Tuning Open Circuit Photovoltages with Tripodal Sensitizers

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The sensitizers $[Ru(bpy)_2(deeb)](PF_6)_2$ (**1**), $[Ru(bpy)_2(bpy)-(E-Ph)-Ad](PF_6)_2$ (**2**), and $[Ru(bpy)_2(bpy)-(E-Ph)_2-Ad](PF_6)_2$ (**3**), where deeb is 4,4′-$(COOCH_2CH_3)_2$-2,2′-bipyridine, E-Ph is phenylethynyl, and Ad are tripod shaped bpy ligands based on 1,3,5,7-tetraphenyladamantane, were anchored to mesoporous nanocrystalline (anatase) TiO_2 thin films and studied in regenerative solar cells with 0.1 M LiI/0.005 M I_2 dichloromethane electrolyte. Over three decades of 488 nm irradiance, the open circuit photovoltage increased markedly with the distance between the Ru center and the surface binding groups, **1** (7 Å) < **2** (18 Å) < **3** (24 Å). The diode equation accurately models the irradiance dependent data and indicates that the $TiO_2(e^-) \rightarrow I_3^-$ (and/or I_2) charge recombination rate constants were decreased by a factor of 20 for **2**/TiO_2 and 280 for **3**/TiO_2 relative to **1**/TiO_2. The results suggest that control of the sensitizer–TiO_2 orientation is important for efficient power optimization.

The fundamental processes for photocurrent generation in dye-sensitized solar cells are well understood at the molecular level and have been optimized such that almost every absorbed photon is converted to an electrical current.[1,2] The open circuit photovoltage, V_{oc}, on the other hand, is not as well understood and remains poorly optimized. The open circuit photovoltage represents the maximum Gibbs free energy that can be abstracted from a regenerative solar cell under conditions of constant irradiance.[3] Previous workers have shown that the "diode equation", eq 1, captures the essential physics of dye sensitzed

$$V_{oc} = \left(\frac{kT}{e}\right) \ln\left(\frac{I_{inj}}{n\sum_i k_i[A]_i}\right) \qquad (1)$$

solar cells and accurately describes the irradiance dependence of the open circuit photovoltage, albeit with "ideality factors" typically of ~2–3.[4,5] Here, n is the concentration of electrons in TiO_2, and the summation is for all electron transfer rate constants, k_i, to acceptors, $[A]_i$. The diode equation predicts a 59 mV increase in V_{oc} for each order of magnitude decrease in the charge recombination rate constant for injected electrons with acceptors, $k_i[A]_i$, at room temperature provided that the electron injection flux into the semiconductor, I_{inj}, is constant. In efficient dye-sensitized solar cells with 1 sun irradiance (100 mW/cm²), the predominant acceptors are thought to be iodide oxidation products, I_2 and/or I_3^-.[1,2]

Our group, as well as others, have previously utilized donor–acceptor sensitizers that promote rapid intramolecular "hole transfer" after electron injection into TiO_2.[5,6] This can increase the lifetime of the interfacial charge-separated states, resulting in a higher V_{oc} value. Grätzel and co-workers have reported increased charge-separated state lifetimes for a series of donor–acceptor sensitizers; however, the increased lifetime did not always lead to an improved V_{oc} value.[6] One possible explanation for the different behavior is that the physical location where iodide oxidation takes place is the key factor. The donor–acceptor compounds previously studied were not rigid and could bind to TiO_2 with a variety of sensitizer–semiconductor orientations.[5,6] In fact, the increased V_{oc} value observed when 4-*tert*-butylpyridine or other Lewis bases were added to the electrolyte has been hypothesized to result from an increased $TiO_2(e^-) \rightarrow I_3^-$ (and/or I_2) charge recombination distance.[7,8] While other explanations for this behavior exist,[8] one reasonable strategy for optimization of V_{oc} is to inhibit recombination with distance while maintaining a high quantum yield for injection. Fundamental studies of this type are critically needed.

Here, we report preliminary photoelectrochemical studies of the irradiance dependence of V_{oc} in regenerative dye-sensitized solar cells with the family of Ru^{II} sensitizers **1**–**3** shown in Figure 1. The sensitizers were designed to gradually increase the distance of the chromophoric and redox active unit from the TiO_2 surface. The three-point attachment of the tripod and the rigidity of the linker were synthesized to achieve some level of control over the orientation.[9] We find that eq 1 accurately predicts V_{oc} with a molecular dependence that can be rationalized by the semiconductor–sensitizer distance. The results suggest a new and general strategy for improving solar energy conversion efficiencies in dye-sensitized solar cells.

The mesoporous nanocrystalline TiO_2 thin films and **1** were prepared as previously described.[10] The synthesis of the tripodal
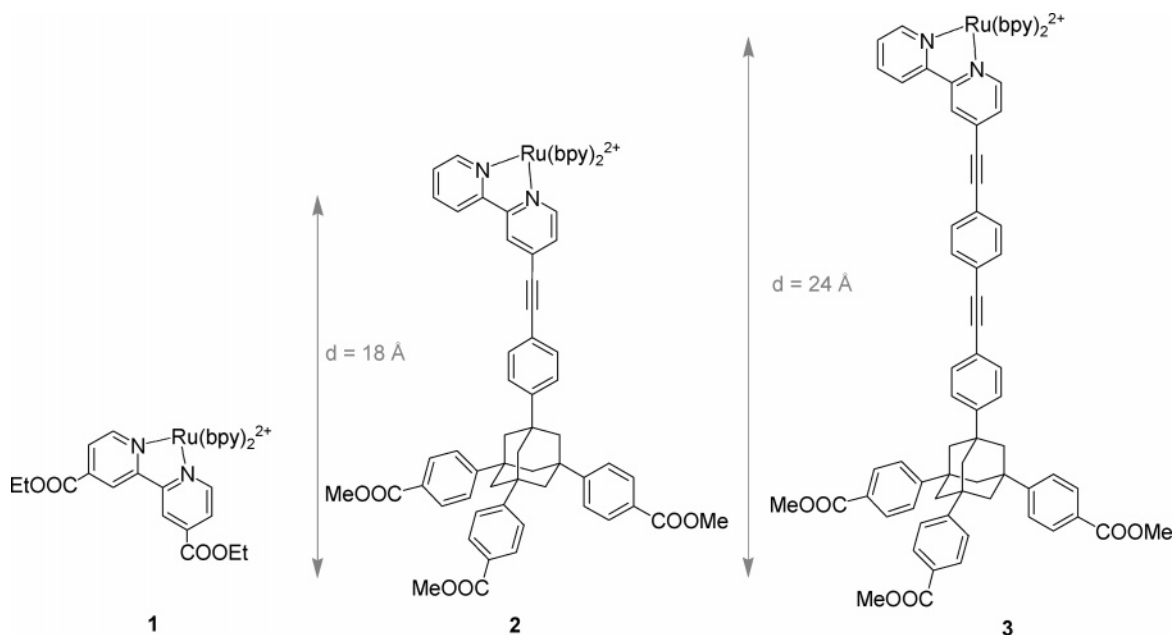
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Figure 1. Molecular structures of the sensitizers [Ru(bpy)$_2$(deeb)](PF$_6$)$_2$ (**1**), [Ru(bpy)$_2$(bpy)−(E-Ph)−Ad](PF$_6$)$_2$ (**2**), and [Ru(bpy)$_2$(bpy)−(E-Ph)$_2$−Ad](PF$_6$)$_2$ (**3**). The distance between the Ru center and the surface binding groups increases in the order **1** (7 Å) < **2** (18 Å) < **3** (24 Å).
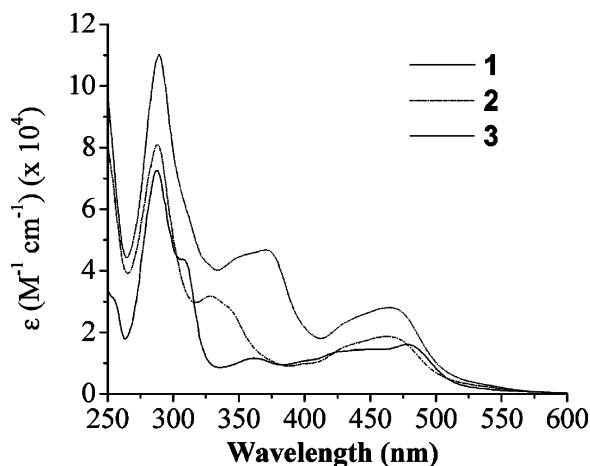

Figure 2. UV−visible absorbance spectra of **1**, **2**, and **3** in dichloromethane.

Figure 3. Open circuit photovoltage, V_{oc}, vs log(irradiance) for the indicated sensitizers in regenerative solar cells with 0.1 M TBAI/0.005 M I$_2$ in CH$_2$Cl$_2$.

sensitizers **2** and **3** has been described in the literature.[9,11] The sensitizers were anchored to base pretreated TiO$_2$ thin films as previously described.[12] All photoelectrochemical measurements were performed in 0.1 M LiI/0.005 M I$_2$ in dichloromethane. Photocurrent−voltage data were measured with a Keithley model 617 electrometer. Excitation was achieved with the 488 nm line of an Innova Ar$^+$ ion laser equipped with a Galilean beam expander and appropriate neutral density filters. Photocurrent action spectra were recorded from 360 to 650 nm in 5 nm increments and 3 s integration times with a 150 W Xe lamp optically coupled to a monochromator. Incident irradiances were quantified with a calibrated Si photodiode (Graesby Inc.).

Figure 2 shows the visible absorbance spectra for sensitizers **1**, **2**, and **3** in dichloromethane. The broad visible absorbance was assigned to metal-to-ligand charge transfer (MLCT) transitions. The absorption band at 290 nm has been assigned to the ancillary bpy ligands, and the bands between 325 and 400 nm for **2** and **3** have been assigned to $\pi \rightarrow \pi^*$ transitions of the tripodal ligand.[9] The absorbance spectrum of **2** and **3** anchored to TiO$_2$ was, within experimental error, the same as that in fluid solution. A small shift was observed in the absorbance spectra
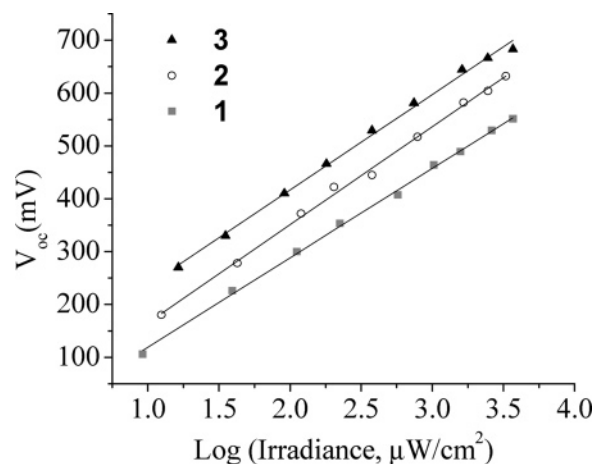
of **1**/TiO$_2$ that has been previously attributed to sensitizer−TiO$_2$ interactions.[12]

Figure 3 shows a plot of V_{oc} versus the logarithm of the 488 nm excitation irradiance. In agreement with eq 1, the data were linear and best-fit lines correspond to ideality factors of ∼3, that is, ∼180 mV/decade. If these data were extrapolated to 100 mW/cm^2, the V_{oc} value would be ∼900 mV for **3**. The absorbed photon-to-current efficiencies were sensitizer independent and were around 50% at 488 nm.

The data in Figure 3 clearly show a relationship between the structural change (length increase) and V_{oc}. The V_{oc} values were 25−30% larger over 3 orders of magnitude change in irradiance for sensitizer **3** relative to **1**. The shorter tripod displayed behavior intermediate between these two extremes. The results suggest that the strategy of positioning the redox active unit of the sensitizer (in this case the Ru^{III} center) farther from the semiconductor surface to increase V_{oc} is valid.[5,6] Presumably, this results from inhibited recombination of the TiO$_2$ electrons with the iodide oxidation products and/or the oxidized sensitizer. This allows the quasi-Fermi level of the semiconductor to increase relative to the Pt electrode. We emphasize that diffusion

of the oxidized iodide species toward the TiO$_2$ surface cannot be ruled out. Nevertheless, assuming that the diode equation accurately models the sensitized interface, the TiO$_2$(e$^-$) → I$_3^-$ (and/or I$_2$) charge recombination rate constants were decreased by a factor of 20 for **2**/TiO$_2$ and 280 for **3**/TiO$_2$ relative to **1**/TiO$_2$.

An alternative interpretation of the results was considered but was ultimately rejected. Sugihara, Arakawa, and co-workers have recently reported compelling evidence for a ligand-mediated reduction of the redox mediator by TiO$_2$ conduction band electrons.[13] This pathway also appears to lower V_{oc} in the novel near-IR absorbing Os^{II} polypyridyl sensitizers reported by Bignozzi.[14] Both authors observed surprisingly small V_{oc} values. Sugihara has shown that the ligand reduction potential for these sensitizers is energetically proximate to the conduction band edge, E_{cb}.[13] Indeed, by tuning E_{cb} with aqueous base, it has been possible to trap injected electrons on these types of ligands.[15] The first ligand reduction potentials of sensitizers **1**−**3** are in the range −1.0 to −1.3 V versus SCE, with the deeb ligand being the most easily reduced.[9,16,17] While such a pathway could result in the lower V_{oc} observed for compound **1**, (**1**$^{2+/+}$) = −1.0 V versus SCE,[16] it does not account for the significantly different V_{oc} values observed for the tripodal sensitizers, whose ligand reduction potentials are nearly identical, (**Ru**$^{2+/+}$) = −1.25 ± 0.01 V versus SCE.[9,17] Therefore, ligand-mediated reduction of the redox mediator is not a likely mechanism for the trend in V_{oc} values reported here.

In summary, we report a relationship between V_{oc} and the distance between the sensitizer binding group and the Ru^{III} center. The irradiance dependent results were adequately described by the diode equation and were consistent with a mechanism wherein iodide oxidation takes place farther from the TiO$_2$ surface for sensitizers that give the largest V_{oc} values. We emphasize that these studies were fundamental in nature and were completed with sensitizers and electrolytes that were not optimized for high solar power conversion efficiencies. In fact, the dichloromethane electrolyte was chosen with the hope that sensitizer−iodide ion pairing would help fix the charge recombination distances.[18] Future studies will test the generality of these findings with alternative sensitizers and electrolytes.

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