Modular Assembly of High-Potential Zinc Porphyrin Photosensitizers Attached to TiO₂ with a Series of Anchoring Groups

Lauren A. Martini, Gary F. Moore, † Rebecca L. Milot, Lawrence Z. Cai, Stafford W. Sheehan, Charles A. Schmuttenmaer, * Gary W. Brudvig, * and Robert H. Crabtree *

Yale Energy Sciences Institute and Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107, United States

Supporting Information

ABSTRACT: Efforts to improve the ease of assembly and robustness of photoanodes for light-driven water oxidation have led to the development of a modular assembly method for anchoring high-potential zinc porphyrins to TiO₂ via coordination to surface-bound pyridine linkers. It is essential that the anchoring groups provide strong electronic coupling between the molecular dye and metal oxide surface for optimal electron injection and that they are robust under the operating conditions of the system. Here, four linker molecules functionalized with either carboxylate, phosphonate, acetylacetone, or hydroxamate anchoring groups are compared for their relative water stability on TiO₂. We also report the relative electron injection efficiencies, as measured by terahertz spectroscopy, for high-potential zinc porphyrins coordinated to TiO₂ via pyridyl linkers with the series of anchoring groups.

INTRODUCTION

Artificial photosynthesis is a challenging yet promising goal for solar energy research. 1-4 Storing the sun’s energy as a chemical fuel requires the integration of visible-light capture and conversion technologies for catalytic water oxidation. Each step presents inherent challenges, and coupling these processes has proven difficult. Inspired by the seminal work on ultraviolet-light-driven water splitting using wide-band-gap titanium dioxide (TiO₂)5 and recent advances in visible-light capturing dye-sensitized solar cells (DSSCs)6-11 for solar-to-electric energy conversion, similar materials are now being explored for the development of solar-to-fuel applications.

In this approach, dye-sensitized photoanodes for solar-driven water splitting incorporate sensitizers that exhibit broad absorption in the visible region, maintain strong attachment to the metal oxide support under operating conditions, and have redox potentials thermodynamically poised for water oxidation. A suitable water-oxidation catalyst should be located in close proximity to the sensitizer to efficiently donate an electron to the photooxidized chromophore. After four successive electron-donation events, the catalyst should be able to oxidize water and release oxygen. However, this approach can be synthetically demanding and few such reports have appeared.12-15

We previously reported an approach that takes advantage of codepositing a sensitizer and catalyst.16 This method avoids elaborate synthesis of linked sensitizer-catalyst complexes, allows variation of the sensitizer to catalyst ratio, and offers a modular design feature for screening different catalysts and light absorbers. Our initial work described a TiO₂ photoanode to which were attached both a high-potential porphyrin dye for light absorption and a Cp*-iridium catalyst for water oxidation. The photoanode optically resembled the porphyrin yet electrochemically responded like the Ir catalyst when immersed in aqueous solutions. Using photoelectrochemical methods, it was demonstrated that illumination of the codeposited anode resulted in enhanced and prolonged photocurrent, providing evidence for visible-light-induced activation of the catalyst.16 Codeposition of a sensitizer and catalyst has also shown promise in recent work by other groups.15,17

Here, we apply an alternative method18 for anchoring high-potential zinc–porphyrin sensitizers to TiO₂. Unlike our previous system, where zinc porphyrins were anchored to TiO₂ nanoparticles via covalently attached carboxylate groups at the meso-position of the porphyrin (Figure 1a), we now exploit the self-assembly chemistry of metalloporphyrins to N-donor ligands.18-29 In this design, the N-donor ligand is functionalized with an anchoring group that binds TiO₂ and serves as the linker between the dye and the metal oxide surface (Figure 1b).

A series of high-potential zinc porphyrins containing two, three, or four meso-substituted electron-withdrawing pentafluorophenyl groups, denoted ZnPF₁₀, ZnPF₁₅, and ZnPF₂₀, respectively (Figure 2), have been prepared and adsorbed onto TiO₂ using the assembly method shown in Figure 1b. The

Received: May 30, 2013
Revised: June 11, 2013
ability to tune the potential of the dye and systematically change the anchoring group provides a promising route to optimizing high-potential photoanodes for solar water splitting. The synthesis of unsymmetric porphyrins can be demanding, making the installation of a variety of anchoring groups on the periphery of the porphyrin synthetically challenging. Also, the most oxidizing of the high-potential porphyrins that we report here contains pentafluorophenyl groups at all four meso-positions, leaving fewer options for the installation of an anchoring group.

The most extensively studied anchoring groups for the attachment of chromophores to TiO₂ are carboxylates and phosphonates. Ruthenium polypyridyl-based and porphyrin-based sensitizers bound to TiO₂ via carboxylic acid anchoring groups can be relatively stable in DSSC applications. However, in an aqueous environment, as demanded in solar-to-fuel applications, the carboxylate anchor can detach from TiO₂. Alternatively, phosphonates have been used as robust anchors under aqueous conditions but are often less effective in promoting favorable interfacial electron-transfer dynamics as compared to carboxylic acids. A number of other substituents, including acetylacetonate and hydroxamic acid, have been proposed by us as suitable anchors for binding molecular chromophores to TiO₂, but a general

Figure 1. TiO₂ nanoparticulate films sensitized with (a) ZnPF₁₀-COOH bound directly via a carboxylic acid anchoring group at its meso-position and (b) ZnPF₁₀-diester bound indirectly via use of a preadsorbed isonicotinic acid linker (L₁).

Figure 2. (top) A series of high-potential zinc porphyrin sensitizers functionalized with two, three, or four pentafluorophenyl groups, denoted ZnPF₁₀-diester, ZnPF₁₅-ester, and ZnPF₂₀, respectively. (bottom) A series of linkers of the form 4-pyridyl-A, where A is anchoring group: carboxylic acid (L₁), phosphonic acid (L₂), acetylacetonate (L₃), or hydroxamic acid (L₄).
comparison of their relative stability on TiO₂ and electron-injection dynamics for the same sensitizer system is lacking. Here, a series of four linkers with different anchors were synthesized and investigated for the surface attachment of high-phosphonic acid (L4), phosphonic acid (L2), acetylacetonate (L3), or hydroxamic acid (L4).

■ METHODS

Sample Preparation and Characterization. All compounds were obtained or synthesized from commercially available starting materials (for experimental procedures, see Supporting Information, Synthesis and Structural Characterization). Absorption spectra were recorded using a Cary 3E UV−vis spectrophotometer (Agilent Technologies). Thin films of TiO₂ were highly scattering so absorbance spectra of all thin films were taken in diffuse reflectance geometry using an integrating sphere.

Preparation of TiO₂ Thin Films. Mesoporous thin films of TiO₂ were prepared using Degussa Aerioxide P25 titanium dioxide nanoparticles either by doctor-blading or, for better reproducibility, by spin-coating. Films for absorbance measurements and water-stability studies were prepared on microscope coverslips (25 × 25 mm for spin-coating, 22 × 50 mm for doctor-blading, Fisherbrand). Films for time-resolved terahertz spectroscopy measurements were prepared on fused quartz microscope slides (1 × 1 in., 1 mm thickness, GM Associates, Inc.). Films for scanning electron microscope (SEM) images were prepared on glass slides coated with conducting fluorine-doped tin oxide (FTO) (TEC 7, 1 × 1 in., 22 mm thickness, Hartford Glass Co, Inc.).

Doctor-Blading Method: A suspension of TiO₂ nanoparticles (1 g) in a 3:2 mixture of ethanol/deionized water (3 mL) was stirred for 24 h with a magnetic stir bar. A 2 × 2 cm area was framed out on the slides using 3M brand Scotch Gift Wrap tape. A thin layer of TiO₂ paste was swept across the surface using a stainless steel blade, and the tape was carefully removed. After drying at room temperature, the films were heated to 450 °C with a ramp rate of 5 °C/min and held at 450 °C for 2 h to sinter the films.

Spin-Coating Method: A suspension of TiO₂ nanoparticles (2 g) in a 1:1 mixture of ethanol/deionized water (8 mL) was sonicated for 1 h. Thin films were prepared by pipetting 0.5 mL of TiO₂ paste onto a slide rotating at 1000 rpm using a Headway PWM 32 spin coater (Headway Research Inc.). Films were dried at room temperature and sintered as described above. Applying a layer of TiO₂ paste at 1000 rpm, heating the slides to 200 °C for 10 min on a hot plate, and depositing a subsequent layer of TiO₂ paste at 1000 rpm yielded thicker films, which were then dried at room temperature and sintered. Single-layer deposition consistently resulted in 3.5 μm films (Figure S2), and double-layer deposition consistently yielded 7 μm films (Figure S3), as measured by SEM. Films with up to four TiO₂ applications (~14 μm) could be reproducibly prepared using this method.

Sensitization of TiO₂ Thin Films. For sensitizers bound directly to TiO₂ via anchoring groups on the porphyrin itself (Figure 1a), bare films were soaked overnight in the dark in a 0.1 mM solution of sensitizer in dichloromethane/ethanol (4:1) and rinsed thoroughly with copious amounts of the soaking solvent to remove unbound sensitizer.

For the modular assembly (Figure 1b), bare films were soaked overnight in the dark in a 0.5 mM solution of the desired linker (L1–L4) in ethanol and thoroughly rinsed with ethanol to remove unbound linker. The films were dried at room temperature for at least 30 min, soaked overnight in the dark in a 0.1 mM dichloromethane solution of the desired zinc porphyrin (ZnPF₁₀-diester, ZnPF₁₅-ester, or ZnPF₂₀), and rinsed with dichloromethane to remove uncoordinated or aggregated sensitizer. As seen in Figure S4, ZnPF₁₀-diester does not bind to TiO₂ in the absence of a linker.

Titration Studies. Stock solutions (100 mL, 0.055 mM) of zinc 5,15-bis(4-carboxyphenethyl)-10,20-bis(mesityl)-porphyrin (ZnPMe₅-diester) (0.48 mg), ZnPF₁₀-diester (0.53 mg), and ZnPF₂₀ (0.57 mg) were prepared in dichloromethane. Stock solutions were added to pyridine (0.56 μL) or 1-phenylimidazole (0.74 μL) to give a 4:1 ligand:porphyrin solution with a total volume of 25 mL. Appropriate volumes of the 4:1 ligand:porphyrin solution and the appropriate porphyrin stock solution were used to prepare solutions with varying molar ratios of ligand to porphyrin. Binding constants were calculated using the Rose–Drago method.⁴⁶

Methods for Water Stability Studies. To determine the water stability of porphyrin sensitizers directly bound to TiO₂ or coordinated via pyridyl linkers (L1–L4), as shown in Figure 1, dye-sensitized TiO₂ films were soaked in water in the dark for varying lengths of time, and changes were monitored using diffuse reflectance UV−vis spectroscopy measured in air. All samples were dried for 30 min at room temperature prior to characterization.

An alternate method was needed to determine the water stability of the linkers (L₁–L₄, Figure 2) on TiO₂ without coordinated porphyrin as the absorption features of the linkers were masked by the strong absorbance of TiO₂ below 400 nm (see Figures S5 and S6). TiO₂ films were sensitized with the desired linker as described above, soaked for 16 h in deionized water in the dark, dried at room temperature for 30 min, and then exposed to a solution of ZnPF₁₀-diester in dichloromethane (0.1 mM) overnight (Figure S7). These sensitized films were characterized by UV−vis spectroscopy in diffuse reflectance mode in air and compared to films sensitized using

![Figure 3. Energy level diagram showing the estimated ground-state and excited-state reduction potentials of the ZnPF₁₀-diester, ZnPF₁₅-ester, and ZnPF₂₀ porphyrin radical cation/porphyrin redox couples as well as the O₂/H₂O couple and the Ecb of TiO₂ at pH = 7. (Porphyrin potentials were obtained using cyclic voltammetry and normalized steady-state absorption and emission spectra (see Figure S1).)](image-url)
the modular assembly method described above, which were never exposed to an aqueous environment. Because the preparation of the TiO₂ thin films by spin-coating was more consistent than by doctor-blading, the resulting comparisons proved to be more reproducible across multiple samples.

Time-Resolved Terahertz (THz) 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 150 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 photoexcitation pump beam. The remainder of the near-IR light was used to generate THz radiation using optical rectification in a ZnTe(110) crystal and detected via free space electro-optic sampling in a second ZnTe(110) crystal. THz data were taken at room temperature, and the average of two samples was taken for each data set. All of the data were taken on the same day to minimize the effects of day-to-day THz signal variation. To analyze electron injection dynamics, the change in THz transmission was monitored as the time delay between the 400 nm pump pulse and the THz probe pulse was varied. Further information on the spectrometer and techniques can be found in the literature.57−49

RESULTS AND DISCUSSION

Optical Studies in Solution. Metalloporphyrins are known to interact with their ligands, such as nitrogenous bases, resulting in five-coordinate or six-coordinate complexes.50 For example, Zn tetraphenylporphyrin (ZnTPP) will coordinate a variety of nitrogen- and oxygen-containing donor ligands to form coordination complexes. A 1:1 ratio of pyridine to Zn porphyrin has been observed.51−53 Steady-state absorption spectra of ZnPF₁₀⁻diester titrated with an increasing concentration of pyridine indicates the formation of a 1:1 host–guest complex with a binding constant of 5.1856 M⁻¹ (Figures 4 and S9). Higher values were obtained for the more electron-deficient ZnPF₁₀⁻ dye (153.422 M⁻¹) and when using a more basic host molecule such as 1-phenylimidazole (288.201 M⁻¹) with ZnPF₁₀⁻, as shown in Table 1. The axial coordination of donor ligands such as pyridine to zinc porphyrins causes a red-shift in the absorption spectrum. For example, titrating ZnPF₁₀⁻diester with pyridine results in a red-shift of 13 nm, as shown in Table 1 and Figure 4.

Optical Studies of Sensitized Films. UV−vis spectroscopy was used to measure the optical transitions of the sensitizers bound to mesoporous nanoparticulate TiO₂ thin films. TiO₂ treated with isonicotinic acid (L₁) followed by ZnPF₁₀⁻-diester, as shown in Figure 1b, gives rise to optical transitions at energies similar to those observed when pyridine coordinates ZnPF₁₀⁻-diester in dichloromethane (Figure S5).

The optical transitions observed for TiO₂ films sensitized with isonicotinic acid (L₁) and ZnPF₁₀⁻-diester were also similar to those observed for TiO₂ sensitized with ZnPF₁₀⁻-COOH, which was anchored directly to the metal oxide surface (Figure S5). Relative to ZnPF₁₀⁻-diester in dichloromethane, a red-shift in the absorption spectrum of ZnPF₁₀⁻-COOH on TiO₂ was observed. This is likely because ethanol, which is used in the deposition solution for ZnPF₁₀⁻-COOH, axially coordinates the Zn metal center in the porphyrin, resulting in a ligand effect similar to that observed when pyridine is added. A similar red-shift in the absorption spectrum is observed when ethanol is added to a solution of ZnPF₁₀⁻-COOH in dichloromethane (see Figure S8).

Sensitizers with strong π−π interactions, such as porphyrins and organic donor−π-acceptor chromophores, can aggregate when immobilized on a surface, which often leads to decreased light-harvesting and electron-injection efficiency.55,56 We observe that zinc porphyrins attached directly to TiO₂ via anchoring groups at the meso-position of the porphyrin give rise to broad peaks in their absorption spectra, while sharper optical transitions are observed for the modular linker assembly on TiO₂, possibly due to a lesser degree of aggregation when using this arrangement. It is also possible that the linkers act as cosorbates to reduce the surface coverage of the porphyrins, which is a common technique used to prevent the aggregation of dyes on TiO₂ photoanodes.57,58 Further, changing the anchoring group on the pyridine linker does not affect the porphyrin transitions in the visible region, as shown in Figure 6.

Water Stability Studies on TiO₂. The water stability of the individual pyridine linkers on TiO₂ was evaluated both with and without coordinated porphyrin. Thin films of TiO₂ sensitized only with linker appeared white in most cases, with the exception of 4-pyridyldihydroxamate (L₄) on TiO₂, which appeared pale yellow (Figure S6). The water stability of each pyridine linker, L₁−L₄, on TiO₂ was tracked prior to porphyrin coordination using diffuse reflectance UV−vis spectroscopy (Figure 6a). TiO₂ thin films were sensitized with linker, soaked in water overnight, and then visualized by treating with ZnPF₁₀⁻-diester. These films were compared to samples that were never exposed to an aqueous environment.

TiO₂ films sensitized with the carboxylate linker (L₁) showed significant changes in absorbance after soaking overnight in water, consistent with dissociation of the linker from TiO₂. Less significant changes were observed in the case of the linkers containing phosphonic acid (L₂), acetylacetonate (L₃), and hydroxamic acid (L₄) anchoring groups, as seen in Figure 6a.

Absorption spectra of sensitized TiO₂ films prepared using the acetylacetonate-functionalized linker (L₃) often exhibited inconsistent absorption intensities despite consistent film preparation, which likely resulted from the instability of 4-pyridylacetylacetonate at room temperature as a solid and in solution. The free linker tends to decompose to the deacetylated 4-pyridylacetone via reverse Claisen condensation, as seen by NMR. However, once coordinated to the TiO₂ surface, the decomposition pathway is blocked.

![Figure 4. Absorption spectra of ZnPF₁₀⁻-diester in dichloromethane titrated with pyridine at room temperature. Ratios indicate the number of equivalents of pyridine added.](image-url)
The water stability of surface-bound linker−porphyrin complexes was also evaluated using UV−vis spectroscopy for samples where the linkers (L1−L4) on TiO2 were soaked in a solution of porphyrin dye (ZnPF10-diester) prior to exposure to water (Figure 6b). In this case the intensity of the absorption remained relatively unchanged for all assemblies even after soaking in water for several days. Additionally, there was little evidence of porphyrin dissociation from the surface, as evidenced by the absorption spectrum of the soaking solution. The porphyrin, thus, protects the anchors and prevents detachment. ZnPF10-COOH anchored directly to TiO2 also appeared stable under aqueous conditions for days. We attribute the stability of these surface-bound complexes to the insolubility of the porphyrin sensitizers in water.

**Time-Resolved Terahertz Studies.** Time-resolved THz spectroscopy (TRTS) was used to compare the relative efficiency of electron injection from the photoexcited sensitizers into the conduction band of the TiO2 nanoparticles. Because mobile electrons in the conduction band of TiO2 decrease the amount of THz radiation transmitted, the change in the THz transmission upon photoexcitation is correlated to a change in electron density in the conduction band. A greater change in THz amplitude (ΔTHz) is therefore associated with increased

![Figure 5. Normalized absorption spectra of a TiO2 thin film treated with isonicotinic acid (L1) followed by ZnPF10-diester taken in diffuse reflectance mode (black), ZnPF10-diester dissolved in dichloromethane treated with pyridine (red), and a TiO2 thin film sensitized with ZnPF10-COOH taken in diffuse reflectance mode (purple).](image1)

![Figure 6. (a) Absorption spectra tracking the water stability of linkers L1−L4 on TiO2: lighter lines correspond to films sensitized with L and then soaked in water overnight before coordinating ZnPF10-diester, and darker lines correspond to films sensitized with L + ZnPF10-diester that were not exposed to water. (b) Absorption spectra tracking the water stability of L + ZnPF10-diester complexes on TiO2 before soaking in water and after 1, 2, and 24 h in water.](image2)

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**Table 1. Binding Constants and UV−vis Parameters for Porphyrin/Ligand Complexes**

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<th>dye</th>
<th>ligand</th>
<th>binding constant (M−1)</th>
<th>dye λmax (nm)</th>
<th>dye ε at λmax (M−1 cm−1)</th>
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<td>23 850</td>
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<tr>
<td></td>
<td>imid</td>
<td>288 201</td>
<td>543</td>
<td>23 850</td>
<td>557</td>
<td>24 982</td>
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*Measured in dichloromethane at rt. Abbreviations: pyr = pyridine; imid =1-phenylimidazole; ZnPMes = zinc 5,15-bis(4-carbomethoxyphenyl)-10,20-bis(mesityl)porphyrin; ZnPF10 = ZnPF10-diester; ZnPF20 = zinc 5,10,15,20-tetra(pentafluorophenyl)porphyrin. For comparison, ZnTPP/pyr complex has a binding constant of 11 000 M−1 ([ZnTPP] = 3.0 × 10−5 M in dichloromethane) at rt.*

*E*
electron density in the conduction band resulting from increased electron injection efficiency.

For all of the species that exhibited electron injection, the rates of electron injection were within the \( \sim 400 \) fs instrument response time of the TRTS setup. These results are consistent with other TRTS measurements for similar porphyrin sensitizers. As a result, differences in injection rate cannot be resolved, only efficiencies.

Figure 7 compares the electron injection efficiency for the directly bound and axially bound versions of ZnPF\(_{10}\). Bare TiO\(_2\)

![Figure 7. Time-resolved THz data showing the relative electron injection of the following on TiO\(_2\): bare TiO\(_2\) (gray), ZnPF\(_{10}\)-diester (pink), L\(_1\) + ZnPF\(_{10}\)-diester (black), and ZnPF\(_{10}\)-COOH (purple).](image)

shows a negligible change in transmitted THz amplitude when illuminated with 400 nm light. Dye-sensitized TiO\(_2\) shows an observable change in THz amplitude when illuminated, as the dye sensitizes the metal oxide surface to absorption in the visible region. Photoexcitation of TiO\(_2\) films sensitized with L\(_1\) followed by ZnPF\(_{10}\)-diester using the modular assembly method resulted in a similar change in THz amplitude as for films sensitized with directly bound ZnPF\(_{10}\)-COOH, indicating similar electron injection efficiencies. When ZnPF\(_{10}\)-diester, which does not contain an anchoring group, was introduced to TiO\(_2\) in the absence of a linker, photoexcitation of the TiO\(_2\) film did not result in a significant change in THz amplitude. In this case, there is likely very little or no dye present on the surface (Figure S4).

Terahertz spectroscopy was also used to compare the relative electron injection onto TiO\(_2\) functionalized with L\(_1\)–L\(_4\) followed by ZnPF\(_{10}\)-diester (Figure 8). The TiO\(_2\) samples prepared with the isonicotinic acid (L\(_1\)) and 4-pyridylhydroxamate (L\(_4\)) linkers exhibited a larger change in the THz amplitude than 4-pyridylphosphonate (L\(_2\)) or 4-pyridylacetylacetonate (L\(_3\)) upon irradiation with light, indicative of more efficient electron injection from the porphyrin through carboxylate and hydroxamate linkers. Since the absorbances of these systems are similar at 400 nm (Figure S7), these differences are not due solely to differences in surface coverage. Additionally, these THz measurements, which indicate observable differences when the anchoring group for surface attachment to TiO\(_2\) is varied, have recently been correlated with molecular conductance calculations to aid in elucidating the effect of the anchor on the photoinduced interfacial electron-transfer efficiency.

In addition, the relative efficiency of electron injection from photoexcited Zn porphyrin dyes to TiO\(_2\) using linkers of varying length and basicity was investigated (Figure S10).

When linker length was increased compared to L\(_1\), by incorporating a phenyl ring between the N-donor pyridyl ligand and carboxylic acid anchoring group, the magnitude of the change in THz amplitude upon illumination of the sensitized films decreased. Similarly, when a more basic N-donor ligand, such as imidazole-benzoic acid, was employed to coordinate the ZnPF\(_{10}\)-diester dye to TiO\(_2\), the magnitude of the change in THz amplitude upon illumination again decreased as compared to L\(_1\) plus ZnPF\(_{10}\)-diester.

![Figure 8. Time-resolved THz data showing the relative electron injection of the following linkers plus ZnPF\(_{10}\)-diester on TiO\(_2\): isonicotinic acid L\(_1\) (black), 4-pyridylphosphonate L\(_2\) (green), 4-pyridylacetylacetonate L\(_3\) (red), and 4-pyridylhydroxamate L\(_4\) (blue).](image)

CONCLUSIONS

The modular assembly of high-potential porphyrin sensitizers on TiO\(_2\) via linkers with a series of different anchoring groups shows promise for testing and optimizing light-harvesting photoanodes for use in a visible-light-driven water-splitting photocell. This modular method offers the possibility for separately tuning the potential of the porphyrin dye and the anchoring group for surface attachment.

Our four classes of anchoring groups for TiO\(_2\)—carboxylates, phosphonates, acetylacetonates, and hydroxamates—were evaluated using this assembly technique. Isonicotinic acid linkers on TiO\(_2\) with coordinated porphyrin sensitizer showed relatively efficient electron injection, as evidenced by THz spectroscopy. However, the carboxylate linkers, without the presence of coordinated porphyrin, desorbed from the surface of TiO\(_2\) when soaked in water overnight. The phosphate linkers did not desorb in the absence of coordinating porphyrin, but dyes using this linkage are less efficient electron injectors. The linkers functionalized with acetylacetonate anchors performed similarly to the phosphate anchoring groups on TiO\(_2\) in terms of water stability and electron injection, but 4-pyridylacetylacetonate was unstable as a solid and in solution at room temperature prior to surface attachment. The hydroxamate linkers were both water-stable on TiO\(_2\) and injected electrons into TiO\(_2\) as well as the carboxylate linkers, proving to be the most practical among the anchoring groups studied here for use in water-splitting technologies.

In summary, the modular assembly method used in this work for the attachment of porphyrin photosensitizers to TiO\(_2\) requires significantly less synthetic effort compared to traditional methods, providing a relatively simple procedure for the preparation and optimization of high-potential, visible-light-harvesting photoanodes for comparing the relative robustness and efficiency of various anchor functionalities. The influence of
the relative surface coverage of each anchoring group will be addressed in upcoming work.

**ASSOCIATED CONTENT**

Synthesis and characterization of linkers L1–L4 and Zn porphyrin photosensitizers; SEM images of spin-coated TiO2 thin films; cyclic voltammetry, absorption spectra, and emission spectra of the high-potential porphyrin dyes; images of sensitized TiO2 thin films; additional solution and surface-bound absorption spectra of linkers L1–L4 and porphyrin dyes; and additional time-resolved terahertz data. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: robert.crabtree@yale.edu (R.H.C.), gary.brudvig@yale.edu (G.W.B.), charles.schmuttermayer@yale.edu (C.A.S.).

**Present Address**
[1] Joint Center for Artificial Photosynthesis (JCAP), Lawrence Berkeley National Laboratory, Berkeley, CA 94720.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the U.S. Department of Energy Grants DE-PS02-08ER15944 (L.A.M.: synthesis, characterization, optical studies) and DE-FG02-07ER15909 (R.L.M.: THz spectroscopy), the Camille & Henry Dreyfus Foundation (G.F.M.), and an NSF Graduate Research Fellowship (S.W.S.). SEM use was supported by the Yale Institute for Nanoscience and Quantum Engineering and NSF MRSEC DMR 1119826. The authors also acknowledge members of the Yale Green Energy Consortium for helpful discussions.

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The Journal of Physical Chemistry C
Supporting Information for

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Lauren A. Martini,a Gary F. Moore,a,b Rebecca L. Milot,a Lawrence Z. Cai,a Stafford W. Sheehan,a Charles A. Schmuttenmaer,a Gary W. Brudvig,a Robert H. Crabtreea

a. Yale Energy Sciences Institute and Department of Chemistry, Yale University, New Haven, CT 06520-8107

b. Currently at Joint Center for Artificial Photosynthesis (JCAP), Lawrence Berkeley National Laboratory, Berkeley, CA 94720

robert.crabtree@yale.edu, gary.brudvig@yale.edu, charles.schmuttenmaer@yale.edu

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Synthesis and Structural Characterization

Commercial reagents were used without further purification unless otherwise noted. Isonicotinic acid (L1) and 4-(1H-imidazol-1-yl)-benzoic acid were purchased from Aldrich and Maybridge, respectively. The photosensitizer ZnPMe$_{5}$ was prepared as previously described in the literature,$^{1}$ as were the high-potential zinc-porphyrin dyes ZnPF$_{10}$-diester and ZnPF$_{10}$-COOH.$^{2,3}$ Tetrakis(pentafluorophenyl)porphyrin was purchased from Aldrich and prior to use was refluxed for 4h in a 7.7 mM solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in bromobenzene (containing 2 equivalents of DDQ per porphyrin). The mixture was filtered through a short silica plug, rinsed through with hot toluene and the solvent was removed at reduced pressure. The residue was purified by column chromatography on silica using toluene as the eluent and converted to ZnPF$_{20}$ using a procedure similar to that used for ZnPF$_{10}$ and as previously described in the literature.$^{4}$ The photosensitizer ZnPF$_{15}$-diester was prepared using a modified literature procedure that is reported here.$^{5-7}$

Dichloromethane was purified on a 1 m alumina column prior to use (Innovative Technologies, Inc.). Analytical thin-layer chromatography was performed using glass plates purchased from EMD Chemicals that were pre-coated with silica gel 60 (250 μm) and impregnated with a fluorescent indicator (254 nm). TLC plates were visualized under ultraviolet (UV) light. Column chromatography was performed using silica gel 60 (40-63 μm particle size) purchased from EMD Chemicals.

NMR spectra were acquired using Bruker spectrometers operating at 400 or 500 MHz at 24 °C. Analytical ultra-high performance liquid chromatography/mass spectrometry (UPLC/MS) was performed on a Waters UPLC/MS instrument equipped with a dual atmospheric pressure chemical ionization (API)/electrospray (ESI) mass spectrometry detector and photodiode array detector. Samples were eluted over a reverse-phase C18 column (1.7 μm particle size, 2.1 x 50 mm) with a linear gradient of 20% acetonitrile–water containing 0.1% formic acid to 100% acetonitrile containing 0.1% formic acid over 3 min at a flow rate of 0.8 mL/min.
Scheme S1. Synthesis of 4-pyridyl-phosphonic acid (L2).

Diethyl-4-pyridyl-phosphonate (2a) was prepared according a modified literature procedure\textsuperscript{8,9} and used as a starting material for the synthesis of L2. 4-bromopyridine hydrochloride (3.11 g, 16 mmol) was neutralized using sodium carbonate (1.9 g, 18 mmol) in water (7 mL), extracted into toluene (15 mL total), and dried over anhydrous potassium carbonate. Diethylphosphite (2.4 mL, 18 mmol) and triethylamine (2.5 mL, 18 mmol) were added to the solution of 4-bromopyridine in toluene, and then cannulated under nitrogen into a round-bottom flask containing tetrakis(triphenylphosphine)palladium (0.93 g, 0.81 mmol), which was first washed with DMSO and dried under vacuum. The reaction mixture was stirred at 80 \degree C for 48 h under nitrogen, poured over 30 mL of toluene and washed with water (2 x 30 mL). The organic layer was dried over anhydrous potassium carbonate, and solvent was removed under reduced pressure. The resulting brown residue was purified by silica chromatography, eluting with ethyl acetate and increasing polarity to 10\% methanol in dichloromethane, to give a yellow oil. Yield: 1.36 g, 40%. \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 8.84 – 8.70 (m, 2H), 7.69 (ddd, $J = 13.3, 4.3, 1.5$ Hz, 2H), 4.33 – 3.96 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 6H).

4-pyridyl-phosphonic acid (L2). The dialkyl phosphonate (2a) was cleaved to yield the phosphonic acid (L2) according to a previously reported method.\textsuperscript{10} Bromotrimethylsilane (3 mL, 22.7 mmol) was added to a solution of 2a (1.36 g, 6.3 mmol) in dichloromethane (15 mL) and stirred at room temperature for 16 h under nitrogen. The solvent was removed to give a yellow precipitate that was dissolved in methanol (25 mL) and stirred at room temperature for 2 h. The resulting precipitate was filtered off, washed with cold ethanol then cold acetone, and dried under vacuum to give a white solid. Yield: 0.570 g, 55%. \textsuperscript{1}H NMR (400 MHz, DMSO) $\delta$ 11.67 (s, 1H), 8.71 – 8.67 (m, 2H), 7.59 (ddd, $J = 12.9, 4.3, 1.6$ Hz, 2H). ESI-MS $m/z$ [M+H]$^+$ calcd for C$_5$H$_6$NO$_3$P: 160.01. Obsd: 159.99. Anal calcd for C$_5$H$_6$NO$_3$P: C, 37.75; H, 3.80; N, 8.80. Found: C, 38.00; H, 3.74; N, 8.81.
3-(4-pyridyl)-acetylacetone \((L3)\) was prepared according to a previously reported literature procedure.\(^{11}\) A solution of 4-picoline (5 mL, 50 mmol) in chloroform (17 mL) was cooled to -20 °C in a bath of ethylene glycol, water, and dry ice. Acetyl chloride (2.9 mL, 40 mmol) was added dropwise via an addition funnel over 75 min under N\(_2\), resulting in a color change from clear to yellow to dark green. The solution was stirred an additional 3 h at -20 °C, solvent was removed under reduced pressure, and the residue was triturated with toluene. After filtering off the resulting red solid, a yellow solution was obtained. The toluene was removed under vacuum and the yellow oil was purified by silica chromatography using a 1:1 hexanes/ethyl acetate mixture and recrystallized from hexanes to give a light yellow solid. Recrystallization from hexanes gave the desired product as a white crystalline solid. The product was unstable at room temperature, both as a solid and in solution, and needed to be stored in a freezer to prevent decomposition to 4-pyridyl-acetone. Yield: 400 mg, 4.5%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 16.76 (s, 1H), 8.66 (d, \(J = 6.0\) Hz, 2H), 7.15 (d, \(J = 6.0\) Hz, 2H), 1.91 (s, 6H).

**Scheme S2.** Synthesis of 4-pyridyl-acetylacetonate (L3).

4-pyridyl-hydroxamic acid \((L4)\) was prepared according to a previously reported literature procedure.\(^{12}\) Hydroxylamine hydrochloride (4.28 g, 66 mmol) was dissolved in a solution of sodium hydroxide (5.28 g, 132 mmol) in water (33 mL) and added dropwise over 30 min to a solution of isonicotinic acid ethyl ester (5 mL, 33 mmol) in methanol (50 mL), resulting in a color change from colorless to yellow. The solution was stirred at room temperature for 72 h and acidified with 5% HCl to pH 5.5. Solvent was removed under reduced pressure. The yellow residue was dissolved in warm methanol, the undissolved sodium chloride was filtered off, solvent was removed from the filtrate under

**Scheme S3.** Synthesis of 4-pyridyl-hydroxamic acid (L4).
reduced pressure, and the resulting residue was recrystallized from water three times to give a white crystalline solid. Yield: 1.01 g, 22%. $^1$H NMR (400 MHz, DMSO) $\delta$ 11.53 (s, 1H), 9.31 (s, 1H), 8.70 (d, $J = 5.6$ Hz, 2H), 7.66 (d, $J = 5.7$ Hz, 2H). ESI-MS $m/z$ [M+H]$^+$ calcd for C$_6$H$_6$N$_2$O$_2$: 139.05. Obsd: 139.00. Anal calcd for C$_6$H$_6$N$_2$O$_2$: C, 52.17; H, 4.38; N, 20.23. Found: C, 52.20; H, 4.38; N, 20.23.

Scheme S4. Synthesis of 5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (PF$_{15}$-ester).

5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (PF$_{15}$-ester). A mixture of 5-(pentafluorophenyl)dipyrromethane$^6$ (1.25 g, 4.00 mmol), 4-carbomethoxybenzaldehyde (329 mg, 2.00 mmol), and pentafluorobenzaldehyde (247 $\mu$L, 2.00 mmol) in chloroform (400 mL) was purged with argon for 20 min before adding BF$_3$(OEt)$_2$ (530 $\mu$L of a 2.5 M stock solution in chloroform). After the mixture was stirred for 24 h at room temperature, DDQ (700 mg, 3.08 mmol) was added and the mixture was stirred for additional 2.5 h. The solvent was removed under 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 4 h. The crude reaction mixture was filtered through a short silica plug and rinsed through with hot toluene. The solvent was removed at reduced pressure and the crude product was purified by column chromatography on silica using toluene as the eluent. Recrystallization from methanol gave a purple crystalline solid. Yield: 283 mg, 15%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.87-8.94 (m, 6H, $\beta$H), 8.83 (d, $J = 4.5$ Hz, 2H, $\beta$H), 8.48 (d, $J = 8.2$ Hz, 2H, ArH), 8.31 (d, $J = 8.2$ Hz, 2H, ArH), 4.13 (s, 3H, CO$_2$CH$_3$), -2.87 (s, 2H, NH). $^{19}$F NMR (400 MHz, CDCl$_3$) $\delta$ -161.61 – -161.34 (m, 6F, ArF), -151.56 (t, $J = 20.7$ Hz, 2F, ArF), -151.50 (t, $J = 20.7$ Hz, 1F, ArF), -136.65 (dd, $J = 8.0$ Hz,
22.9 Hz, 4F, ArF), -136.51 (dd, $J = 8.0$ Hz, 22.9 Hz, 2F, ArF). MALDI-TOF-MS $m/z$ calcd for C$_{46}$H$_{17}$F$_{15}$N$_4$O$_2$: 942.111. Obsd: 942.115.

Scheme S5. Synthesis of Zinc 5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (ZnPF$_{15}$-ester).

Zinc 5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (ZnPF$_{15}$-ester). Zn(OAc)$_2$·2H$_2$O (384 mg, 1.75 mmol) dissolved in methanol (5 mL) was added to a solution of 5-(4-carbomethoxyphenyl)-10,15,20-(pentafluorophenyl)porphyrin (110 mg, 0.117 mmol) in dichloromethane (20 mL) and stirred at room temperature for 1 h. The mixture was then stirred at reflux for 1 h. After cooling to room temperature, the solution was diluted with dichloromethane (50 mL) and washed with water (75 mL) followed by a saturated solution of aqueous sodium bicarbonate (75 mL). The organic phase was dried over sodium sulfate, filtered, and solvent was removed under reduced pressure. The product was purified by silica chromatography using toluene as the eluent to give a dark pink powder. Yield: 112 mg, 95%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.97-9.01 (m, 6H, $\beta$H), 8.92 (d, $J = 4.4$ Hz, 2H, $\beta$H), 8.42 (d, $J = 8.2$ Hz, 2H, ArH), 8.30 (d, $J = 8.2$ Hz, 2H, ArH), 4.08 (s, 3H, CO$_2$CH$_3$). $^{19}$F NMR (400 MHz, CDCl$_3$) $\delta$ -161.96 – -161.68 (m, 6F, ArF), -152.18 (t, $J = 20.7$ Hz, 2F, ArF), -152.12 (t, $J = 20.7$ Hz, 1F, ArF), -136.93 (dd, $J = 8.0$ Hz, 22.9 Hz, 4F, ArF), -136.82 (dd, $J = 8.0$ Hz, 22.9 Hz, 2F, ArF).
Characterization of High-Potential Porphyrin Dyes

**Figure S1.** Cyclic voltammograms (center) recorded in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$), and normalized steady-state absorption (solid lines) and emission (dashed lines) spectra in dichloromethane (right) of (a) ZnPF$_{10}$-diester, (b) ZnPF$_{15}$-ester, and (c) ZnPF$_{20}$.

Cyclic voltammetry was performed with an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat using a glassy carbon working electrode, a platinum counter electrode, and a silver wire pseudoreference electrode in a conventional three-electrode cell. The potential of the
pseudoreference electrode was determined using the ferrocenium/ferrocene redox couple as an internal
standard (E_{1/2} taken as 0.690 V vs. NHE in dichloromethane).^{13} The voltammograms were recorded at a
100 mV/s scan rate. All reduction potentials are referenced to the normal hydrogen electrode (NHE).

Absorbance spectra were measured using a Cary 3E spectrophotometer and emission spectra were
measured using a Shimadzu RF 5301-PC spectrometer.

The coordination of pyridine to the high-potential Zn porphyrin dyes (ZnPF_{10}, ZnPF_{15}, ZnPF_{20}) will
alter the optical and electronic properties of the porphyrins. The pyridine-porphyrin complexes will
have slightly smaller E^{00} values (resulting in a red-shift in the absorption spectrum) and more oxidizing
ground-state reduction potentials (more positive E_{1/2} values) than the porphyrin dyes alone. However, as
shown by THz spectroscopy, the photoinduced electron injection from pyridyl-bound porphyrins into
TiO_{2} is still favorable (Figures 7 and S10).
SEM Images of Spin-Coated TiO₂ Thin Films

Images of TiO₂ thin films were obtained using a Hitachi SU-70 scanning electron microscope (SEM).

**Figure S2.** Single application of TiO₂ spin-coated at 1000 rpm consistently gave ~3.5 µm thin films. Image shows TiO₂ on FTO-coated slide.

**Figure S3.** Double application of TiO₂ spin-coated at 1000 rpm consistently gave ~7 µm thin films. Image shows TiO₂ on FTO-coated slide.
Images of Sensitized TiO₂ Thin Films

**Figure S4.** TiO₂ nanoparticulate films sensitized with (a) ZnPF₁₀-COOH bound directly via a carboxylic acid anchoring group at its meso-position, (b) ZnPF₁₀-diester bound indirectly via use of a preadsorbed isonicotinic acid linker (L₁), and (c) ZnPF₁₀-diester, containing no anchoring groups, in the absence of any linkers. (Inset: Photographs of sensitized TiO₂ thin films doctor-bladed onto FTO slides.)
Figure S5. Absorption spectra of 4-pyridyl-A (0.3 mM in 95% ethanol), where A is carboxylic acid (L1, $\varepsilon = 2505 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda = 272\text{ nm}$) (black), phosphonic acid (L2 $\varepsilon = 3896 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda = 263\text{ nm}$) (green), or hydroxamic acid (L4, $\varepsilon = 4314 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda = 263\text{ nm}$) (blue). The solution absorption spectrum of 4-pyridyl-acetylacetone L3 is not included as it decomposes to a yellow oil at room temperature.
Figure S6. Absorption spectra of a TiO$_2$ thin film (gray) and 4-pyridyl-A on TiO$_2$, where A is carboxylate L1 (black), phosphonate L2 (green), acetylacetonate L3 (red), and hydroxamate L4 (blue), taken in diffuse reflectance mode.
Figure S7. Absorption spectrum of a TiO$_2$ thin film (gray) compared to TiO$_2$ films treated with 4-pyridyl-A followed by ZnPF$_{10}$-diester, where A is carboxylate L1 (black), phosphonate L2 (green), acetylacetonate L3 (red), and hydroxamate L4 (blue), taken in diffuse reflectance mode.
Figure S8. Normalized absorption spectra comparing a TiO$_2$ thin film treated with ZnPF$_{10}$-COOH taken in diffuse reflectance mode (*purple*), ZnPF$_{10}$-COOH in dichloromethane solution (*dashed gray*), and ZnPF$_{10}$-COOH in dichloromethane solution in the presence of ethanol (*gray*).
Job Plot

It is possible to use the titration data in Figure 4 to construct a Job Plot in order to verify that the ZnP:Pyridine complexes are indeed 1:1 host-guest complexes. ZnPF_{10}-diester will be referred to as ZnP, pyridine will be referred to as Py, and the complex that is formed will be referred to as ZnP-Py\(_n\). The goal is to determine whether \(n = 1\) or \(n = 2\).

The blue line in Figure 4 of the main text is for pure ZnP at a relative concentration of 1. The red line is for pure ZnP-Py\(_n\) at a relative concentration of 1, where \(n\) is equal to either 1 or 2. This is because the Py does not absorb in this region of the spectrum, and when the relative concentration of Py is 40 times greater than that of ZnP, all of the ZnP is in the complexed form of ZnP-Py\(_n\).

The equilibrium in question is: ZnP + \(n\) Py \(\rightleftharpoons\) ZnP-Py\(_n\). At equilibrium, the relative concentration of ZnP-Py\(_n\) will be \(y\), leaving behind a relative concentration of \((1.0 - y)\) of ZnP since the initial relative concentration of ZnP is 1.0 in each spectrum.

The measured spectrum at a given relative concentration of Py is a linear combination of the blue spectrum and the red spectrum in Figure 4, where the blue is multiplied by \((1 - y)\) and the red is multiplied by \(y\). The beautiful isosbestic point assures us that all of these intermediate spectra are linear combinations of the two individual spectra.

Furthermore, we can determine the value of \(y\) using only the values of the absorbances at 559 nm, the wavelength of the peak value of the spectrum of the ZnP-Py\(_n\) complex (red curve in Figure 4).

For each spectrum, the absorbance at 559 nm, denoted \(A_{559}\), is a linear combination of that for ZnP at 559 nm \((A_{ZnP,559})\) and ZnP-Py\(_n\) at 559 nm \((A_{ZnP-Py\_n,559})\). Thus, \(A_{559} = (1.0 - y)A_{ZnP,559} + yA_{ZnP-Py\_n,559}\). Upon
rearrangement: 

\[ y(\Delta A_{\text{ZnP-Py,559}} - \Delta A_{\text{ZnP,559}}) = A_{\text{559}} - A_{\text{ZnP,559}}, \]

and we can now solve for \( y \):

\[ y = \frac{A_{\text{559}} - A_{\text{ZnP,559}}}{A_{\text{ZnP-Py,559}} - A_{\text{ZnP,559}}}. \]

A Job Plot (Figure S9) is made by plotting \( \frac{y}{[\text{ZnP}]_0 + [\text{Py}]_0} \) as a function of \( \frac{[\text{ZnP}]_0}{[\text{ZnP}]_0 + [\text{Py}]_0} \). From this, it is clear that it is a 1:1 host-guest complex since the peak value occurs at 0.50. If it were a 1:2 complex, then the Job Plot would have its peak value at 0.333.

\[ \frac{y}{[\text{ZnP}]_0 + [\text{Py}]_0} \]

\[ \frac{[\text{ZnP}]_0}{[\text{ZnP}]_0 + [\text{Py}]_0} \]

**Figure S9.** Job Plot constructed from the titration data in Figure 4 in the manner described above.
Additional Time-Resolved Terahertz Data

Figure S10. Time-resolved THz data showing the relative electron injection of linkers of varying length and basicity plus ZnPF$_{10}$-diester on TiO$_2$, including isonicotinic acid L1 (*black*), 4-pyridinylbenzoic acid (denoted 4-pyr-Ph-COOH) (*dark red*), and 4-(1H-imidazol-1-yl)-benzoic acid (denoted imidazole-Ph-COOH) (*dark blue*).

The relative efficiency of electron injection from photoexcited Zn-porphyrin dyes to TiO$_2$ using linkers of varying length and basicity was also investigated. We found that when the more basic N-
donor imidazole-benzoic acid ligand (Imidazole-Ph-COOH) was used, the magnitude of the change in THz amplitude upon photoexcitation decreased as compared to when a less basic pyridine ligand was employed. When linker length was increased compared to \textit{L1} by incorporating a phenyl ring between the N-donor ligand and carboxylic acid anchoring group, as in the case of both imidazole-benzoic acid and 4-(4-pyridyl)benzoic acid (\textit{4-pyr-Ph-COOH}), the magnitude of the change in THz amplitude upon illumination of the sensitized films also decreased. The observed decrease in efficiency of electron transfer when employing longer linkers, as evidenced by THz spectroscopy, is consistent with a similar trend reported in the literature for the rate of forward electron transfer from photoexcited ZnTPP donors coordinated to C\textsubscript{60} acceptors using either pyridyl linkers or longer phenyl-imidazole linkers. In this system, the rate of forward electron transfer for the shorter pyridyl linker was about 20 times greater than the rate observed for the longer phenyl-imidazole linker, as observed by time-resolved transient absorption spectroscopy.\textsuperscript{14}
References


