Hydroxamate Anchors for Improved Photoconversion in Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: We present the first analysis of performance of hydroxamate linkers as compared to carboxylate and phosphonate groups when anchoring ruthenium-polypyridyl dyes to TiO₂ surfaces in dye-sensitized solar cells (DSSCs). The study provides fundamental insight into structure/function relationships that are critical for cell performance. Our DSSCs have been produced by using newly synthesized dye molecules and characterized by combining measurements and simulations of experimental current density–voltage (J–V) characteristic curves. We show that the choice of anchoring group has a direct effect on the overall sunlight-to-electricity conversion efficiency (η), with hydroxamate anchors showing the best performance. Solar cells based on the pyridyl-hydroxamate complex exhibit higher efficiency since they suppress electron transfer from the photoanode to the electrolyte and have superior photoinjection characteristics. These findings suggest that hydroxamate anchoring groups should be particularly valuable in DSSCs and photocatalytic applications based on molecular adsorbates covalently bound to semiconductor surfaces. In contrast, analogous acetylacetone anchors might undergo decomposition under similar conditions suggesting limited potential in future applications.

INTRODUCTION

The efficient utilization of solar energy is a promising solution to current energy and environmental concerns.¹ Traditional photovoltaic devices, however, are based on costly p-n junctions of high-quality silicon wafers, making solar cells affordable only at a moderate scale, or for specific applications (e.g., satellites).²,³ Therefore, there has been significant interest in the development of alternative solar cells based on inexpensive materials such as dye-sensitized solar cells (DSSCs) made of sensitized nanoparticulate thin-films.⁴ Since the work by O’Regan and Grätzel in 1991,⁵ DSSCs quickly reached conversion efficiencies >10%.⁶ However, only modest improvements in efficiency have been reported over the last 20 years since these initial breakthroughs.⁷–⁹ This has been partially due to the lack of understanding of how the various redox/transport processes determine the overall cell performance and how they are affected by the nature of the assembly components. In this article, we focus on the effect of anchoring groups on the overall sunlight-to-electricity conversion. To the best of our knowledge, this is the first analysis of performance of hydroxamate linkers as compared to carboxylate and phosphonate groups when anchoring ruthenium-polypyridyl dyes to TiO₂ surfaces, in complete dye-sensitized solar cells (DSSCs).

Figure 1 shows a schematic diagram of a DSSC, including the photoexcitation, redox, and transport processes initiated by absorption of visible light. While the TiO₂ band gap lies in the UV region (at approximately 3.0–3.2 eV),¹⁰ functionalization of TiO₂ surfaces with dye molecules sensitizes them to absorption of visible light. Electrons are transferred to the conduction band of the semiconductor upon photoexcitation of a dye to an excited electronic state that is isoelectronic with electronic states in the TiO₂ conduction band. The injected electron can flow through an external circuit and be collected by the counter-electrode. A redox mediator, most commonly I⁻/I⁺, then accepts the electron from the cathode and fills the hole left on the dye.⁴ Important aspects for optimization of the cell performance are, thus, selection of the dye and its attachment motif to the semiconductor surface.

Many of the most efficient DSSC dyes are ruthenium-polypyridyl complexes.⁶,⁷,¹¹–¹³ Small variations in the dye structure can lead to large changes in the overall cell performance.¹⁴ Ligand exchange affects the visible absorption, and thus the overall efficiency, of Ru(dcbpy)₂X₂ (dcbpy = 2,2′-bipyridyl-4,4′-dicarboxylate, X = Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻) with the thiocyanate complex giving the best performance.⁸ Other important changes that can dramatically affect solar cell efficiency are the protonation state of the carboxylate anchoring groups in Ru(dcbpy)₂(NCS)₂¹³ and modifications of the pyridyl-based ligands.⁹ Impressively, Ru(dcbpy)₂(NCS)₂, and other analogous complexes have been shown to have incident photon to charge carrier conversion efficiencies of unity across portions of the visible spectrum.⁶,⁷,¹²,¹³

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Though effective in DSSCs, dyes bearing carboxylate anchors have been shown to have limited stability in aqueous and highly oxidizing conditions.15,16 This would make them unsuitable for use in an artificial photosynthetic cell. In such a device the redox mediator is removed and the acetonitrile solvent is replaced by water. The circuit is then closed by oxidation of water to dioxygen at the anode and cathodic reduction of the generated protons to dihydrogen.10,17 A few examples of functional water-splitting cells based on such scheme have been reported,18−22 showing promise of a viable way of capturing and storing solar energy.

Many water stable anchoring groups have been suggested as replacements for carboxylates in DSSC and artificial photosynthetic applications. Phosphonate anchors are the most commonly implemented,15,16,23,24 although hydroxamate,25−27 catecholate,28,29 and acetylacetonate anchors have also been explored. To date, however, most reported water-splitting devices based on molecular catalysts have employed phosphonates to anchor the dye molecules to TiO2 thin-films.21,22

Phosphonate anchors bind to TiO2 surfaces more tightly than carboxylates.16 However, they are usually less efficient than carboxylates at facilitating interfacial electron transfer.34,35 Additionally, the decrease in injection rate does not always correlate with a decrease in photoconversion efficiency. In fact, there are examples of systems in which ruthenium dyes bound through phosphonic acid anchors outperform their carboxylate counterparts because of differential rates of other charge transfer processes required for cell operation.24,37 Recently, an attempt to combine the binding affinity of the phosphonate anchor with the electron injection efficiency of carboxylates was reported.38 Though this method proved successful for the reported sensitizer, applications may be limited because of the geometric constraints imposed by this strategy.

In contrast to phosphonates, hydroxamates have been shown to bind more tightly to semiconductor surfaces and inject electrons into TiO2 more efficiently than the industry-standard carboxylates, thus resolving both issues with a single anchor.25,39 These advantages are presumably due to dianionic character. Specifically, hydroxamic acids, R-CONHOH, can undergo facile double deprotonation, thus providing dianionic anchoring groups that readily form oxidation- and water-stable 5-membered chelate rings with suitable metal ions (eq 1). In this way, hydroxamic acids find use in both pharmacological and bioinorganic applications, acting as metal-binding groups in drugs and siderophores, respectively.40 While ruthenium complexes with acetylacetonate anchors have been studied,33 ruthenium complexes bearing hydroxamate anchors have not been investigated for solar applications, probably because of the lack of previously established synthetic pathways. Additionally, the direct effect of the hydroxamate anchor on sunlight-to-electricity conversion efficiency has not been previously investigated. In fact, to the best of our knowledge, no DSSC data has been previously reported for a dye bearing a hydroxamate anchor.

This paper focuses on the synthesis of ruthenium dyes that differ only in their anchoring group and the analysis of their performance in DSSCs. We analyze our own series of new dyes of the form [Ru(terpy)(tbbpy)L][BF4]2 (terpy = 2,2′;6,2″-terpyridine, tbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine, L = anchoring ligand), that have been synthesized, characterized spectroscopically, and tested for their efficiency in complete DSSC assemblies. Their relative performance is assessed through measurements of the current−voltage (J−V) characteristic curves and simulations of the J−V curves based on an equivalent circuit model, as in previous work.41 The analysis shows how different anchoring groups affect photoconversion efficiency by changing the various current components, including photoinjection, recombination, and the shunt current. Hydroxamate complexes
are shown to give the highest overall sunlight-to-electricity conversion efficiency ($\eta$), while acetylacetonate dyes are shown to be susceptible to decomposition, limiting their potential in DSSC applications. We propose, based on our findings, that hydroxamate anchors are a viable, synthetically accessible alternative to carboxylates for future artificial photosynthesis devices.

### RESULTS AND DISCUSSION

**Synthesis and Characterization.** Recently we published a report detailing thiocyanate linkage isomerism in $[\text{Ru(terpy)}(\text{tbbpy})\text{SCN}][\text{SbF}_6]_{\text{4}}$.\textsuperscript{42} In the synthesis of this complex, halide was first abstracted from the chloride precursor, $[\text{Ru(terpy)}(\text{tbbpy})\text{Cl}]\text{Cl}$ (1), in ethanol and potassium thiocyanate added to the resulting solvento intermediate. Using this route as a model, we were able to isolate the aqua complex $[\text{Ru(terpy)}(\text{tbbpy})\text{OH}_2][\text{BF}_4]$ (2) after anion metathesis with silver tetrafluoroborate in a 3:1 mixture of acetone and water. The bound water can then exchange with other ligands, but only slowly at room temperature. Full conversion to the dimethyl sulfoxide complex in $d_6$-dimethyl sulfoxide requires several hours, as shown by $^1$H NMR data. As a result of this ligand exchange and the limited solubility of the aqua complex in water, we were unable to record a $^{13}$C NMR spectrum of the aqua complex,\textsuperscript{2}

Encouraged by this isolation of 2, we then set out to synthesize complexes of the form $[\text{Ru(terpy)}(\text{tbbpy})(\text{pyr-L})][\text{BF}_4]_{\text{2}}$ where pyr-L is isonicotinic acid (pyr-COOH), N-hydroxyisonicotinamide (pyr-hydrox), pyridin-4-ylphosphonic acid (pyr-phos), and 3-(pyridin-4-yl)pentane-2,4-dione (pyr-acac) so as to equip the complex with a series of anchor groups. The complex $[\text{Ru(terpy)}(\text{tbbpy})(\text{pyr-COOH})][\text{BF}_4]_{\text{2}}$ (3) was generated in good yield by adding an excess of isonicotinic acid to 2 in refluxing methanol (Scheme 1). Unfortunately, simple addition of pyr-hydrox or pyr-phos\textsuperscript{39} to the starting aqua species generated an inseparable mixture of products.

Assuming that the problem with the hydroxamate and phosphonate syntheses was caused by unwanted coordination of the acid groups to ruthenium, a protection–deprotection strategy was devised. Refluxing tetrahydropyran-protected pyr-hydrox\textsuperscript{43} and 2, in the presence of silver tetrafluoroborate in methanol, followed by washing with aqueous tetrafluoroboric acid, generated $[\text{Ru(terpy)}(\text{tbbpy})(\text{pyr-hydrox})][\text{BF}_4]_{\text{2}}$ (4) in a two-step, one-pot synthesis. The ethyl-protected phosphonate complex, $[\text{Ru(terpy)}(\text{tbbpy})(\text{pyr-PO(OEt)}_2)][\text{BF}_4]_{\text{2}}$ (5), was likewise generated by addition of pyridin-4-yl diethylphosphonate (pyr-PO(OEt))\textsuperscript{44} to 2 in refluxing methanol in the presence of silver tetrafluoroborate. Exposure of 5 to bromotrimethylsilane in dry dichloromethane yielded the desired phosphonate complex, $[\text{Ru(terpy)}(\text{tbbpy})(\text{pyr-phos})][\text{BF}_4]_{\text{2}}$ (6) (Scheme 2).

Synthesis of the 3-(pyridin-4-yl)pentane-2,4-dione complex proved to be much more difficult. Pyr-acac was synthesized by a literature method, recrystallized from hexanes, and isolated as a white crystalline solid.\textsuperscript{45} However, on standing at room temperature, the complex rapidly decomposed to 1-(4-pyridinyl)-propan-2-one (pyr-acetone), presumably in a water-assisted deacetylation. As a result of this decomposition, addition of pyr-acac to 2 in refluxing methanol always generated a mixture of $[\text{Ru(terpy)}(\text{tbbpy})(\text{pyr-acac})][\text{BF}_4]_{\text{2}}$ (7) and $[\text{Ru(terpy)}-$
Instead, a strategy for synthesizing aryl acetylacetonates from 3,5-dimethylisoxazole precursors was explored. However, the conversion of the ruthenium-bound 3,5-dimethyl-4-(pyridin-4-yl)isoxazole to pyr-acac, which requires vigorous reflux in the presence of Mo(CO)₆ or other harsh conditions, was unsuccessful (Scheme 3).

Unsure if the mixture of complexes 7 and 8 would lead to a mixture of surface bound complexes as well, we set out to synthesize 8 in pure form. Addition of 1-(pyridin-4-yl)propan-2-one to 2 in refluxing methanol generated 8 in modest yield. Unfortunately, titanium dioxide films sensitized with 8 did show visible absorption indicating a weak interaction with the semiconductor surface (vide infra). To examine if this adsorption was covalent or electrostatic, the complex [Ru(terpy)(tbbpy)-(pyridine)][BF₄]₂ (9) was synthesized in a similar manner. Even without an anchoring moiety, the pyridine complex (9) exhibited a similar visible absorption as 8 on the surface of titanium dioxide indicating that an electrostatic interaction could be sufficient for weak binding (vide infra). This does not, however, exclude the possibility of the tautomerization of 8 to the enol followed by deprotonation in the presence of titanium dioxide to form the enolate, which could subsequently bind the metal oxide surface.

Comparing the performance of all four anchoring groups was complicated by the instability of pyr-acac, and led us to switch from pyridine-based ligands to N-phenylimidazole-based ligands. N-phenylimidazole was chosen for its greater length, possibly allowing for better accessibility of the anchoring moiety to the titanium dioxide surface, and because its lone pairs are slightly more basic than those of pyridine, which could help stabilize coordination of this monodentate ligand to ruthenium during solar cell operation. Synthesis of the carboxylate complex was achieved by refluxing 4-(1H-imidazol-1-yl)benzoic acid (im-ph-COOH) and 2 in ethanol for 48 h to form [Ru(terpy)(tbbpy)-(pyr-acetone)][BF₄]₂ (8) consisting mostly of the pyr-acetone complex. Instead, a strategy for synthesizing aryl acetylacetonates from 3,5-dimethylisoxazole precursors was explored. However, the conversion of the ruthenium-bound 3,5-dimethyl-4-(pyridin-4-yl)isoxazole to pyr-acac, which requires vigorous reflux in the presence of Mo(CO)₆ or other harsh conditions, was unsuccessful (Scheme 3).

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The hydroxamate and phosphonate N-phenylimidazole complexes were also obtained in a procedure similar to that used for their pyridyl analogues. 4-(1H-imidazol-1-yl)-N-(((tetrahydro-2H-pyran-2-yl)oxy)benzamide (11) was made from 4-(1H-imidazol-1-yl)benzoic acid by conversion to the acid chloride in neat thionyl chloride followed by treatment with O-((tetrahydro-2H-pyran-2-yl)hydroxylamine in dry dichloromethane under nitrogen. 11 was then mixed with 2 in refluxing.
methanol in the presence of silver tetrafluoroborate. After washing with aqueous HBF₄, [Ru(terpy)(tbbpy)(im-ph-hydrox)][BF₄]₂ (im-ph-hydrox = N-hydroxy-4-(1H-imidazol-1-yl)benzamide) (12) was obtained (Scheme 5).

Similarly, diethyl(4-(1H-imidazol-1-yl)phenyl)phosphonate (im-ph-PO(OEt)₂, 13), which was formed by cross-coupling 1-(4-bromophenyl)-1H-imidazole and diethyl phosphate in toluene in the presence of triethylamine and Pd(dppf)-Cl₂-dichloromethane (dppf = 1,1'-bis-diphenylphosphinoferro-cene) as catalyst, 48 was mixed with 2 in refluxing methanol in the presence of silver tetrafluoroborate to give [Ru(terpy)(tbbpy)-(im-ph-PO(OEt)₂)][BF₄]₂ (14). Treatment of 14 with bromo-trimethylsilane44 in dichloromethane yielded the deprotected phosphonic acid complex, [Ru(terpy)(tbbpy)(im-ph-phos)][BF₄]₂ (15) (im-ph-phos = 4-(1H-imidazol-1-yl)phenyl)-phosphonic acid) (Scheme 5).

Finally, a strategy for synthesizing the acetylacetonate N-phenylimidazole complex, again from its 3,5-dimethylisoxazole precursor, was explored. Suzuki coupling of 1-(4-bromophenyl)-1H-imidazole and 4-(4,5-dimethyl-1,3,2-dioxaborolan-2-yl)-3,5-dimethylisoxazole using Pd(PPh₃) and Ba(OH)₂47 as base in a 9:1 mixture of dimethoxysilane and water gave 4-(1H-imidazol-1-yl)phenyl)-3,5-dimethylisoxazole (16). Treatment of 16 with Mo(CO)₆ in vigorously refluxing acetonitrile/water (1:1, v:v) followed by addition of oxalic acid in aqueous ethanol yielded 3-(4-(1H-imidazol-1-yl)phenyl)-2,4-pentanedione (im-ph-acac, 17) in high purity after several recrystallizations from hexanes. 17 is a white crystalline solid and, unlike its pyridyl analogue, is stable for several weeks at room temperature or indefinitely if stored in a freezer. All attempts to metatlate 17 resulted in a mixture of the desired im-ph-acac product 18 and its deacetylated analogue 19. Unfortunately, 18 could not be isolated from the mixture (Scheme 6).

Because of these synthetic difficulties and the need for analytically pure material, we then stopped pursuit of the acetylacetonate complexes. This deacetylation pathway is likely to hinder other systems seeking to use acetylacetonate functionalized at the 3 position to anchor sensitizers to titanium dioxide. In the best case, it will limit yields of synthesized dyes, and in the worst case, as we have observed here, it could make synthesis of pure species impossible.

**Spectroscopic Characterization.** The visible absorption characteristics of our catalog of complexes were measured in two ways. First, absorption spectra were recorded in ethanol solution at a concentration of 0.1 mM. Results are displayed in Figure 2, and show similar spectral characteristics for all of the synthesized complexes, regardless of the anchoring moiety present. Complexes with pyridyl-based anchoring ligands show two absorbance maxima, at 425 and 466 nm, with maximal molar extinction coefficients between 8000 and 10300 M⁻¹ cm⁻¹.

Figure 2. UV/visible spectra of newly synthesized dyes in 0.1 mM ethanol solution. Top: [Ru(terpy)(tbbpy)(pyr-L)][BF₄]₂. Bottom: [Ru(terpy)(tbbpy)(im-ph-L)][BF₄]₂. 

Complexes with imidazole-based anchoring ligands have red-shifted absorbance maxima, resulting in a broad peak with shoulders at either 469 or 488 nm. Molar absorptivities for the imidazole complexes range between 7200 and 8800 M⁻¹ cm⁻¹.

Next, emission spectra and cyclic voltammograms of dyes 3, 4, and 6 bearing pyridyl ligands were recorded (see Supporting Information). The aqua complex, 2, was also investigated in this manner. As can be seen in Figure 3, the energy levels for both the ground state oxidation (E_{1/2}) and the first excited state (S*) are not greatly perturbed by the variation in the anchoring moiety. Interestingly, the spectra of 2 also show very similar ground and excited state energies. Importantly, each of the newly synthesized dyes has an excited state which is poised to inject electrons into TiO₂ and a ground state which is thermodynamically capable of oxidizing I⁻ to close the circuit in a functioning DSSC. Given the similarities between these dyes, it can be assumed that dyes 10, 12, and 15 will also not show great variance in their electronic characteristics.

Finally, to determine how the absorbance features of the complexes change upon binding to TiO₂, visible absorption spectra of nanoparticle films sensitized with the dye molecules were recorded (Figure 4). For the most consistent and comparable data, films for UV/vis were made by spin-coating colloidal titanium dioxide (1.0 g TiO₂ suspended in 4 mL of 1:1
ethanol:water) onto glass coverslips at 1000 rpm. Films were then sintered at 450 °C for 2 h. Finally, slides were soaked in 0.3 mM ethanolic solutions of dye for 36 h to ensure maximum coverage. Because the spectra were recorded using diffuse reflectance with an integrating sphere we cannot directly estimate dye surface coverage from the UV−vis data. However, the spectra were highly reproducible for sensitized films prepared from the same dye solution across multiple sample preparations. Thus, it would seem that there is differentiation among the various anchoring moieties in their ability to bind the surface. Our data are consistent with previous work suggesting a higher TiO2 binding affinity for phosphonates compared to carboxylates.23,35,49

The presence of any absorbance features in the visible region indicates the presence of dye on the surface of titanium dioxide. This is especially significant in the cases of aqua complex 2, pyr-acetone complex 8, and pyridine complex 9 as they do not bear traditional anchoring groups. We believe that they are most likely held near the surface by electrostatic attraction between the dicationic complex and anionic oxygen atoms on the oxide surface. Such complexes would not be expected to perform as well in photoelectrochemical cells as those bearing anchoring groups that coordinate the metal oxide surface because of a lack of direct electronic communication between the complex and the nanoparticulate surface (vide infra).

In general, the absorption spectra of the ruthenium-polypyridyl dyes bearing varying anchoring groups are not much altered by titanium dioxide sensitization. This is likely because the anchoring group does not play a significant role in the metal-to-ligand charge transfer responsible for the transitions observed in the visible region. Also, the wavelengths of maximum absorption are conserved for both sets of complexes on the semiconductor surface. For dyes bearing pyridyl ligands, the λ_{max} are centered at 476 and 444 nm. For dyes bearing N-phenylimidazole ligands, the absorption maximum appears at 477 nm with a shoulder at 450 nm. This conservation of absorption features among the different photosensitizers is essential to compare their relative performance in dye-sensitized solar cells.

**Photovoltaic Cell Current Density−Voltage Characteristics.** Solar cells were constructed using the newly synthesized series of ruthenium complexes bearing varying anchoring groups. A 7-μm film of titanium dioxide was deposited on fluorine-doped tin oxide (FTO) conducting glass by spin coating (see Experimental Details). The mesoporous TiO2 film was reduced in area to approximately 0.5 cm by 0.5 cm by removing excess titanium dioxide using a template, then scanned to calculate surface area with higher accuracy. The electrodes were then soaked in 0.3 mM solutions of dye for a minimum of 3 days to ensure maximum surface coverage. A platinized counter-electrode was fashioned by a previously described method.41 Cells were then assembled using our electrodes separated by a 60-μm plastic thermal spacer (SX1170-60, Solaronix SA, Switzerland) held together with binder clips. The electrolyte consisted of 0.6 M tert-butylammonium iodide, 0.05 M iodine, 0.1 M lithium iodide, and 0.5 M tert-butyl pyridine (tBP) in a 1:1 mixture of valeronitrile and acetonitrile. The J−V curves were measured in quadruplicate from independent preparations of dye molecule and sensitization.

Representative J−V curves for solar cells sensitized with each new dye are shown in Figure 5, and all photovoltaic parameters are reported in Table 1. We also report the J−V curve and corresponding parameters for a TiO2 anode sensitized with N719 operating under our conditions.

Table 1 shows that the hydroxamate anchors give the best overall efficiencies for both the pyridyl- and the N-phenyl-
imidazole-based complexes. Consistent with their poor electron injection,
the phosphonate complexes showed the lowest overall solar-to-electric conversion. Meanwhile, the carboxylate-anchored complexes showed intermediate conversion. It is notable that all of our measured efficiencies for the newly synthesized dyes are an order of magnitude lower than those measured for N719. However, the low efficiency of our dye molecules only serves to magnify the relative effect of the anchoring moiety. It is likely that the observed increases in efficiency would be conserved in “champion” dyes upon switching from carboxylate to hydroxamate, though the relative percent increase in efficiency would be lower. Investigations of highly efficient dyes with hydroxamate anchors are currently underway.

Further insight into the anchor-dependent TiO2 surface chemistry, device photophysics, and cell electrochemistry can be gained by analyzing the solar cell J-V characteristics with an equivalent circuit model. Parameters readily obtained from the experimental data such as the short-circuit photocurrent, open-circuit voltage, and fill factor of the cell provide a useful starting point for comparison as they ultimately make up the solar-to-electrical energy conversion efficiency. However, direct relation of these parameters to the many device processes that influence them is difficult. The equivalent circuit model breaks down the complexity of the DSSC into components, thus unraveling the various fundamental processes controlling device efficiency and enabling them to be studied and compared independently.

The device parameters shown in Table 1 were extracted from the J-V curves based on the equivalent circuit shown in Figure 6 and the modified nonideal diode equation:

\[ J = J_L - J_0 \exp \left( \frac{e(V + JAR_sh)}{nkT} \right) - 1 \frac{V + JAR_s}{AR_sh} \]

where \( J_L \) is the photogenerated current density, \( R_s \) is the series resistance, \( kT \) is the thermal energy, \( e \) is the elementary charge, \( A \) is the device area, and \( n \) is the ideality factor. The solar cell shunt resistance \( R_{sh} \) and reverse saturation currents \( J_0 \) are parameters extracted from the J-V curves that quantify the various loss mechanisms in solar cells. High leakage currents in DSSCs are generally attributed to undesired recombination of carriers with the redox mediator in the electrolyte, either at regions of FTO directly exposed to the electrolyte or, the putative more dominant mechanism, via the nanoporous metal oxide. Increasing the device shunt resistance improves device efficiency because of both higher fill factors and larger open circuit voltages. A global value of the ideality factor \( (n = 2) \) was used in this systematic study for better comparison of \( J_0 \) values. Table 1 shows that the values of the series resistance, which result primarily from the electrode and ionic resistances of the cell, are similar for all devices, indicating that the fabrication procedure yields consistent metal oxide film thickness and porosity (as confirmed experimentally). Equation 1 has been used to model J-V characteristics in a wide variety of solar cell technologies including hydrogenated amorphous silicon p-i-n cells, Cu-(In,Ga)Se2 cells, organic bulk heterojunction cells, and DSSCs. This model has been shown to work well for DSSCs, particularly when performing a comparative analysis of a series of device architectures in which cell components are systematically varied, as in the present study.

The biggest systematic difference between the anchoring groups is evident in the \( J_L \) values. It is readily apparent from eq 2 that \( J_L \) is approximately equal to the photocurrent at zero bias \( J_0 \) for moderate to large shunt resistances. Table 1 shows that the shunt resistance is high enough in all devices as to not greatly affect the short-circuit current \( J_{sc} \approx J_L \). In both the pyridyl and the n-phenylimidazole cases, dyes bearing hydroxamate anchors have the highest values of \( J_L \) (0.70 and 0.51 respectively), while the carboxylate and phosphonate have very similar, lower calculated values (pyr-COOH = 0.40, pyr-phos = 0.43, im-ph-COOH = 0.41, im-ph-phos = 0.39). Though other factors may also be involved, this suggests that the improved electron injection observed for hydroxamates indeed has a measurable effect on the solar cell performance. However, to achieve high overall efficiency, higher \( J_L \) and \( J_0 \) values need to be coupled with low reverse saturation currents and/or high shunt resistance.

### Table 1. Measured Characteristics and Calculated Fitting Parameters of Solar Cells Based on the New Dyesa

<table>
<thead>
<tr>
<th>dye</th>
<th>R (mA/cm²)</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
<th>( J_{sc} ) (mA/cm²)</th>
<th>( J_{0} ) (mA/cm²)</th>
<th>AR_s (kΩ-cm²)</th>
<th>AR_sh (kΩ-cm²)</th>
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<td>1.7 × 10⁻⁸</td>
<td>0.082</td>
<td>4.46</td>
</tr>
<tr>
<td>12 im-ph-hydrox</td>
<td>0.51</td>
<td>0.38</td>
<td>0.48</td>
<td>0.09</td>
<td>0.53</td>
<td>2.2 × 10⁻⁸</td>
<td>0.072</td>
<td>2.75</td>
</tr>
<tr>
<td>15 im-ph-phos</td>
<td>0.39</td>
<td>0.38</td>
<td>0.45</td>
<td>0.07</td>
<td>0.41</td>
<td>1.9 × 10⁻⁸</td>
<td>0.15</td>
<td>3.18</td>
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<tr>
<td>blank</td>
<td>0.16</td>
<td>0.47</td>
<td>0.60</td>
<td>0.05</td>
<td>0.16</td>
<td>1.6 × 10⁻⁸</td>
<td>0.029</td>
<td>20.44</td>
</tr>
<tr>
<td>N719</td>
<td>7.52</td>
<td>0.73</td>
<td>0.54</td>
<td>2.91</td>
<td>7.76</td>
<td>6.0 × 10⁻⁸</td>
<td>0.025</td>
<td>1.14</td>
</tr>
</tbody>
</table>

aReported values are the average of values obtained from two to four cells across multiple preparations.

![Figure 6. Equivalent circuit for modeling solar cells using the modified nonideal diode equation](image-url)
to facilitate sustained photocurrent as a function of voltage, that is, larger fill factors and open circuit voltages. Unfortunately, attempts to directly measure electron injection across our series of dye molecules by THz spectroscopy suffered from a poor signal-to-noise ratio resulting from the low amount of carriers generated by dye excitation.

Looking at the performance of the newly synthesized dyes as a whole, solar cells based on the pyridyl-hydroxamate anchor not only give the highest photoinjection current densities but they are also significantly more efficient. The average measured efficiency is 0.20%, while all other dyes, including the N-phenylimidazolone-hydroxamate-based complex, gave efficiencies in the range of 0.04—0.09%. Given this great difference, it is not surprising that the pyr-hydroxyl cell also has a reverse saturation current that is significantly lower than all the rest. This indicates that, in addition to the photophysical properties of the attached dye, the hydroxamate anchor increases suppression of electron transfer from the photoanode to the electrolyte.

The trends in $R_{sh}$ and $J_0$ in Table 1 are also consistent with expected surface binding and its mitigation of the effects of tBP. The addition of 0.5 M tBP to the DSSC electrolyte solution, as is common practice in the literature, is known to increase the $V_{oc}$6,14,53—56 and is attributed, in part, to a decrease in the amount of electron recombination in TiO$_2$ by blocking access of triiodide to the TiO$_2$ surface and/or by iodine complexation.54 These effects can account for an increase in the $R_{sh}$, which is evident from the J–V curves showing a decrease in the magnitude of the slope of the current density at low voltages. A second effect of tBP is a lowering of the reverse saturation current density $J_0$ as observed by a shift in the sharp onset of the recombination current (near $V = V_{oc}$) to higher voltages.6,56 This can be explained by a decrease in the number of positive ions (protons and Li$^+$) adsorbed to the TiO$_2$ surface, leading to a shift in the conduction band minimum of nanoporous TiO$_2$ to higher energies (more negative potentials).14,53—55 The hydroxamate-, carboxylate-, and phosphate-anchored complexes in the present study have lower shunt resistances compared to cells made with unsensitized TiO$_2$ photoanodes, which is consistent with dye attachment interfering with the ability of tBP to block recombination sites on the TiO$_2$ surface. The values of $J_0$ are generally larger since binding of dye molecules competes with tBP and its effect on the conduction band minimum of TiO$_2$. The pyr-hydroxyl anchor seems to be the exception since it has a larger photoinjection current density, while maintaining a low $J_0$.

It is also interesting to note that solar cells sensitized with the pyridine complex 9 give an appreciably larger photoresponse than unsensitized cells. This suggests that an electrostatic attraction with the semiconductor surface is not only sufficient for binding dye molecules, but that it also can hold sensitizers tightly enough to facilitate through-space electron transfer. It is notable that pyr-acetone complex 8 gives a lower overall sunlight-to-electricity conversion efficiency than 9 with a very similar value calculated for $J_0$. This suggests that the association of 8 to the semiconductor surface may not be covalent. However, a tautomerization to the enolate form of pyr-acetone followed by weak binding through an alkoxide cannot be excluded. Unfortunately, this also prohibits titanium dioxide sensitization using a mixture of 7 and 8 or 18 and 19. While it is likely that binding acetylacetone to titanium dioxide would be thermodynamically preferred over either the alkoxide or a pure electrostatic attraction, it is impossible to rigorously prove that all surface-bound molecules resulting from a sensitizing mixture bear acetylacetone moieties. Additionally, because some current could be derived from deacetylated species adsorbed to TiO$_2$, we cannot say that all photocurrent was obtained from the desired acetylacetone complexes. This reinforces the need for analytically pure dyes in sensitization,7$^\text{7}$ and severely diminishes the utility of acetylacetone as an anchor for DSSC applications. Unless an analogue is found in which the acetylacetone does not deacetylate under solution conditions, or where it can be proven that the deacetylated species has no interaction with the semiconductor surface, acetylacetone should not be used.

In regard to solar fuels production, it is highly advantageous that the hydroxylate species produce the best measured efficiencies ($\eta$). Hydroxylate anchors, unlike carboxylate, are stable under aqueous conditions over a wide range of pH values when the corresponding dye is soluble in water.$^{25,30}$ This feature will be essential for any water-oxidation/proton reduction dye-sensitized solar cell.$^{13}$ It would seem that, owing to the relative ease of synthesis, strong binding, compatibility with water oxidation catalysis, and the relatively high overall photovoltaic efficiency afforded, a hydroxamate anchor is a leading candidate for any dye molecule to be used in a photoelectrochemical water oxidation cell.

**CONCLUSIONS**

Our analysis of a series of anchoring groups for covalent attachment of ruthenium-polypyrpyridyl dyes of the form $[\text{Ru}$(terpy)$(tbbpy)L][\text{BF}_4]$ to TiO$_2$ surfaces predicts that hydroxylate anchors should lead to improved performance of DSSCs. Solar cells were constructed by using newly synthesized photosensitizers and tested under AM 1.5 illumination. Hydroxamic acid anchoring groups were found to give superior photogenerated current densities, when compared to other anchors, including carboxylate groups used in traditional DSSCs. Analysis by the nonideal diode equivalent circuit model shows that solar cells based on the pyridyl-hydroxamate anchor give significantly higher efficiencies because the current density–voltage characteristics show increased suppression of electron transfer from the photoanode to the electrolyte. In addition, we see better photoinjection properties that are characteristic of the hydroxamate anchor. Since hydroxamates provide stable attachment in aqueous environments and have demonstrated improved performance over carboxylates in this system, they are a good candidate for applications in artificial photosynthesis devices.

**EXPERIMENTAL DETAILS**

$[\text{Ru}(\text{terpy})(\text{tbbpy})(\text{Cl})]^{2+}$ and diethyl pyridin-4-ylphosphonate$^{39}$ were synthesized by literature methods. Dichloromethane, toluene, and acetonitrile were dried on a Grubbs-type solvent purification system.58 All other reagents and solvents were commercially available and used without further purification unless specified. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. $^1$H NMR spectra were recorded on a 400 MHz Bruker spectrometer and referenced to the residual solvent peak (6 in ppm, $\delta$ in Hz).$^{13}$ $^{13}$P NMR spectra were recorded on a 500 MHz Varian spectrometer and referenced to the solvent peak. $^{19}$P NMR spectra were recorded on a 300 MHz Varian spectrometer. High-resolution ESI mass spectra were collected by the Mass Spectrometry and Proteomics Resource at the W.M. Keck Foundation Biotechnology Resource Laboratory (Yale University). Elemental analysis was performed by Robertson Microlit Laboratories (Ledge-wood, NJ) and Atlantic Microlab, Inc. (Norton, CA).

$[\text{Ru}(\text{terpy})(\text{tbbpy})(\text{OH}_2)][\text{BF}_4]$ (2). A 2.08 g portion (2.99 mmol) of $[\text{Ru}(\text{terpy})(\text{tbbpy})\text{Cl}]$ and 1.947 g (10.0 mmol) of silver tetrafluoroborate were dissolved in 200 mL of 3:1 acetonitrile:water. The
resulting solution was refluxed overnight in the dark under the air. The volume of the solution was then reduced to approximately 25 mL, and 48 wt % HBF₄ (aq) was added. The resulting suspension was cooled in a freezer for 1 h. The brown precipitate was then filtered off, washed with 1 M HBF₄ (aq), and dried. The dimethyl sulfoxide adduct was prepared by dissolving [Ru(terpy)(tbbpy)(OH)][BF₄]₂ in a 2-dimethyl sulfoxide solution, and the solution was heated to 65 °C, held at 65 °C for 3 h, and then cooled to 0 °C. The solution was then filtered, and the filtrate was added to the reaction vessel.

The resulting solution was dried in vacuo. The small brown solid was then collected by filtration, and the filtrate was dried to constant weight.

The resulting solution was then stirred at room temperature overnight. The solution was then filtered through Celite, and the filtrate was added to the reaction vessel. The solution was then filtered, and the filtrate was added to the reaction vessel.

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The resulting solution was dried in vacuo. The small brown solid was then collected by filtration, and the filtrate was dried to constant weight.

The resulting solution was then stirred at room temperature overnight. The solution was then filtered through Celite, and the filtrate was added to the reaction vessel. The solution was then filtered, and the filtrate was added to the reaction vessel.
methane under nitrogen. Two milliliters of diethylisopropylamine was layer was dried with sodium sulfate and solvent was removed. The

\[ \text{d} (t, J = 6.0, 1.7, 2H), 7.85 - 7.78 (m, 2H), 7.19 (s, 1H), 4.31 - 3.95 (m, 4H), 1.32 (q, J = 6.9 Hz, 6H). \]

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\[ \text{d} (t, J = 6.0, 1.7, 2H), 7.85 - 7.78 (m, 2H), 7.19 (s, 1H), 4.31 - 3.95 (m, 4H), 1.32 (q, J = 6.9 Hz, 6H). \]

\[ \text{d} (t, J = 6.0, 1.7, 2H), 7.85 - 7.78 (m, 2H), 7.19 (s, 1H), 4.31 - 3.95 (m, 4H), 1.32 (q, J = 6.9 Hz, 6H). \]

\[ \text{d} (t, J = 6.0, 1.7, 2H), 7.85 - 7.78 (m, 2H), 7.19 (s, 1H), 4.31 - 3.95 (m, 4H), 1.32 (q, J = 6.9 Hz, 6H). \]

\[ \text{d} (t, J = 6.0, 1.7, 2H), 7.85 - 7.78 (m, 2H), 7.19 (s, 1H), 4.31 - 3.95 (m, 4H), 1.32 (q, J = 6.9 Hz, 6H). \]
dimethylisoxazole, 370 mg (0.320 mmol) of freshly purified 4,10-Pt(Ph3)2 and 5.630 g (32.7 mmol) of barium hydroxide were heated at 80 °C for 18 h under nitrogen in 200 mL of 9:1 1,2-dimethoxyethane-water. The solution was cooled to room temperature, washed with 1 M HCl, and extracted into dichloromethane. The aqueous layer was basified with potassium carbonate and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and the solvent of the filtrate removed. The product was purified by alumina chromatography using 1% methanol in dichloromethane as eluent and recovered as a white solid. Yield: 660 mg, 62%. 1H NMR (400 MHz, CD2Cl2) δ 7.90−7.84 (m, 1H), 7.73−7.46 (m, 2H), 7.42−7.37 (m, 2H), 7.36 (t, J = 1.3 Hz, 1H), 7.19−7.14 (m, 1H), 2.42 (s, 3H), 2.27 (s, 3H). 13C{1H} NMR (126 MHz, CD2Cl2) δ 165.94, 158.85, 138.76, 135.90, 130.93, 130.85, 130.22, 122.05, 118.49, 115.99, 118.10, 109.96. Elemental Analysis for C14H13N3O: Calculated: C 69.34; H 5.91; N 11.72. 

Prior to DSSC assembly, the electrodes were removed from dye solution and rinsed thoroughly with absolute ethanol. Platinum counter electrodes and iodide/triiodide redox electrolyte were prepared by methods outlined previously. Solar cells were assembled prior to testing using a 60-μm plastic thermal spacer (SX1170–60, Soloranix SA, Switzerland) between electrodes and were held together with metal binder clips. Photocurrent–voltage measurements were performed using a 300 W Ozone-free xenon lamp with an AM 1.5G filter (Newport, U.S.A.) as a light source and were recorded using a Keithley 2400 digital source meter. The light intensity of the AM 1.5G filtered xenon lamp was adjusted to 100 mW/cm² prior to testing. Exact solar cell surface areas were confirmed by scanning the working electrodes with a 1200 dpi scanner.

**ASSOCIATED CONTENT**

**Supporting Information**

Selected 1H NMR spectra, emission spectra, cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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