Efficiency of Interfacial Electron Transfer from Zn-Porphyrin Dyes into TiO₂ Correlated to the Linker Single Molecule Conductance

Christian F. A. Negre,†‡ Rebecca L. Milot,† Lauren A. Martini,† Wendu Ding,† Robert H. Crabtree,*,†‡ Charles A. Schmuttenmaer,†‡§, † and Victor S. Batista*,†‡

†Department of Chemistry, Yale University, 225 Prospect St., P.O. Box 208107, New Haven, Connecticut, 06520-8107 United States
‡Energy Sciences Institute, Yale University, P.O. Box 27394, West Haven, Connecticut, 06516-7394 United States

Supporting Information

ABSTRACT: High performance dye-sensitized solar cells (DSSCs) rely upon molecular linkers that allow efficient electron transport from the photoexcited dye into the conduction band of the semiconductor host substrate. We have studied photoinduced electron injection efficiencies from modular assemblies of a Zn-porphyrin dye and a series of linker molecules which are axially bound to the Zn-porphyrin complex and covalently bound to TiO₂ nanoparticles. Experimental measurements based on terahertz spectroscopy are compared to the calculated molecular conductance of the linker molecules. We find a linear relationship between measured electron injection efficiency and calculated single-molecule conductance of the linker employed. Since the same chromophore is used in all cases, variations in the absorptivities of the adsorbate complexes are quite small and cannot account for the large variations in observed injection efficiencies. These results suggest that the linker single-molecule conductance is a key factor that should be optimized for maximum electron injection efficiencies in DSSCs. In addition, our findings demonstrate for the first time the possibility of inferring values of single molecule conductance for bridging molecules at semiconductor interfaces by using time-resolved THz spectroscopy.

1. INTRODUCTION

Ever since the seminal work of O’Regan and Grätzel,¹ dye-sensitized solar cells (DSSCs) have continued to raise significant interest as promising alternatives for solar-to-electric energy conversion. DSSCs are particularly attractive since they are based on inexpensive semiconductor materials (typically nanoporous TiO₂, ZnO, or SnO₂)²–⁵ sensitized to visible light absorption with dyes covalently attached to the semiconductor surface. Nevertheless, axial linkers have been incorporated in some of the most efficient DSSCs to date,²⁰,²¹ are particularly attractive since they have high molar absorptivity. In addition, the spectral and electronic properties can be tuned by varying both the centrally coordinated metal ion and the peripheral substituents.²²–²⁴ Metal porphyrins can bind directly to the semiconductor surface via built-in anchoring groups at the beta- and meso-positions or alternatively through linkers that coordinate to the metal center in the axial position (Figure 1a).²⁵–²⁶ The advantage of the axial binding motif is that it separates the design and synthesis of the linker from the development of the porphyrin dye, thereby simplifying the design of the chromophore/redox active center and assembly of the molecular framework to the semiconductor surface. Nevertheless, axial linkers have been much less investigated, compared to anchoring groups substituting at the beta or meso positions of the porphyrin ring. It is therefore important to analyze the efficiency of photoinduced electron injection as a function of the linker structure²⁵ and explore structure/function relations that might...
correlate the resulting interfacial electron transfer efficiency with the electrical properties of the linkers.

High-potential porphyrin dyes have been assembled in photoanodes for DSSCs29 as well as in photocatalytic cells for light-driven water splitting when codeposited with a water oxidation catalyst on TiO2 thin films.30 They were found to be quite versatile since they could be optimized to give sufficiently positive redox potentials, as necessary to activate catalysts for water oxidation. Furthermore, when covalently bound to semiconductor surfaces, they were stable under oxidative and aqueous conditions, as necessary for photocatalytic water oxidation. However, the reported cells have shown low efficiency calling for fundamental studies of the factors responsible for efficiency loss.

In addition to the optimization of the spectral and electrochemical properties of the dye, optimum performance requires assemblies that maximize electron injection into the semiconductor.31−35 For metal-porphyrins bound through axial coordination, electron injection can be optimized through suitable design and refinement of the molecular linker.36 Two photoinjection mechanisms are possible: photoexcitation of the dye, followed by injection through the molecular linker (type-I), or direct injection from the ground state of the dye to the CB of the semiconductor (type-II).37−40 While both mechanisms involve ultrafast time scales,37,42 the type-I process is usually favored in porphyrin dyes as well as in the molecular assemblies most commonly used in DSSCs.43 Therefore, it is important to focus on optimization of interfacial electron injection by design of molecular linkers that provide proper alignment of electronic states and strong electronic coupling with the semiconductor CB.

Several experimental techniques have been used to study photoinjection mechanisms in DSSCs and to determine the efficiency and time scales of interfacial electron transfer at a variety of semiconductor surfaces, including transient absorption spectroscopy, electron paramagnetic resonance, and time-resolved terahertz (THz) spectroscopy.3,44−50 In addition, analytical studies and computational simulations of interfacial electron transfer have advanced our understanding of the complex interrelationship between the dye and the semiconductor surface.23,40,51−59 These studies have shown that highly conductive linkers, such as molecular frameworks with conjugated double bonds, usually inject carriers much faster than aliphatic linkers. In addition, several studies have focused on the differences in electron injection observed for different anchoring groups.25,60−63 However, a systematic study of the molecular origin of differences in the efficiency of interfacial electron injection has yet to be reported. In this work, we employ a series of modular linker-porphyrin assemblies that vary in their anchoring group for surface attachment. We find that the efficiency of interfacial electron injection as probed by THz spectroscopy correlates with the single molecule conductance of the linkers binding Zn-porphyrin dyes to TiO2 surfaces. The resulting insight is particularly relevant to the design of linker-porphyrin assemblies when combined with optimization of photoabsorption and redox properties by inverse design techniques.36 These findings also demonstrate for the first time the possibility of inferring values of single molecule conductance by using time-resolved THz spectroscopy for molecules bridging electron donor adsorbates at semiconductor interfaces.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Sample Preparation. All compounds were obtained or synthesized from commercially available starting materials and were used without further purification unless otherwise noted. Isonicotinic acid (L1) and 4-pyridyl-boronic acid (L5) were obtained from Aldrich. The molecular linkers 4-pyridyl-phosphonic acid (L2), 4-pyridyl-acetylacetonate (L3), and 4-pyridyl-hydroxamic acid (L5) were synthesized according to a previously reported literature procedure.64−68 The high-potential zinc porphyrin dye ZnPF10-diester was also synthesized according to a previously reported literature procedure.59,30

Mesoporous thin films of TiO2 were prepared using Degussa Aerosioxide P25 titanium dioxide nanoparticles by either doctor-blading or spin-coating. Films used for absorbance measurements were prepared on microscope coverslips (25 × 25 mm for spin-coating, 22 × 50 mm for doctor-blading, Fisherbrand, USA). Films used for time-resolved THz spectroscopy measurements were prepared on fused quartz microscope slides (1 × 1 in, 1 mm thickness, GM Associates, Inc., USA). Bare TiO2 thin films were soaked overnight in the dark in a 0.5 mM solution of the desired linker (L1-L5) 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 ZnPF10-diester porphyrin, and rinsed well with
dichloromethane to remove any uncoordinated or aggregated porphyrin.

Absorption spectra were recorded using a Cary 3E UV–
visible 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 attachment.

2.2. Time-Resolved THz Spectroscopy (TRTS) 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 ~130 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 (3.1 eV) light for the pump beam. The remainder of the near-IR light was used to generate THz radiation via optical rectification in a ZnTe(110) crystal and detect it using free space electro optic sampling in a second ZnTe(110) crystal. Terahertz data were taken at room temperature, and the average of two samples was taken for each data set. Further information on the spectrometer and technique can be found in the literature.45,69

2.3. Conductance and Electronic Structure Calculations. The steady state current flowing through the molecular linker has been computed according to the Landauer–Büttiker formula

\[ I = \frac{2e}{h} \int_{\mu_L}^{\mu_R} T(E) \mathrm{d}E \]  

where \( e \) is the electron charge, \( h \) is Planck’s constant, \( \mu_L \) and \( \mu_R \) are the chemical potentials for the electron in the left and right leads, respectively (Figure 2), and \( E \) is the energy of the

conducting channel. The transmission function \( T \) is calculated by using the Fisher–Lee formula74

\[ T = \text{Tr}(g_{\text{dev}}^+(E)\Gamma_L(E)g_{\text{dev}}^-(E)\Gamma_R(E)) \]  

where \( g_{\text{dev}}(E) \) is the advanced nonequilibrium Green’s function (NEGF) operator for the system consisting of the device attached to one-dimensional leads, as shown in Figure 2.75

The NEGF operator can be written, as follows:

\[ g_{\text{dev}}(z) = (zS - H_{\text{dev}} - \Sigma_L(z) - \Sigma_R(z))^{-1} \]  

where \( z \) is the generalized complex energy variable, \( S \) is the overlap matrix, \( H_{\text{dev}} \) is the Hamiltonian of the molecule, and \( \Sigma_L \) and \( \Sigma_R \) are the self-energy operators corresponding to the left and right leads, respectively. \( \Gamma \) is defined as follows:

\[ \Gamma_{L/R} = i(\Sigma_L^+(E) - \Sigma_R^-(E)) \]  

where \( \Sigma_L^+(E) \) and \( \Sigma_R^-(E) \) are the advanced and retarded self-energy operators for the left (L) and right (R) contacts, respectively.

The electronic structure and transport properties of the linkers were determined by using the semiempirical extended-Hückel (EH) Hamiltonian in conjunction with the NEGF methodology.76–78 In the basis of localized atomic orbitals, the matrices \( \Sigma_{L/R} \) are assumed to be diagonal with nonzero elements \( (\Sigma_{L/R})_{11} = \gamma_{\text{NN}}^L(E) \) and \( (\Sigma_{L/R})_{NN} = \gamma_{\text{NN}}^R(E) \) where the indices \( 1 \rightarrow N \) label the atomic orbitals of the linker that have significant overlap with the left and right leads. The parameter \( \gamma \) defines the effective electronic coupling with the contacts and is assumed to the same for s, p, and d orbitals. The Green’s function for the isolated left and right contacts, \( E_{\text{L/R}} = -i\beta/\beta \), are defined to mimic semi-infinite one-dimensional nanowires as described by a nearest-neighbor tight-binding Hamiltonian with constant intersite coupling \( \beta \).79 The value of \( \gamma^2/\beta = 2.0 \text{ eV} \) was chosen to ensure that the conductance of a linear chain of gold atoms at 0 V bias is equal to the unit of quantum conductance (i.e., \( G_0 = 2e^2/h \)) when connected to the model nanowire leads, as recently reported.76 All calculations of conductance were performed at 0 V bias. Hence

\[ G = \frac{2e^2}{h} T(E_F) \]  

where \( G \) is the molecular conductance (in Siemens), and the transmission function \( T \) is evaluated at the device Fermi level \( E_F \). The geometries of the linkers (Figure 3) correspond to optimized minimum energy configurations, obtained via density functional theory (DFT) at the B3LYP/LANL2DZ level, as implemented in Gaussian 09.80

Figure 2. Scheme depicting the coupling of 4-pyridyl-carboxylic acid to the semi-infinite leads in monodentate (a) and bidentate (b) binding motifs.

Figure 3. Linker molecules (L) substituted with different anchoring groups (A) that covalently bind Zn-porphyrin sensitizers to TiO2 surfaces. Linkers have the structure 4-pyridyl-A, where the anchoring group A is either carboxylic acid (L1), phosphonic acid (L2), acetylacetonate (L3) hydroxamic acid (L4), or boronic acid (L5).
3. RESULTS AND DISCUSSION

Figure 3 shows the structures of the linkers analyzed in this study. All the linkers have the form 4-pyridyl-A where the anchoring group A is either carboxylic acid (L1), phosphonic acid (L2), acetylacetonate (L3), hydroxamic acid (L4), or boronic acid (L5). Hydroxamic acid is treated in both of its two tautomers L4a and L4b. These anchoring groups are known to bind strongly to semiconductor surfaces while the pyridyl group axially coordinates to the metal center of the porphyrin ZnPF10 through the pyridyl nitrogen, sensitizing the TiO2 surface (Figure 1). These surface-bound complexes are collectively denoted L-ZnPF10, with L = L1 − L5.

Figure 4 shows the UV−vis diffuse reflectance spectra of the L-ZnPF10 assemblies bound to TiO2 showing only small differences in the molar absorptivity of the chromophore-linker assemblies. In fact, Figure 4 shows that L1-ZnPF10, L2-ZnPF10, and L4-ZnPF10 have nearly the same absorbance at around 400 nm, which is the wavelength of the pump pulse in our THz measurements, while the absorptivities of L3-ZnPF10 (shown) and L5-ZnPF10 (not shown) are only slightly lower. Therefore, differences in the observed photoinjection yields of these assemblies cannot be attributed to differences in light-harvesting efficiency.

Figure 5 shows the change in transmitted THz amplitude as a function of time after the TiO2 thin-films sensitized with L-ZnPF10 are photoexcited with a pump pulse at 400 nm. The attenuation of THz amplitude is a measure of the efficiency of electron injection, since it is proportional to the concentration of free charge carriers injected into the semiconductor conduction band (denoted state B in Figure 6). As a control experiment, we note there is no detectable attenuation of THz transmittance when ZnPF10 is merely physisorbed on the TiO2 surface, whereas all of the L-ZnPF10 complexes covalently bound to the surface show measurable attenuation. We also performed a second control experiment that shows no injection from porphyrin-free L1-sensitized anatase compared to the full system (L1-ZnPF10; see Figure S4). Since the predominant porphyrin excitation near 400 nm (the Soret or B band) arises from the S2 ← S0 transition, which is π* ← π, these results suggest that the photoinjected carriers must travel through the linkers (or through space) in order to be injected into TiO2. From the THz data alone, however, we see significant differences in the efficiency of electron injection for the different anchoring groups. The efficiencies of electron injection for the various L-ZnPF10 complexes can be ranked according to the order: L4 > L1 > L2 ≈ L3 ≈ L5.

Figure 6 shows a schematic diagram of the photoinjection process. Upon photoexcitation of the dye, electrons are transferred through the pyridyl ligand and anchoring group to the semiconductor surface (D* → X). This is an ultrafast electron transmission process that takes a few femtoseconds prior to the interfacial injection of free carriers into the conduction band (X → B with an injection rate constant k1 of tens to hundreds of femtoseconds). The kinetic model also includes trapping (B → C) and detrapping (C → B) dynamics with rate constants k2 and k3, respectively. According to this
kinetic model, the concentration of free carriers \(B\), as a function of time \(t\), is given by the following equation:

\[
B(t) = X_0(\theta_1 + \theta_2 e^{-k_1 t} + \theta_3 e^{-(k_2 + k_3) t})
\]

where

\[
\theta_1 = \frac{k_3}{k_2 + k_3}
\]

\[
\theta_2 = \frac{(k_1 - k_3)}{-k_1 + k_2 + k_3}
\]

\[
\theta_3 = \frac{k_2 k_3}{(k_2 + k_3)(k_1 - k_2 - k_3)}
\]

The derivation of eqs 6 and 7 is provided in the Supporting Information (SI). Equation 6 provides a description of the time-dependent concentration of free carriers that should be proportional to the observed attenuation of THz transmitted amplitude for the different anchoring groups. The trapping and detrapping rate constants \(k_1\) and \(k_3\) are assumed to depend only on the nature of the semiconductor and therefore are treated as global fitting parameters common to all anchoring groups. The parameter \(X_0\), which is reported in Table 1 for each linker, gives a measure of the efficiency of photoinjection as probed by THz spectroscopy since it is proportional to the THz amplitude at the time of maximum attenuation, \(t_m\), and therefore proportional to the concentration of electrons injected into the semiconductor conduction band.

For comparison, Table 1 also reports the values of single molecule conductance computed for each linker by using the EH NEGF methodology outlined in section 2.3. Values for L3 and L4 were calculated assuming a bidentate binding mode, while L1, L2, and L5 were assumed to have monodentate binding. The attachment mode (bidentate for L3 and L4 and monodentate for L1, L2, and L5) is determined for each ligand according to the DFT minimum energy configuration (Figure S5, SI). Our results are consistent with the special arrangement of oxygen atoms, separated by more than two bonds in L3 and L4 anchoring groups, leading to a configuration that is more favorable for bidentate binding with Ti\(^{4+}\) octahedral sites.\(^{49,50}\) Monodentate binding is found to be most stable for L1, L2, and L5, consistent with previous reports for L1,\(^{85}\) L2,\(^{61}\) and L5.\(^{86,87}\) Also, crystallographic data for the dyes absorbed onto novel (TiO\(_2\))\(_{17}\) clusters shows a bidentate chelating mode for L3.\(^{88}\)

The case of L4 has been previously modeled showing a favorable bidentate oxygen vacancy mode.\(^{50}\)

The conductance value for L4 was taken as the average between the conductance values for L4a and L4b\(^{81}\) because the DFT computed energy difference between the two conformers is less than 0.1 eV.

Figure 7 shows the correlation of the maximum change in THz amplitude \(X_0\) as a function of the linker conductance in the L-ZnPFO\(_{10}\) complexes. The linear relationship \((R^2 = 0.9851)\), suggests that the transport properties of the different linkers have a direct effect on the electron injection and efficiency. The observed correlation between electron injection efficiency and calculated molecular conductance provides a valuable guideline for designing new sensitizers. To understand why different linkers have different values of conductances, we analyze the electronic structure/function relations for the different linkers as correlated to their transport properties.

Figure 8 displays the frontier molecular orbitals of linkers L1 and L3 that are primarily responsible for electron transport.

![Figure 7](image-url)  
*Figure 7. Change in THz amplitude (\(X_0\)) at the time of maximum attenuation (\(t_m\)) versus conductance \(G\) computed for the various linkers. The best linear fit is given by \(X_0 = 0.7212G + 1.9943\), with \(R^2 = 0.9851\).*

![Figure 8](image-url)  
*Figure 8. Frontier orbitals calculated within the EH level of theory for L1 and L3.*

(Alogous frontier orbitals for L2, L4, and L5 are provided in the SI, Figure S2.) Although L1 and L3 are both known to bind well to the TiO\(_2\) surface,\(^{7,49}\) L1 has higher conductance and yields much more efficient electron injection than L3. Figure 8 shows that these differences can be attributed to differences in the electronic structure since the pyridine ring of L3 is rotated...
nearly perpendicularly to the anchoring group and therefore is not conjugated with the electronic structure of the anchor as in L1. Furthermore, the LUMO orbital of L3 is localized on the anchor and therefore does not provide good electronic coupling with the pyridine moiety. In contrast, the LUMO of L1 is delocalized along the entire linker, providing an efficient channel for electron transport.

The analysis of L2 and L5 suggests that phosphonic acid (L2) and boronic acid (L5) functional groups decrease the overall conductance since those functional groups inhibit electron tunneling when bound to the semiconductor surface. In contrast, the hydroxamate linker L4 binds as a bidentate ligand, leading to a more efficient injection than through the monodentate L1 linker. When compared to the bidentate L3 ligand, L4 also leads to much more efficient electron injection due to the extended conjugation and delocalization of the LUMO over the entire linker. EH Frontier orbitals for all the ligands are plotted in Figure S2 in the SI.

The Dπ* → X transition is the primary electron transfer event in porphyrin type-I modular assemblies following photo-absorption at 400 nm due to π* ← π photoexcitation. The photoabsorption and Dπ* → X transport events, however, are dynamically decoupled since the transition dipole moment of the Soret band lies in the plane of the porphyrin ring which is parallel to the TiO2 surface. The resulting decoupling with respect to the adiabatic photoinjection is consistent with the observation that the photoabsorption features remain almost unchanged when using linkers with different electron transport efficiency. Figure 9 shows the projected DOS (pDOS) for two

during electron photoinjection from the photoabsorption properties of the porphyrin dye.

4. CONCLUSIONS

We have studied the efficiency of interfacial electron injection from Zn-porphyrin dyes bound to TiO2 surfaces via axially coordinated pyridine ligands with a variety of different anchoring groups. The photoconversion efficiency has been characterized by the attenuation of transmitted time-resolved terahertz (THz) signal after photoexcitation and interfacial electron transfer. We found a linear relationship between the interfacial electron injection efficiency and the single molecule conductance of the linker computed according to the nonequilibrium Green’s function formalism. This simple relationship suggests that pyridyl linkers in the surface-bound L-ZnPF10 complexes function as effective molecular wires, transmitting photoexcited electrons from the light-absorbing porphyrin sensitizer into the conduction band of TiO2. These results are particularly relevant for optimization of DSSCs that rely upon molecular linkers mediating electron transport from the dye into the conduction band of the semiconductor host substrate. In addition, these findings demonstrate for the first time the possibility of inferring values of single molecule conductance by using time-resolved THz spectroscopy to probe bridging molecules that covalently bind dyes to semiconductor surfaces, while keeping constant the other components of the molecular assembly, such as the nature of the dye and the semiconductor material.

ASSOCIATED CONTENT

Supporting Information

Kinetic model and derivation of eq 6; additional figures with the analysis of relaxed configurations, THz analysis; density of states, frontier orbitals, and absorption spectra; coordinates for optimized structures; sample input file for geometry optimizations in SIESTA; and full Gaussian 09 reference. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: robert.crabtree@yale.edu.
*E-mail: charles.schmuttenmaer@yale.edu.
*E-mail: victor.batista@yale.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge support by the U.S. Department of Energy Grant DE-FG02-07ER15909 (C.A.S.) and DE-PS02-08ER15944 (R.H.C.). Computational work was supported as part of the Argonne-Northwestern Solar Energy Research (ANSER) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001059 (V.S.B.). Computer resources were provided by NERSC and by the High performance Computing facilities at Yale University.

REFERENCES


NOTE ADDED AFTER ASAP PUBLICATION
This paper was published ASAP on November 8, 2013, with an error to the affiliations and reference errors to Sections 2 and 3. The corrected version was reposted November 11, 2013.