon}
\]

where \(E°(P°+/P)\) is the excited-state potential for the porphyrin-radical cation/singlet state excited porphyrin couple, \(E°(P°+/P)\) is the ground state potential for the porphyrin-radical cation/porphyrin couple, \(E°(P \rightarrow P°)\) is the estimated \(E°\) porphyrin ground state to porphyrin singlet state transition energy (S0 – S1 energy difference), and \(\epsilon\) is the elementary charge of an electron.

In this report, the S2 state reduction potentials were approximated by adding the energy (in eV) at the Soret band maximum to the ground-state potential for the P°+/P couple. T1 state energies were estimated in a similar fashion using electrochemical and emission data for meso-tetraphenylporphyrin (TPP) analogues of the PF15 porphins. \text{29}

The values of these excited-state reduction potentials (Figure 3 and Table S1) are pertinent because they determine the thermodynamic feasibility of photoinduced electron transfer into the metal oxide conduction band. As seen in Figure 3, all of the S2 potentials are more negative (higher in energy) than the conduction band edge of both TiO2 and SnO2, so electron injection into either material is possible from these states. The potentials of the S1 states of the PF15 compounds are closer to the TiO2 conduction band edge potential. The ZnPF15 potential is 0.09 \text{ V} negative of the conduction band, whereas the potentials for H2PF15 and PdPF15 are 0.250 and 0.08 \text{ V} positive of it, respectively. The potentials of CuPF15 and NiPF15 are nearly isoeenergetic with the conduction band. As a result, electron injection into TiO2 from S1 is expected to occur for ZnPF15 only.

For SnO2, however, the potentials of the S1 states of the PF15 compounds range from 0.2 to 0.6 \text{ V} negative of the conduction band edge, so electron injection is thermodynamically possible from all of them. Although none of the T1 states are more negative than the TiO2 conduction band edge, all of them except for H2PF15 are negative of the SnO2 band edge, indicating that electron injection from T1 into SnO2 is possible (except for H2PF15).

Time-Resolved THz Spectroscopy. Time-Resolved THz Spectroscopy (TRTS) is a proven method for measuring subpicosecond electron-injection dynamics and efficiency in dyesensitized nanoparticulate systems. \text{13,17,24–27,34,49,50} TRTS employs an ultrafast optical pump pulse followed by a THz probe pulse and is unique in that it is a noncontact electrical probe capable of monitoring photococnductivity on a subpicosecond time scale. Because mobile conduction band electrons alter the transmission of THz radiation, a change in THz amplitude upon photoexcitation is attributable to a change in conductivity. The change in THz amplitude as a function of the pump–probe delay time provides information about both the dynamics and efficiency of electron injection. While arbitrary units for the change in THz transmission are used in Figures 4 and S1, the same arbitrary units are used for all samples studied, and thus, they may be directly compared to each other.

Since conductivity is proportional to the product of the carrier density and carrier mobility, \text{39,51} TRTS provides a direct measure of electron injection efficiency if the mobility is constant, as is the case with a series of sensitizers all bound to a particular metal oxide. Results from TiO2 and SnO2 will therefore be discussed separately, since SnO2 has a higher mobility than TiO2.\text{17}

TiO2. The electron injection efficiencies and dynamics of the porphyrin dyes bound to TiO2 nanoparticles are shown in Figure 4. A control sample with no dye (denoted “bare TiO2”) was measured to demonstrate that there is almost no direct carrier generation from either two-photon absorption or excitation from band edge or midgap states. Of all of the porphyrins examined here, only ZnPF15 exhibits significant electron injection into TiO2. CuPF15 and H2PF15 show a very small amount of electron injection, and the signals of the NiPF15 and PdPF15 samples are indistinguishable from that of bare TiO2.

Electron injection from ZnPF15 into TiO2 occurs faster than the \(~400\) fs time resolution of the TRTS setup.\text{39,40} This time
scale. As seen in Figure 3 and discussed previously, the \( S_1 \) reduction potential of ZnPF\(_{15} \) is higher in energy than the TiO\(_2 \) band edge, whereas the reduction potentials of the other dyes are either nearly isoelecteric with or positive of the conduction band edge. Thus, significant electron injection is observed only for ZnPF\(_{15} \) because it has a relatively long \( S_1 \) excited state lifetime and an \( S_1 \) state energy slightly above the conduction band minimum.

A small amount of electron injection is also observed when using CuPF\(_{15} \) and H\(_2\)PF\(_{15} \) as sensitizers. Since the \( S_1 \) state is the only excited state for H\(_2\)PF\(_{15} \) higher in energy than the TiO\(_2 \) conduction band, the observed electron injection must come from this state. In the case of CuPF\(_{15} \), electron injection is unlikely to originate from the \( S_1 \) state as the \( S_1 \) state lifetimes of copper porphyrins are typically less than 100 fs.\(^{34} \) Given that the \( S_2 \) state for CuPF\(_{15} \) lies slightly above the conduction band edge of TiO\(_2 \), electron injection from it is possible. Although similar reasoning could be employed for NiPF\(_{15} \), both the \( S_1 \) and \( S_2 \) lifetimes of Ni porphyrins typically range from 100 to 350 fs,\(^{55,56} \) and the lack of injection from NiPF\(_{15} \) is consistent with these short lifetimes.

**SnO\(_2\)**. The conduction band edge reduction potential of SnO\(_2\) is \( \sim 0.5 \) V positive of the conductive band edge of TiO\(_2\).\(^{57,58} \) Therefore, electron injection from the \( S_1 \) state of all of the sensitizers is thermodynamically possible and, as seen in Figure 5, is indeed observed for all sensitizers reported here except NiPF\(_{15} \). Electron injection into SnO\(_2\) is significantly slower than that into TiO\(_2\) and continues for tens to hundreds of picoseconds after photoexcitation. A similar trend has been observed previously by other researchers who attribute this decrease in rate to a decrease in the density of states in the conduction band of SnO\(_2\) as compared to TiO\(_2\).\(^{17,21,26,59} \)

Electron injection dynamics were quantified by fitting eq 2 to the measured data (excluding NiPF\(_{15} \)) using the Levenberg–Marquardt nonlinear least-squares fitting algorithm.

\[
\Delta THz = \Delta THz_0 \left[ A_1 \left( e^{-t/\tau_1} - 1 \right) + A_2 \left( e^{-t/\tau_2} - 1 \right) + \left( 1 - e^{-t/\tau_1} \right) \right] \tag{2}
\]

Electron injection is modeled as a double exponential with time constants \( \tau_1 \) and \( \tau_2 \) and relative amplitudes \( A_1 \) and \( A_2 \) (where \( A_1 + A_2 = 1 \)), and the \( 1 - e^{-t/\tau_1} \) term accounts for recombination. The measured change in THz amplitude as a function of pump/probe delay time is denoted \( \Delta THz \), and \( \Delta THz_0 \) is a scaling factor that indicates the relative injection efficiency. \( \Delta THz \) and \( \Delta THz_0 \) have the same arbitrary units, and no further scaling of individual traces is performed.) Thus, the change in THz amplitude is a measure of the amount of charge injection from a particular photoexcited chromophore. If \( \tau_1 \) is long compared to \( \tau_2 \) then \( \Delta THz_0 \) represents the maximum change in THz amplitude. A global fit of all four data sets was performed in which \( \tau_1 \) was a shared parameter because loss of mobility over this short injection time scale is due mainly to trapping in the SnO\(_2\) nanoparticles and not to reduction of the sensitiser cation. The results are shown in Table 3.

For all of the porphyrins studied, the values of \( \Delta THz_0 \) are similar. The slightly lower value for PdPF\(_{15} \) is due to its lower absorbance at 400 nm (see Figure S1). These \( \Delta THz_0 \) values quantify the overall trend seen in Figure 5A: The photoinjected electron density is slightly lower for PdPF\(_{15} \) than for the other three dyes.
Table 3. Fitted Parameters of eq 2

<table>
<thead>
<tr>
<th>porphyrin</th>
<th>ΔτH20 (arbitrary units)</th>
<th>A1 (τ1 (ps))</th>
<th>A2 (τ2 (ps))</th>
<th>τc (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2PF15</td>
<td>24</td>
<td>0.19</td>
<td>1.20</td>
<td>0.81</td>
</tr>
<tr>
<td>ZnPf15</td>
<td>23</td>
<td>0.38</td>
<td>0.44</td>
<td>0.62</td>
</tr>
<tr>
<td>CuPF15</td>
<td>26</td>
<td>0.30</td>
<td>10.5</td>
<td>0.70</td>
</tr>
<tr>
<td>PdPF15</td>
<td>21</td>
<td>0.44</td>
<td>5.14</td>
<td>0.56</td>
</tr>
</tbody>
</table>

In contrast, the time constants for electron injection, τ1 and τ2, span an order of magnitude for the different dyes. While electron injection is completed within 20 ps for ZnPf15 and within 40 ps for H2PF15, it continues for about 200 ps for both CuPF15 and PdPF15. Overall, the ordering of electron injection rates is ZnPf15 > H2PF15 > PdPF15 ≈ CuPF15. Although many researchers have observed a decrease in electron injection rate with increasing reduction potential,15,20,60 this relationship is not found in the results shown in Table 3. Specifically, if only the estimated reduction potentials of the S1 states are considered, then the rates would be in the order of ZnPf15 > CuPF15 > PdPF15 > H2PF15. This lack of correlation indicates that factors in addition to the photoelectrochemical properties of the porphyrin singlet states determine the rate of electron injection.

The TRTS results for PF15-sensitized SnO2 can be rationalized by considering the kinetic competition between electron injection from the dyes and relaxation of the porphyrin excited states via other processes. If the rate of electron injection from a particular excited state is greater than the rate of deactivation, then electron injection may occur. If the converse is true, electron injection is disfavored. In the TRTS experiments described previously, the photoexcitation energy was 3.1 eV (400 nm), which is slightly greater than the S0 – S1 transition energy for all of the porphyrins used in this study. The presence of so many of three porphyrin excited states above the SnO2 conduction band edge (see Figures 1B and 3) allows for many different electron injection pathways.

Soret (S1) excitations can lead to internal conversion to the S0 state which may be followed by intersystem crossing to a S2 state. Since S2 lifetimes for Zn porphyrins are generally on the order of nanoseconds52,62,63 and the slow injection component observed for ZnPf15 is 18.1 ps, this slower component is attributed to electron injection from the S2 state. Furthermore, τ1 for ZnPf15 is the actual electron injection time constant, unlike τc which is a measure of the excited state lifetime.

A similar rationale is applied to the data for H2PF15, for which τ1 = 1.20 ps and τ2 = 37.4 ps. Reported lifetimes of the free-base S2 state are typically less than 100 fs,53,60 which is seemingly inconsistent with the observed 1.20 ps electron injection time of H2PF15. However, it is known that a small energy gap between the Q and B bands in free-base porphyrins leads to a strong coupling between them, as manifested in an enhanced Q band intensity relative to the B band, and this coupling promotes the rapid deactivation of the free-base S2 state.29 As seen in the UV–vis spectra in Figure 2B, the enhancement of the Q band at 500 nm relative to the B band at 590 nm is less pronounced when H2PF15 is bound to SnO2 compared to solutions in dichloromethane. Thus, the coupling is not as strong when bound to SnO2, and the measured 1.20 ps electron injection time is the lifetime of the S2 state. Lifetimes of the H2PF15 S1 states range from 9.8 to 11.2 ns.52,68,69 Accordingly, the observed 37.4 ps component of electron injection from H2PF15 is the time constant for injection from the S1 state.

Phosphorescent. Pd porphyrins are typically classified as phosphorescent.29,31 Electron injection from PdPF15 is much slower than that from H2PF15 and ZnPf15, and the values of τ1 and τ2 for PdPF15 are 5.14 and 197 ps, respectively. For Pd porphyrins, the lifetimes of porphyrin S1 and S2 states are shortened due to spin–orbit coupling and the heavy atom effect. Instead of fluorescence from S1, intersystem crossing to a triplet state T1 occurs. As compared to the nanosecond S1 lifetimes of Zn and free-base porphyrins, Pd porphyrin S1 lifetimes are much shorter and range from 13 to 20 ps.29 Triplet states, however, are much longer lived. For PdTPP, T1 lifetimes on the order of microseconds have been reported.29,70,71 Therefore, the measured τ1 time constant is actually the S1 → T1 intersystem crossing time constant. Since τ2 is orders of magnitude smaller than the triplet state lifetime, it accurately represents the electron injection time constant from the T1 state.

Luminescent. The emission from Cu(II) porphyrins cannot be considered either purely fluorescent or phosphorescent, and thus, they are classified as luminescent.29,31 Because they are paramagnetic and have an unpaired electron in the d8(3g) orbital of the Cu(II) cation, their first excited triplet states (T1) are split into a tripboublet (3T1g) and tripquartet (3T1u), which are separated by 200–700 cm−1 depending on the substituents.29 For CuPF20, this splitting is 270 cm−1 and intersystem crossing from the 3S1 state to the 3T1 state occurs in less than 350 fs.82 Following intersystem crossing, an equilibrium is established between the 3T1 and 4T states.82,96 Overall luminescence lifetimes of copper porphyrins range from 10 to 300 ns,83,84,74 and the luminescence lifetime of CuPF20 in energy transfer before undergoing internal conversion,53,63–66 and the S1 lifetime of ZnPf20 is 0.19 ps.52 The time constant of the fast electron injection component, τ1 for ZnPf15 is 0.44 ps, which is slightly longer than the lifetime of ZnPf20. Because the instrument response time of the TRTS apparatus is ∼400 fs,94,40 τ1 represents an upper limit for electron injection, and the actual value could be closer to the ZnPf20 S1 lifetime. Therefore, this fast component corresponds to injection from the S2 state. Since S1 lifetimes for Zn porphyrins are generally on the order of nanoseconds,52,62,63 and the slow injection component observed for ZnPf15 is 18.1 ps, this slower component is attributed to electron injection from the S1 state. Furthermore, τ1 for ZnPf15 is the actual electron injection time constant, unlike τc which is a measure of the excited state lifetime.
dichloromethane is 155 ns.\textsuperscript{45} Cu porphyrins also exhibit (\(\pi, d\)) ligand-to-metal charge transfer (LMCT) states that lie close in energy to the triplet manifold.\textsuperscript{29,75,76} The position of the LMCT state relative to the \(2T\) and \(4T\) states can vary with different ring substituents and is between the \(2T\) and \(4T\) states for CuTPP.\textsuperscript{77}

CuPF\textsubscript{15} exhibits comparatively slow electron injection dynamics into SnO\textsubscript{2} (\(\tau_1 = 10.5\) ps and \(\tau_2 = 180\) ps). Assigning the two time constants to a particular state is more difficult in this case due to the increased number of possible excited states. A LMCT state can be ruled out, since (\(\pi, d\)) LMCT states involve the transfer of electrons from the porphyrin’s ligands to the central metal ion and would quench electron injection. Given that the faster injection time constant in CuPF\textsubscript{15} is near that of the singlet state of PdPF\textsubscript{15}, and the slower one is close to that from the triplet state of PdPF\textsubscript{15}, \(\tau_1\) is assigned to the lifetime of a singlet doublet (\(2S_1\)) state of CuPF\textsubscript{15} and \(\tau_2\) to the injection time constant from its triplet doublet (\(2T_1\)) state.

**Radiationless.** Electron injection was not observed for NiPF\textsubscript{15} bound to SnO\textsubscript{2} even though the reduction potential of its \(S_1\) state lies about 0.5 eV negative of the conduction band edge of SnO\textsubscript{2}. A significant difference between Ni porphyrins and the others is that they are radiationless and are known to have sub-picosecond \(S_1\) and \(S_2\) excited state lifetimes due to relaxation into empty d orbitals on the Ni(II) cation (which has a \(d^8\) configuration). Furthermore, these d states are highly localized on the Ni atom and lack electronic coupling to the SnO\textsubscript{2} conduction band. As a result, electron injection does not occur.

### CONCLUSION

Electron-injection dynamics have been investigated using TRTS for a selection of high potential porphyrin dyes bound to TiO\textsubscript{2}, and SnO\textsubscript{2} nanoparticles. Electron injection into TiO\textsubscript{2} or lack thereof, is determined by the energetic positioning of the singlet excited state of the dye molecule relative to the metal conduction band edge. Because ZnPF\textsubscript{15} is the only sensitizer studied here with an \(S_1\) state higher in energy than the TiO\textsubscript{2} conduction band, it is the only sensitizer to demonstrate significant electron injection. Given that the TiO\textsubscript{2} conduction band is unfavorably positioned with respect to the sensitizer excited state, these results suggest that TiO\textsubscript{2} may not be the best choice of semiconductor for these high-potential porphyrin sensitizers.

For SnO\textsubscript{2}, all of the sensitizers studied in this report have excited states higher in energy than the SnO\textsubscript{2} conduction band edge. Accordingly, all of the porphyrins inject electrons upon photoexcitation except for NiPF\textsubscript{15}. Changing the central substituent of the porphyrin ring changes the photoluminescent properties of the dye, leading to different pathways of excited state deactivation (fluorescence, phosphorescence, luminescence, or radiationless decay) and resulting in a range of excited state lifetimes. Since electron injection competes with this deactivation, it is strongly influenced by the identity of the central substituent. Therefore, the electron injection time constants obtained can be either indicators of the excited state lifetime or the actual electron injection time scale. For the biphatic dynamics observed, the shorter time constant represents the lifetime of a higher lying state, and the longer one is an intrinsic electron injection time constant for the lower lying state.

### ASSOCIATED CONTENT

#### Supporting Information

Synthesis and characterization, additional UV–vis and emission spectra, cyclic voltammograms, and electrochemical values. 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.

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### REFERENCES


Supporting Information for

Electron Injection Dynamics from Photoexcited Porphyrin Dyes into SnO₂ and TiO₂ Nanoparticles

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Synthesis and characterization.

5-(Pentafluorophenyl)dipyrromethane. A solution of pentafluorobenzaldehyde (2.0 mL, 16.2 mmol) in freshly distilled pyrrole (50 mL, 720 mmol) was degassed with a stream of argon for 20 min before adding trifluoroacetic acid (120 µL, 1.62 mmol). The mixture was stirred for 30 min at room temperature, diluted with CH₂Cl₂ (400 mL), and then washed with 0.1 M NaOH (400 mL). The organic phase was washed with water (400 mL) and dried over Na₂SO₄. Evaporation of the solvent at reduced pressure gave a brown oil. Unreacted pyrrole was removed under high vacuum, yielding a tacky solid that was flashed on a column of silica using a mixture of hexanes:ethylacetate:triethylamine (80:20:1) as the eluent. The product was recrystallized from dichloromethane/hexanes to yield 3.29 g of 5-(pentafluorophenyl)dipyrromethane as a white powder (65% yield). 1H NMR (400 MHz, CDCl₃): δ 5.90 (1H, s, CH), 6.00 – 6.05 (2H, m, ArH), 6.14– 6.19 (2H, m, ArH), 6.71 – 6.75 (2H, m, ArH), 8.06 (2H, brs, NH); 19F NMR (400 MHz, CDCl₃): δ -160.98 – -161.40 (2F, m, ArF), -155.71 (1F, t, J = 21.0 Hz, ArF), -141.43 (2F, brd, J = 20.7 Hz, ArF).

5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin. A portion of 5-(pentafluorophenyl)dipyrromethane (1.25 g, 4.00 mmol), 4-carbomethoxybenzaldehyde (329 mg, 2.00 mmol) and pentafluorobenzaldehyde (247 µL, 2.00 mmol) in chloroform (400 mL) was purged for 20 minutes with argon before adding BF₃(OEt₂) (530 µL of a 2.5 M stock solution in chloroform). After 24 h, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (700 mg, 3.08 mmol) was added and the mixture was stirred for an additional 24 h. The solvent was evaporated at reduced pressure and the residue was redissolved in bromobenzene. The solution was treated with a second portion of DDQ (700 mg, 3.08 mmol) and refluxed for 3 h. The solvent was removed at reduced pressure and the crude product was purified by column chromatography on silica using toluene as the eluent. (18% yield). 1H NMR (400 MHz, CDCl₃): δ -2.87 (2H, s, NH), 4.13 (3H, s, CO₂CH₃), 8.31 (2H, d, J = 8.3 Hz, ArH), 8.48 (2H, d, J = 8.3 Hz, ArH), 8.83 (2H, d, J = 4.5Hz, βH), 8.87-8.94 (6H, m, βH); 19F NMR (400 MHz, in CDCl₃): δ -161.61 – -161.34 (6F, m, ArF), -151.50 (1F, t, J = 20.7 Hz, ArF), -151.51 (2F, dd, J = 8.0 Hz, 22.9 Hz, ArF), -136.64 (4F, dd, J = 8.0 Hz, 22.9 Hz, ArF); MALDI-TOF-MS m/z. calcd. for C₄₆H₁₇F₁₅N₄O₂ 942.111, obsd. 942.115; UV-vis (CH₂Cl₂) 413, 507, 536, 583, 637 nm.

5-(4-Carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (PF15). A portion of 5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (100 mg, 0.11 mmol) was dissolved in a mixture of trifluoroacetic acid and conc. HCl (1:2, 80 mL) at 90 °C for 24 h. The reaction mixture was diluted with dichloromethane (80 mL), washed twice with an equal volume of water, and then neutralized with a saturated solution of aqueous sodium bicarbonate. The organic phase was dried over sodium sulfate, filtered, and the solvent removed at reduced pressure. The crude product was purified by column chromatography on silica using a gradient of 1% methanol in dichloromethane to 10% methanol in dichloromethane as the eluent to give 96 mg of the desired porphyrin (98% yield). 1H NMR (400 MHz, CDCl₃): δ -2.86 (2H, s, NH), 8.38 (2H, d, J = 8.3 Hz, ArH), 8.60 (2H, d, J = 8.3 Hz, ArH), 8.87 (2H, brd, J = 4.3 Hz, βH), 8.88-8.89 (6H, brm, βH); 19F NMR (400 MHz, in CDCl₃): δ -161.59 – -161.30 (6F, m, ArF), -151.31 (2F, t, J = 20.7 Hz, ArF), -151.46 (1F, t, J = 20.7 Hz, ArF), -136.64 (4F, dd, J = 8.0 Hz, 22.9 Hz, ArF), -136.51 (2F, dd, J = 8.0 Hz, 22.9 Hz, ArF); MALDI-TOF-MS m/z. calcd. for C₄₅H₁₅F₁₅N₄O₂ 928.096, obsd. 928.098. UV-vis (CH₂Cl₂) 413, 507, 536, 637 nm.

Zinc 5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin. Zn(OAc₂)₂H₂O (82 mg, 0.37 mmol) was added to a solution of 5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (35 mg, 0.04 mmol) in a mixture of dichloromethane and methanol (80:20, 40 mL). After cooling to room temperature, the solution was diluted with dichloromethane (20 mL) and washed with water (70 mL), then a saturated solution of aqueous sodium bicarbonate (70
mL). The organic phase was dried over sodium sulfate, filtered, and the solvent evaporated at reduced pressure. The product was purified by column chromatography on silica using toluene as the eluent to give 37 mg of the desired porphyrin (99% yield). 1H NMR (400 MHz, CDCl3): δ 4.08 (3H, s, CO2CH3), 8.30 (2H, d, J = 8.2 Hz, ArH), 8.42 (2H, d, J = 8.2 Hz, ArH), 8.92 (2H, d, J = 4.4Hz, βH), 8.97-9.01 (6H, m, βH); 19F NMR (400 MHz, in CDCl3): δ -161.96 – -161.68 (6F, m, ArF), -152.18 (2F, t, J = 20.7 Hz, ArF), -152.12 (1F, t, J = 20.7 Hz, ArF), -136.93 (4F, dd, J = 8.0 Hz, 22.9 Hz, ArF), -136.82 (2F, dd, J = 8.0 Hz, 22.9 Hz, ArF); UV-vis (CH2Cl2) 415, 544, 578 nm.

**Zinc 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (ZnP15).**

Zn(OAc2).2H2O (83 mg, 0.38 mmol) was added to a solution of 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (35 mg, 0.04 mmol) in a mixture of dichloromethane and methanol (80:20, 40 mL). After stirring for 15 h, the solution was heated at reflux for 4 h. After cooling to room temperature, the solution was diluted with dichloromethane (20 mL) and washed with water (70 mL), then a saturated solution of aqueous sodium bicarbonate (70 mL). The organic phase was dried over sodium sulfate, filtered, and the solvent evaporated at reduced pressure. The product was purified by column chromatography on silica using 5% methanol in dichloromethane as the eluent to give 36 mg of the desired porphyrin (97% yield). 1H NMR (400 MHz, CDCl3): δ 8.37 (2H, d, J = 8.3 Hz, ArH), 8.54 (2H, d, J = 8.3 Hz, ArH), 8.95 (2H, d, J = 4.5Hz, βH), 8.98-9.07 (6H, m, βH); 19F NMR (400 MHz, in CDCl3): δ -161.91 – -161.61 (6F, m, ArF), -152.09 (2F, t, J = 20.7 Hz, ArF), -152.04 (1F, t, J = 20.7 Hz, ArF), -136.91 (4F, dd, J = 8.0 Hz, 22.9 Hz, ArF), -136.81 (2F, dd, J = 8.0 Hz, 22.9 Hz, ArF).

**Palladium 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (PdPF15).**

Palladium (II) chloride (67 mg, 0.38 mmol) was added to a solution of 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (35 mg, 0.04 mmol) in N,N-dimethylformamide (15 mL). The mixture was stirred for 7 h at reflux under an argon atmosphere. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica using 5% methanol in dichloromethane as the eluent to give 36 mg of the desired porphyrin (92% yield). 1H NMR (400 MHz, CDCl3): δ 8.26 (2H, d, J = 8.2 Hz, ArH), 8.50 (2H, d, J = 8.2 Hz, ArH), 8.75 (2H, d, J = 4.7Hz, βH), 8.83-8.89 (6H, m, βH); 19F NMR (400 MHz, in CDCl3): δ -161.51 – -161.19 (6F, m, ArF), -151.52 (2F, t, J = 21.8 Hz, ArF), -151.45 (1F, t, J = 21.8 Hz, ArF), -136.93 (4F, dd, J = 8.0 Hz, 22.9 Hz, ArF), -136.39 (2F, dd, J = 8.0 Hz, 22.9 Hz, ArF); UV-vis (CH2Cl2) 410, 520, 553 nm.

**Nickel 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (NiPF15).**

Ni(OAc2).4H2O (94 mg, 0.38 mmol) was added to a solution of 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (35 mg, 0.04 mmol) in N,N-dimethylformamide (25 mL). The mixture was stirred for 24 h at reflux under an argon atmosphere. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica using 5% methanol
in dichloromethane as the eluent to give 33 mg of the desired porphyrin (89% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (2H, d, $J = 8.2$ Hz, ArH), 8.47 (2H, d, $J = 8.2$ Hz, ArH), 8.72 (2H, d, $J = 4.8$ Hz, $\beta$H), 8.74-8.79 (4H, m, $\beta$H) 8.81 (2H, d, $J = 4.8$ Hz, $\beta$H); $^{19}$F NMR (400 MHz, in CDCl$_3$): $\delta$ -161.45 – -161.24  (6F, m, ArF), -151.62 (2F, t, $J = 21.8$ Hz, ArF), -151.57 (1F, t, $J = 21.8$ Hz, ArF), -136.78 (4F, dd, $J = 8.0$ Hz, 22.9 Hz, ArF), -136.63  (2F, dd, $J = 8.0$ Hz, 22.9 Hz, ArF); UV-vis (CH$_2$Cl$_2$) 406, 524, 557 nm.

**Copper 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (CuPF15).** Cu(OAc)$_2$·H$_2$O (68 mg, 0.38 mmol) was added to a solution of 5-(4-carboxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (35 mg, 0.04 mmol) in dichloromethane (40 mL). After stirring for 12 h, the solution was heated at reflux for 3 h. After cooling to room temperature, the solution was diluted with dichloromethane (20 mL) and washed with water (70 mL), then a saturated solution of aqueous sodium bicarbonate (70 mL). The organic phase was dried over sodium sulfate, filtered, and the solvent evaporated at reduced pressure. The product was purified by column chromatography on silica using 5% methanol in dichloromethane as the eluent to give 34 mg of the desired porphyrin (91% yield); UV-vis (CH$_2$Cl$_2$) 409, 535, 570 nm.
Figure S1. UV-vis and emission spectra. Left: normalized absorption (solid line) and emission (dashed line) spectra of PF$_{15}$ methyl esters in dichloromethane. The wavelength of the highest energy Q-band transition was chosen for excitation to obtain the emission spectra. Due to low emission, the spectrum for NiPF$_{15}$ has been given the same scaling as that of CuPF$_{15}$. Right: absorption spectra of the PF$_{15}$ methyl esters in dichloromethane (medium), for the PF$_{15}$ dyes on the TiO$_2$ surface (light), and for the PF$_{15}$ dyes on the SnO$_2$ surface (dark).
Figure S2. Unscaled emission spectra. Concentrations of all species have been approximately absorbance matched, and spectra have been divided into parts A and B to highlight order of magnitude differences in emission intensity.

![Unscaled emission spectra]

Figure S3. Cyclic voltammograms of the PF$_{15}$ methyl esters. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane, and the scan rate was 100 mV/s. First and second oxidations are observed for H$_2$PF$_{15}$, ZnPF$_{15}$, and CuPF$_{15}$. Only the first oxidation is observed for NiPF$_{15}$ and PdPF$_{15}$ due to the limitations of the solvent window.

![Cyclic voltammograms]
**Table S1. Electrochemical values.**

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>$P^+/P$ (V)$^a$</th>
<th>$P^+/P^*$ (V)$^b$</th>
<th>$P^+/P(S1)^*$ (V)$^c$</th>
<th>$E_0^0$ (eV)</th>
<th>$P^+/P(S2)^*$ (V)$^d$</th>
<th>$E_{Soret}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$<em>2$PF$</em>{15}$</td>
<td>1.68</td>
<td>0.18</td>
<td>-0.25</td>
<td>1.93</td>
<td>-1.33</td>
<td>3.01</td>
</tr>
<tr>
<td>ZnPF$_{15}$</td>
<td>1.47</td>
<td>-0.20</td>
<td>-0.66</td>
<td>1.47</td>
<td>-1.52</td>
<td>2.99</td>
</tr>
<tr>
<td>CuPF$_{15}$</td>
<td>1.63</td>
<td>-0.08</td>
<td>-0.55</td>
<td>2.10</td>
<td>-1.40</td>
<td>3.03</td>
</tr>
<tr>
<td>NiPF$_{15}$</td>
<td>1.68</td>
<td>–</td>
<td>-0.55</td>
<td>2.10</td>
<td>-1.37</td>
<td>3.05</td>
</tr>
<tr>
<td>PdPF$_{15}$</td>
<td>1.73</td>
<td>-0.03</td>
<td>-0.49</td>
<td>2.22</td>
<td>-1.29</td>
<td>3.02</td>
</tr>
</tbody>
</table>

$^a$ Ground state reduction potentials as determined by cyclic voltammetry.

$^b$ Triplet state reduction potentials estimated using electrochemical data for free-base, zinc, and palladium tetraphenylporphyrin (TPP) and the maximum value of triplet emission spectrum of CuTPP.

$^c$ $S_1$ state reduction potentials estimated by adding the $E_0^0$ transition energies to the corresponding ground state potentials.

$^d$ $S_2$ state reduction potentials calculated using the energy of the Soret band maximum.