HETEROLEPTIC OSMIUM(II) POLYPYRIDINE COMPLEXES
AND CARBAZOLE-BASED CHROMOPHORES
AS SENSITIZERS IN DYE-SENSITIZED SOLAR CELLS

ANTHONY CHINEDU ONICHA

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Committee:
Dr. Felix N. Castellano, Advisor
Dr. Margaret M. Yacobucci
Graduate Faculty Representative
Dr. John R. Cable
Dr. Thomas H. Kinstle
Several osmium(II) polypyridine complexes bearing modified terpyridine and bipyridine ligands were designed, synthesized and characterized in this work. The photophysical and electrochemical properties of the complexes were studied and the results confirm the suitability of these complexes to serve as sensitizers in dye-sensitized solar cells (DSSCs).

Operational DSSCs incorporating these complexes as sensitizers were fabricated and the photovoltaic properties of these sensitizers were evaluated. Device photovoltaic properties were acquired by measuring the external quantum efficiency (EQE) as a function of wavelength and the current-voltage (I-V) curves, the latter under simulated AM1.5G one sun illumination. Initial photovoltaic evaluation of their associated solar cells indicated that TD-1 has the best photovoltaic properties. Further device optimization was carried out using this sensitizer. It was demonstrated that the photovoltaic properties of the Os(II)-based sensitizers can be improved by making variations in the composition of the redox electrolyte used in the operational DSSCs. The results indicate that an abundance of I⁻ appears to be crucial for the effective regeneration of surface-bound osmium sensitizers and hence the production of higher photocurrents in these devices. Most importantly, an unprecedented power conversion efficiency for an Os(II)-based DSSC of 5.03% was achieved with the TD-1 sensitizer.
Electrochemical and photovoltaic studies were also carried out on sensitizers based on metal-free carbazole-based chromophores. Two of the sensitizers incorporate a carbazole linker and displayed impressive photovoltaic properties with EQE’s of about 75%, fill factors above 70% and power conversion efficiency of 2.70%. Short-term light-soaking indicated the potential stability of these sensitizers towards prolonged exposure to solar irradiation.
To my parents,

Chief Livinus and Theresa Onicha,

for their love and support, their love of education,

and the enormous sacrifices they made

to ensure that we went to school.
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CHAPTER I

Introduction
1.1. Photoelectrochemical Processes

Significant interest arose in solar cell technology as an alternative source of energy for terrestrial use in the mid-1970s after the political unrest in the Middle East and the oil embargo that followed. This interest was again rekindled in the last few years, especially with the recent economic downturn and the realization of the negative effect of fossil fuels on the environment. Over the years, environmental and economic concerns have motivated research into alternative sources of energy that could replace fossil fuels. Solar energy is the most abundant, clean and safe energy source that could also be harnessed in remote areas.

The average power of sunlight just above the Earth’s atmosphere is over 1300 W/m², but at noon on a cloudless day, an average power of about 1000 W/m² reaches the Earth’s surface. Reflection and absorption of light during its passage through the atmosphere account for the losses. Even when these losses are taken into consideration, the amount of energy reaching the surface of the earth makes it clear that solar power is an abundant resource and potentially a major player in the world’s energy market.

Solar photovoltaic energy conversion is an energy conversion process that transforms solar energy into electrical energy. Solar cells are photovoltaic cells that absorb sunlight and convert it directly and continuously into electricity, usually without a net chemical change within the device. This is explained based on ideas from quantum theory. Light consists of packets of electromagnetic energy, called photons, whose energy depends solely on its frequency, or color. Photons with sufficient energy can excite electrons in the lower energy levels of metals into higher energy levels where they have freedom of motion. The absorbed energy could be sufficient to completely liberate the electrons from the surface of the metal, the photoelectric effect, or to drive the electrons through an external circuit, the photovoltaic effect, if there is some built-in spatial asymmetry that pulls the electrons away before they can relax. The
photovoltaic effect was reportedly first discovered in 1839 by Becquerel when he found that silver-coated platinum electrodes, immersed in a suitable electrolyte, produced a small amount of current and voltage when exposed to sunlight. This was the pioneering work on photoelectrochemical cells using a semiconductor/liquid junction setup. The energetics of the semiconductor/liquid junctions have been extensively studied and a detailed explanation of the semiconductor-electrolyte interface can be found elsewhere. The first solid state photovoltaic devices were made in 1876 by Adams and Day and in 1954, a diffused silicon p-n junction photovoltaic device was reported which served as a forerunner for the present widespread silicon solar cell technology. The well-known concept of p- and n-doping of semiconductors and the working principle of p-n junction devices can be found elsewhere. Also in 1954, the first cuprous sulfide/cadmium sulfide heterojunction solar cells were reported, paving the way for intense research on thin film solar cell devices. The first real impact of solar cell technology came with the advent of space exploration and was occasioned by the demand for reliable, long-lasting power sources.

The most obvious photoelectrochemical process is photosynthesis – a process by which solar energy is converted into chemical fuel by green plants. Research has focused on two types of photoelectrochemical cells (Figure 1.1) that can be used to achieve solar energy conversion and storage. The first is the photosynthetic cell, modeled after photosynthesis, which converts light energy to chemical energy in the form of chemical fuel. Incident photons with energy greater than the bandgap of the semiconductor generate electron-hole pairs, which are separated by the electric field of the space-charge layer. The electrons (e⁻) in the conduction band migrate through the bulk semiconductor and the external circuit to the counter electrode from where they reduce the redox molecule to form a reduction product (Red.). The holes (h⁺) in the valence band are driven to the surface of the semiconductor where they are scavenged by the redox molecule to
form an oxidation product (Ox.). The favored redox molecule is water which gives hydrogen (H₂) and oxygen (O₂) as reduction and oxidation products, respectively. The second type of photochemical cell is the regenerative cell and operates on a similar principle. In this case, the redox molecule is also oxidized at the semiconductor surface, but the oxidation product is not evacuated, as in the previous case, but migrates to the counter electrode where it is reduced back to its initial form. This results in no net chemical change within the system and the product of the process is the current that flows in the external circuit. Prior research on regenerative cells had focused on n-type (electron-doped) II/VI or III/V semiconductors using electrolyte based on sulfide/polysulfide or vanadium(II)/vanadium(III) and conversion efficiencies of up to 19.6% have been reported for multi-junction regenerative photoelectrochemical cells.⁵,⁸

**Figure 1.1.** Schematic representation of a photoelectrochemical cell.
1.2. The Dye-Sensitized Solar Cell

A relatively new kind of regenerative photoelectrochemical cell is the dye-sensitized solar cell (DSSC). The original breakthrough in the concept of dye-sensitized solar cell was achieved by O’Regan and Grätzel in 1991, and was preceded by a successful sensitization of wide band gap semiconductors, such as TiO$_2$, by a ruthenium-based sensitizer. This further permitted a complete departure from classical solid state solar cells as DSSCs are devices based on interpenetrating solid/liquid network junctions. Poor light harvesting properties of the nanocrystalline TiO$_2$ were overcome by anchoring molecular sensitizers with a broad range of visible light absorption to the nanoparticles. Only surface-anchored sensitizers, as a rule, can contribute to the sub-band gap photoresponse of the device. This is because most sensitizers, when in solution, have excited state lifetimes that are too short to allow for any homogenous bimolecular electron-transfer process. The DSSC is the only photovoltaic device that absorbs photons using molecules and converts them to electric charges without the use of intermolecular transport of electronic excitation; and also the only solar cell that separates the two functions of light harvesting and charge-carrier transport. Other photovoltaic devices, such as the conventional ones and all of the other known organic photovoltaic devices, carry out both functions simultaneously.

1.3. The Structure of the Dye-Sensitized Solar Cell

The DSSC is a multilayer device which consists of three distinct parts: the photoanode, the redox electrolyte and the cathode (Figure 1.2). The photoanode and cathode usually have a substrate which in most cases is a transparent conductive glass (TCG). The transparent conductive glass is coated on one of the sides (the conductive face of the glass) with fluorine-doped tin oxide (SnO$_2$: F, FTO) or indium-tin oxide (In$_2$O$_3$-SnO$_2$, ITO) to make it conductive.
Figure 1.2. Schematic representation of the dye-sensitized solar cell.

The photoanode, which performs the function of a working electrode, is made up of a nanocrystalline semiconductor thin film, deposited and sintered onto the TCG, with a monolayer of sensitizer molecules anchored on the surface of the nanoparticles. The counter electrode is usually a TCG coated with a thin film of platinum particles. The redox electrolyte contains, as a rule, a redox mediator which is usually the iodide/triiodide (I⁻/I₃⁻) redox mediator. Apart from the
three parts already mentioned, the photoanode and the cathode are usually separated by an inert polymer spacer such as hotmelt gasket or surlyn film. The polymer film is cut to expose the photoactive area of the photoanode to the redox electrolyte and serves as a sealant between the photo-inactive area of the anode and the cathode, preventing short-circuiting of the device.

1.4. Operational Principle of the Dye-Sensitized Solar Cell

The operational principle of the dye-sensitized solar cell\textsuperscript{13} is illustrated in Figure 1.3 with a generic energy level diagram. Photoexcitation of the sensitizer promotes its ground state electron to the excited state from where the electron is injected into the conduction band of the semiconductor. The injected electron flows through the network of semiconductor nanoparticles to the TCG substrate from where it is relayed through the external circuit to the cathode. The oxidized sensitizer is regenerated/reduced back to its ground state by electron donation from the electrolyte, usually an organic solution containing a redox mediator/hole conductor such as the iodide/triiodide redox mediator, which intercepts the recapture of the conduction band electron by the oxidized sensitizer. The iodide/triiodide redox mediator is, in turn, regenerated at the counter electrode, thus completing one full cycle of operation. The cycle of operation of DSSCs involve electron transfer processes, whose theory will be discussed later. It has been shown that the sensitizer regeneration process does not produce the sensitizer that was initially photoexcited, but instead is succeeded by a slow (\textmu s to ms) cation transfer process that yields the initial sensitizer.\textsuperscript{14} A more detailed study revealed an underlying Stark effect, wherein electron injection into the conduction band of the nanocrystalline \text{TiO}_2 creates an electric field resulting in the perturbation of the metal-to-ligand charge transfer electronic transitions of the sensitizer.\textsuperscript{15} The decay of this Stark effect in the presence of iodide donors was attributed to ionic reorganization at the sensitized interface which results in a more effective screening of the field
from the sensitizers, which in turn is expected to increase the lifetime of the interfacial charge-separated states and hence the open-circuit voltage of the dye-sensitized solar cell.

**Figure 1.3.** Principle of operation of the dye-sensitized solar cell. M(III/II) and M(III/II)* represent the molecular sensitizer in the ground and excited states, respectively. $V_{\text{max}}$ represents the maximum possible voltage from the device.

Electron injection from the excited state of the sensitizer into the conduction band of TiO$_2$, $k_{\text{inj}}$, is known to occur on the sub-picosecond time scale$^{16-19}$ with high yield, provided that the excited-state of the sensitizer lies above the conduction band of the TiO$_2$. Where electron injection is inefficient, nonradiative decay of the excited state, $k_d$, or trapping of the excited-state electron by the redox mediator$^{20}$ (if the excited state is long-lived enough for a bimolecular quenching process) may become the dominant loss pathway. The injected electron can percolate
to the TCG to be collected \((10^{-6} \text{ – } 10^{-3} \text{ s})\),\(^{21}\) or can be lost by recombination with the oxidized sensitizer \((10^{-8} \text{ – } 10^{-3} \text{ s}, \text{ rate constant } k_{cr}\)\(^{22}\) or by reaction with the redox mediator in the electrolyte solution, \(k_{br}\). Although these loss pathways generally take place on larger timescale, they can still contribute to loss of photocurrent in the external circuit if the system is not optimized. Regeneration of the oxidized sensitizer, \(k_{reg}\), generally takes place within \(10^{-11} \text{ – } 10^{-9} \text{ s}\), but this rate strongly depends on the nature of the sensitizer.\(^{13}\)

1.5. Characterization of Photovoltaic Devices

The photovoltaic performance of solar cells is evaluated by measuring the incident photon-to-current conversion efficiency (IPCE) and the current-voltage (I-V) characteristics. The IPCE, also referred to as the external quantum efficiency (EQE), is the ratio of the observed photocurrent to the incident photon flux, measured as a function of wavelength. This parameter serves as an indicator of the ability of the solar cell to convert light of specific wavelengths into current and is used to evaluate the photoaction of the solar cell at various regions of the electromagnetic spectrum. The EQE can be calculated using equation (1.1).\(^{23,24}\)

\[
\text{EQE}(\lambda) = \frac{1240 \times \text{photocurrent density (A/cm}^2\text{)} \times 100}{\lambda \text{ (nm)} \times \text{photon flux (W/cm}^2\text{)}}
\] (1.1)

The EQE depends on the light-harvesting efficiency (LHE) of photons of wavelength \(\lambda\), the quantum yield of electron injection from the excited state of the sensitizer to the conduction band of the semiconductor oxide (\(\Phi_{inj}\)), and the electron collection efficiency (\(\eta_{coll}\)) according to equation (1.2). The LHE depends on the absorption properties of the sensitizer, \(\Phi_{inj}\) depends on the excited-state oxidation potential of the sensitizer and its lifetime, while \(\eta_{coll}\) is dependent on
the structure and morphology of the mesoscopic film and also on the effectiveness of the sensitizer regeneration process which intercepts charge recombination.\textsuperscript{13,24}

\[
\text{EQE} (\lambda) = \text{LHE} \times \Phi_{\text{inj}} \times \eta_{\text{cell}}
\] (1.2.)

The current-voltage characteristics of solar cells can be obtained by three different methods: diode forward, $P$-$N$ junction, and photovoltaic output methods.\textsuperscript{25} The diode forward method tests the solar cell like a diode without applying any illumination, but by supplying a DC power from an external source. The current going into the terminals of the solar cell and the voltage across them are measured. This method differs from the rest in that there is no light-generated current. In the $P$-$N$ junction method, the solar cell is illuminated with variable light intensity. The short-circuit current and the open-circuit voltage are determined for every light intensity setting, with which the desired current-voltage curve is plotted. The value of the light intensity does not have to be known if the value of the light–generated current can be determined. The most commonly used method is the photovoltaic output method in which the solar cell is illuminated with light of known and constant intensity and a resistive load is varied between short-circuit and open-circuit conditions while measuring current and voltage across the terminals of the solar cell.
The current-voltage characteristics of a solar cell consist of four important parameters: the short-circuit current density ($J_{SC}$), the open-circuit voltage ($V_{OC}$), the fill factor ($ff$) and the power conversion efficiency ($\eta$). Figure 1.4 shows a typical current voltage curve. The short-circuit current is the current that flows across the terminals of the device when there is no resistance in the external circuit and represents the maximum possible value of current that the device can generate. The open-circuit voltage is the voltage across the terminals of the device when there is infinite resistance to current flow and represents the maximum possible value of voltage from the device. The fill factor is the ratio of the maximum output power, $P_{max}$, of the device (shaded area of the graph) to the theoretical maximum power output ($J_{SC} \times V_{OC}$) and...
indicates the degree of internal resistance within the device. The closer the value of the fill factor is to unity (or 100 %), the lesser the internal resistance and the greater the power conversion efficiency. The fill factor is calculated according to equation 1.3.

\[
\text{ff} = \frac{P_{\text{max}}}{J_{\text{SC}} \times V_{\text{OC}}} = \frac{J_{\text{Pmax}} \times V_{\text{Pmax}}}{J_{\text{SC}} \times V_{\text{OC}}}
\]  

(1.3.)

The power conversion efficiency is the fraction of incident light power that is converted into electrical power and can be obtained as a product of the integral photocurrent density (\(J_{\text{SC}}\)), the open-circuit voltage (\(V_{\text{OC}}\)), the fill factor (ff) and the intensity of the incident light (\(I_{\text{s}}\)), according to equation 1.4.

\[
\eta = \frac{J_{\text{SC}} \times V_{\text{OC}} \times \text{ff}}{I_{\text{s}}}
\]

(1.4.)

For terrestrial applications, the global air mass 1.5 spectrum (AM1.5 G) at a constant intensity of 100 mW/cm\(^2\) at 25 °C represent the standard conditions for the acquisition of the current-voltage characteristics of a solar cell. The passage of sunlight through the atmosphere is accompanied by losses in the form of absorption, reflection, and scattering by atmospheric gases and dust particles. Wavelengths of light less than 300 nm are filtered out by atomic and molecular oxygen, ozone, and nitrogen while water and carbon dioxide absorb mainly in the infrared.\(^2\) These losses result in a continuous spectrum with sharp peaks at various wavelengths (Figure 1.5) and a reduction in the average power of the sunlight reaching the Earth’s atmosphere to 1000 W/m\(^2\) (or 100 mW/cm\(^2\)).
Air mass (AM) is an astronomical term which expresses the effect of the Earth’s atmosphere on the solar spectrum and is associated with a coefficient that characterizes the solar spectrum after the solar irradiation has passed through the atmosphere. The air mass coefficient, $\eta_{\text{AirMass}}$, is defined as follows:\(^2\)

$$\eta_{\text{AirMass}} = \frac{\text{Optical path length to sun}}{\text{Optical path length if sun is directly}} = \csc \gamma_s \quad (1.5.)$$

where $\gamma_s$ is the angle of elevation of the sun, as shown in Figure 1.6. The AM $\eta_{\text{AirMass}}$ solar spectrum is therefore an extraterrestrial solar spectrum attenuated by $\eta_{\text{AirMass}}$ thickness of an Earth atmosphere of standard thickness and composition. AM1.5 corresponds to the sun being at

![AM1.5G Spectrum](image)
an angle of elevation of 42°. Two types of AM1.5 spectra are the direct AM1.5 spectrum that includes only the direct sunlight, and the global AM1.5 spectrum (AM1.5 G) which includes both the direct and the diffuse sunlight.26

Figure 1.6. The air mass definition scheme.

1.6. Characterization of Photoinduced Processes

Absorption of light and the processes triggered can be represented by a general Jablonski diagram as shown in Figure 1.7. From a molecular point of view, absorption of a photon promotes an electron from the ground state to the corresponding excited state. The ground state of most molecules is singlet in nature (S₀) and absorption of a photon promotes an electron to the singlet excited states (S₁, S₂, S₃, etc) in a vertical transition within a time frame (~ 10⁻¹⁵ s) that is too short for any nuclear displacement, according to the Frank-Cordon principle.27 The excited state usually possesses many vibrational states from where the excited state electron relaxes by internal conversion (IC) within 10⁻² s to the lowest vibrational state of the lowest energy excited state. The singlet excited state can then be deactivated radiatively (hνᵣ, rate constant ¹kᵣ),
nonradiatively (rate constant $1k_{nr}$) or by intersystem crossing (ISC) to the triplet excited state (rate constant $1k_{isc}$). Intersystem crossing occurs when the electron in $S_1$ undergoes spin conversion to the triplet, $T_1$, excited state from where it can decay radiatively ($h\nu_p$, rate constant $3k_r$), or nonradiatively (rate constant $3k_{nr}$). Radiative decay from the singlet excited state is termed fluorescence ($h\nu_f$) and such decays from the triplet excited state are referred to as phosphorescence ($h\nu_p$). Fluorescence is a kinetically fast process since it is allowed by the spin-selection rule$^{27,28}$ while the spin forbidden phosphorescence is a kinetically slow process.

Figure 1.7. Jablonski diagram showing the energy levels that are accessible to molecules upon photoexcitation.
The characteristics of the excited state can be obtained experimentally by measurement of the photophysical properties of the compound. The quantum yield (Φ) is the ratio of the number of emitted photons to the number of absorbed photons and is normally measured versus a standard. The expression for the quantum yield can be written as:29

\[
\Phi = \frac{k_r}{k_r + \sum k_{nr}} \quad (1.6.)
\]

where \( \sum k_{nr} \) is the sum of all the nonradiative decay processes. The excited state lifetime (\( \tau \)), defined as the average time the molecule spends in the excited state, can be measured and used in conjunction with the quantum yield to determine the various rate constants as expressed in the following equations:27,29

\[
\tau = \frac{1}{k_r + \sum k_{nr}} \quad (1.7.)
\]

\[
k_r = \frac{\Phi}{\tau} \quad (1.8.)
\]

\[
k_{nr} = \frac{1 - \Phi}{\tau} \quad (1.9.)
\]

It is clear from the above equations that the quantum yield will be close to unity (or 100%) if \( \sum k_{nr} << k_r \). The excited state of a molecule can be deactivated by various means as mentioned earlier and this decreases or quenches the emission (fluorescence or phosphorescence). The
photophysical properties of compounds in combination with their electrochemical properties offer useful insights on possible application of these compounds as sensitizers for DSSCs. The excited state of the sensitizer is quenched by electron injection to the conduction band of the semiconductor TiO₂ in DSSCs.

1.7. Charge-Transfer Complexes

Mixtures of molecules with low ionization potential (electron donors) or high electron affinity (electron acceptors) may exhibit absorption or emission properties that are different from those of the separate molecules. The new bands are due to electron donor-acceptor or charge-transfer complexes (CT).\(^{27}\) Charge-transfer transitions are generally broad and devoid of any vibrational structure due to the small binding energies of these complexes, which allow many different structural configurations to exist in equilibrium with one another. Each structural configuration has a corresponding absorption spectrum and contributions from all the available configurations cause a broadening of the band. An important characteristic of a CT band is its sensitivity to solvent polarity. The energy required for absorption decreases as the solvent polarity increases (given that the excited state is more polar than the ground state) due to solvation of the charged species by the solvent molecules. There is also a decrease in total energy of the charge-transfer complex.\(^{29}\) Many charge-transfer complexes are designed and synthesized as single molecules bearing the donor and acceptor units which may be separated by a linker. The excited states of such complexes can be experimentally tuned by making variations in the choice of the donor and acceptor units, and this is crucial towards greater light harvesting by sensitizers in DSSCs.

Metal-to-ligand charge-transfer complexes (MLCT) are organometallic CT complexes where the metal center is the electron donor and the ligand is the electron acceptor. A simplified Jablonski diagram of MLCT transitions in transition metal complexes is presented in Figure 1.8.
Photon absorption by the metal complex promotes the ground state (S_0) electron to the singlet metal-to-ligand charge-transfer (^{1}\text{MLCT}) excited state from where the electron rapidly crosses to the triplet metal-to-ligand charge-transfer (^{3}\text{MLCT}) excited state via intersystem crossing. The presence of the heavy metal center creates internal heavy atom effects which promote spin-orbit interactions that enhance intersystem crossing (rate constant k_{isc}).\(^{27}\) The ^{3}\text{MLCT} excited state decays radiatively (rate constant k_r) or non-radiatively (rate constant k_{nr}) to the ground state. The magnitude of the spin-orbit coupling can be high enough to enable spin-forbidden transitions,\(^{27}\) promoting electrons from the ground state directly to the triplet MLCT excited-state, as is exemplified in osmium(II) polypyridyl complexes.\(^{30-33}\)

Osmium, a third row transition metal, is part of Group 8 in the periodic table of chemical elements and forms a stable 2+ oxidation state which gives it a d^6 configuration. The complexes of Ru(II), Os(II) and other d^6 systems are of intense photochemical and spectroscopic interest due to the fact that a variety of these complexes can be designed to possess radically different types of excited states, lowest in energy and accessible with near-ultraviolet, visible and near-
infrared radiation. The preferred geometry adopted by Os(II) complexes is octahedral and is explained based on the ligand field theory. A free transition metal ion has five degenerate d-orbitals whose energy increases due to electron-electron repulsion in a spherical field. The five degenerate d-orbitals are split by the ligand field during complex formation into different sublevels dictated by the symmetry, with some d-orbitals stabilized while the rest are destabilized. A detailed description of the different splitting patterns in various geometrical fields can be found elsewhere. In an octahedral ligand field, the perturbation of the d-orbitals results in splitting into two sets (Figure 1.9): the stabilized triply degenerate t$_{2g}$ orbitals ($d_{xy}$, $d_{xz}$ and $d_{yz}$) and the destabilized doubly degenerate e$_g$ orbitals ($d_{z^2}$ and $d_{x^2-y^2}$). The t$_{2g}$ orbitals are bonding, while the e$_g$ orbitals are antibonding with respect to metal-ligand bonds. The energy separation between the t$_{2g}$ and the e$_g$ orbitals is the crystal field splitting parameter, $\Delta_0$ or 10Dq, whose magnitude is determined by the strength of the ligand field and the identity and oxidation state of the metal ion. Ligands are placed according to their field strength in the spectroelectrochemical series of ligands and can be divided into two groups: the weak field ligands and the strong field ligands. Metal ions can also be placed in a spectroelectrochemical series, independent of the ligands.
Figure 1.9. Perturbation of d-orbital energies during the formation of an octahedral complex.

The orbital dispositions for a strong field $d^6$ octahedral complex are shown in Figure 1.10 and include three different case scenarios.\textsuperscript{34} Case A is when intraligand $\pi \rightarrow \pi^*$ electronic transitions are the lowest energy transitions. This is possible if the filled metal $t_{2g}$ orbitals lie below the filled orbitals of the ligand and the $e_g$ orbitals lie above the $\pi^*$ orbital set, and is exemplified in rhenium trisbipyridine and trisphenanthroline complexes. Case B is when the filled metal $t_{2g}$ orbitals lie above the filled ligand orbitals and the metal $e_g$ orbitals lie below the ligand $\pi^*$ orbitals. The lowest energy electronic transitions obtainable in the case are the metal-centered Laporte-forbidden\textsuperscript{28} $d \rightarrow d^*$ transitions ($t_{2g} \rightarrow e_g$) and are typically exhibited by the hexacyanocobalt(III) ion. The third situation (Case C) is found in most Os(II) and Ru(II) complexes. This case is obtainable when the filled metal $t_{2g}$ orbitals lie above the filled ligand orbitals and the $\pi^*$ ligand orbital lies below the metal $e_g$ orbital. The lowest energy electronic transitions possible in such complexes are $d \rightarrow \pi^*$ ($t_{2g} \rightarrow \pi^*$) transitions, which are also typical of weak field ligands. This type of transition is typically exemplified in metal-to-ligand charge-transfer transitions (Figure 1.8).
1.8. Tuning of MLCT Transitions

The polypyridyl complexes of transition metals have been greatly explored owing to their useful properties as sensitizers in various photonic and optoelectronic devices. In their non-complexed form, the polypyridyl ligands (all nitrogen heterocycles) that are the main components in these complexes possess non-bonding electrons on their nitrogen atoms that can be promoted into the antibonding $\pi^*$ orbitals on the aromatic ring upon photoexcitation. The first $n \rightarrow \pi^*$ transitions, for pyridine, are usually the lowest energy transitions, followed closely by $\pi \rightarrow \pi^*$ transitions. Upon complexation of the polypyridine ligand to a metal center, the $n$-electrons of the nitrogen atom form a $\sigma$–bond with the metal ion which effectively lowers the
energy of the electrons so that they can no longer be excited by low energy light. This is true only for n-electrons that are involved in the formation of a metal complex. Unlike the \( n \rightarrow \pi^* \) transitions, the \( \pi \rightarrow \pi^* \) transitions on the ring are not greatly shifted by complexation and usually lie in the same region as in the free ligand.\(^{34}\) This permits tuning of the excited state properties of \( d \rightarrow \pi^* \) MLCT complexes through the use of ligands that have low-lying \( \pi \rightarrow \pi^* \) transitions (\( \pi^* \)-tuning) that can be exploited to extend \( d \rightarrow \pi^* \) MLCT transitions to lower energies.\(^24\) The other approach used in the tuning of excited state properties towards achieving lower energy transitions involve the tuning on the metal \( t_{2g} \) orbital (\( t_{2g} \)-tuning). Figure 1.11 illustrates both strategies. The energy level of the metal \( t_{2g} \) orbital is largely determined by the electron density at the metal center and electron donating substituents on the polypyridine ring raise this energy level, decreasing the energy associated with the MLCT transitions. Electron-withdrawing substituents lower this energy level and increase the energy associated with these transitions.

\[ \pi^* \text{-tuning with low-lying } \pi^* \quad \text{and} \quad t_{2g} \text{-tuning with donor} \]

**Figure 1.11.** Schematic representation of \( t_{2g} \)- and \( \pi^* \)-tuning of MLCT transitions in polypyridine complexes.
1.9. Marcus Theory of Electron Transfer

The dynamics of electron transfer reactions can be accurately predicted by Marcus theory which predicts that the rate of energy transfer \( k_{ET} \) between a donor and an acceptor is controlled by the Gibbs free energy \( (\Delta G_{ET}) \) and the total reorganization energy \( (\lambda) \) at a given temperature.\(^{35,36}\) The general expression for the Marcus theory is given below:

\[
k_{ET} = \frac{2\pi}{h} |H_{AB}|^2 \frac{1}{\sqrt{4\pi \lambda k_b T}} \exp \left( -\frac{(\lambda + \Delta G_{ET})^2}{4\lambda k_b T} \right)
\]

where \( h \) is the Planck’s constant \((1.05457266 \times 10^{-34} \text{ J } \text{s})\), \( k_b \) is the Boltzman constant \((1.380658 \times 10^{-23} \text{ J } \text{K}^{-1})\), \( |H_{AB}| \) is the electronic coupling between the initial and final states. The pre-exponential expression defines the nature of the electron transfer reaction while the Gibbs free energy \( (\Delta G_{ET}) \) in this equation is related to the activation free energy \( (\Delta G^*) \) as follows:\(^{37}\)

\[
\Delta G^* = \frac{(\Delta G_{ET} + \lambda)^2}{4 \times \lambda}
\]

A plot of \( \ln k_{ET} \) vs \( \Delta G_{ET} \) is presented in Figure 1.12. From equation 1.11 it is evident that an activationless \( (\Delta G^* = 0.0) \) electron transfer reaction proceeds when \( -\Delta G_{ET} = \lambda \) with the fastest rate. When \( -\Delta G_{ET} < \lambda \), the activation free energy for electron transfer will decrease with increasing \( \Delta G_{ET} \), increasing the rate of electron transfer and represent the normal region of the Marcus curve. In the inverted region of the Marcus curve, \( -\Delta G_{ET} > \lambda \) and the activation free energy increases with increasing \( \Delta G_{ET} \), resulting in a decreasing rate of electron transfer.
The electron transfer processes that characterize DSSC operation fall into the various regions of the Marcus curve. Electron injection into the conduction band of the semiconductor TiO$_2$ is kinetically near optimal ($\Delta G^* \approx 0.0$) as a result of strong coupling between the adsorbed sensitizer and the conduction band. Charge recombination falls in the inverted Marcus region.
and could be up to six orders of magnitude slower than the electron injection process. Likely factors contributing to the slow rate of charge recombination include delocalization of injected electrons in the conduction band and carrier trapping in remote defects of the semiconductor.\textsuperscript{38}

\textbf{1.10. General Design of Molecular Sensitizers}

Progress has been made in the optimization of the sensitizer component of the DSSC through the systematic variation of the metal center, the ligands, and other substituents groups.\textsuperscript{12,24,39} The systematic variations have resulted in the development of sensitizers based on Ru(II),\textsuperscript{12,40} Os(II),\textsuperscript{41-43} Pt(II),\textsuperscript{44} Fe(II),\textsuperscript{45} Re(I),\textsuperscript{46} amongst others. In addition to transition metal complexes, various classes of organic compounds such as coumarin,\textsuperscript{47-49} cyanine,\textsuperscript{50,51} hemicyanine\textsuperscript{52,53} indoline,\textsuperscript{54,55} merocyanine,\textsuperscript{56,57} phenothiazine,\textsuperscript{58} tetrahydroquinoline,\textsuperscript{59,60} and triphenylamine\textsuperscript{51,61,62} have been used as sensitizers in DSSCs. Porphyrin\textsuperscript{63} and phthalocyanine\textsuperscript{64} sensitizers have also been explored.

For a compound to effectively function as a sensitizer for DSSCs, it has to conform to a number of essential requirements. The compound has to (a) absorb all visible light, (b) carry attachment groups to firmly anchor it to the surface of the semiconductor, (c) inject electrons with a quantum yield of unity upon photoexcitation, (d) have a redox potential that is sufficiently high to enable regeneration of the oxidized sensitizer by the redox mediator or hole conductor, (e) be stable enough to sustain up to 100 million turnovers corresponding to about 20 years of exploitation under natural light.\textsuperscript{39,65} For electron injection and sensitizer regeneration to be thermodynamically favored, the excited state oxidation potential of the sensitizer has to be higher than the semiconductor conduction band potential and the ground state oxidation potential has to be lower than the potential of the redox mediator, respectively. Developments in sensitizer design have focused on enhanced spatial charge separation to minimize charge recombination,
the use of hydrophobic sensitizers to prevent desorption of the anchored sensitizer, extension of spectral coverage and enhancement of the molar extinction coefficients of the sensitizers to facilitate greater light-harvesting.66

1.11. The Goal of this Project

Ever since the introduction of the DSSC, significant attention has focused on modification of the dye-sensitizer, with ruthenium(II) polypyridine sensitizers arguably being the most extensively studied.67-72 Some of the reported ruthenium sensitizers include molecules coded as N3,73 N719,74 Z907,75 C103,76 C104,77 K-19,78 the black dye,79 amongst others. Despite the various sensitizers that have been made and the various attempts at improving photovoltaic performance of DSSCs, the highest power conversion efficiencies remain 11.18 % and 11.1 % for N71974 and the black dye,80 respectively. The approach of replacing the ruthenium metal center with osmium in the transition metal complexes used to sensitize nanocrystalline TiO2 has been explored by other researchers.81-85 This choice of osmium (Os) over ruthenium (Ru) is based on similarities in properties. The presence of the heavy metal center in these complexes produces a heavy atom effect which promotes spin-orbit interactions that enhance intersystem crossing. Metal-ligand bond lengths are very similar due to the lanthanide contraction and this minimizes differences in steric effects and solvation.33 There are significant differences that are associated with electronic factors33,86 which are expected to enhance the potential of Os(II) complexes to act as sensitizers in DSSCs as compared to their Ru(II) counterparts. Based on these potential advantages, Os(II) polypyridine sensitizers are known to give additional photoconversion efficiency in the red-to-near-infrared and are expected to give a higher integrated photocurrent density, relative to that of ruthenium sensitizers, provided that the excited state in the osmium complex effectively injects an electron into the conduction band of
This property can be properly harnessed to yield greater photovoltaic performance for Os(II) sensitizers. The extended spectral response could result in an excited state that is not thermodynamically favored towards electron injection to the conduction band of TiO$_2$ and care has to be taken in choice of ligands to avoid such situations. Most polypyridine complexes of Os(II) exhibit remarkable photochemical stability. This stability is a direct consequence of the larger crystal field splitting parameter as compared to Ru(II), which raises the energy of the low-lying metal-centered dd states beyond significant thermal population at room temperature.

This dissertation focuses on the development of new heteroleptic osmium(II) polypyridyl sensitizers bearing 2,2'-bipyridine-4,4'-dicarboxylic acid and 2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid as anchoring groups. The photophysical, electrochemical, and photovoltaic properties of the sensitizers were investigated. Various techniques, such as the use of a scattering layer of TiO$_2$ particles and surface protection of the transparent conductive glass substrate, that were geared towards the optimization of the photovoltaic performance of the sensitizers were evaluated. The last part of this dissertation describes the investigation of DSSCs incorporating metal-free organic sensitizers bearing carbazole donor and cyanoacrylic acceptor units with either carbazole or thiophene linkers. Metal-free organic sensitizers offer unique advantages over organometallic sensitizers, such as lower cost, low toxicity and higher molar extinction coefficients, which make them promising candidates for use in DSSCs.
1.12. References


Chapter II

Instrumentation and Experimental Techniques
2.1 Synthesis and Characterization Methods

All synthetic procedures were performed using standard organic and inorganic techniques in reagent grade solvents. Purification of metal complexes was carried out using either size-exclusion column chromatography on Sephadex LH-20 using methanol as eluent or ion-exchange chromatography on DEAE Sephadex A-25 using water as eluent. Purification of organic ligands was carried out by standard purification techniques and where chromatography was necessary, activated neutral aluminum oxide (Sigma-Aldrich) or silica gel 60 (EM Science) was used with select solvents or mixtures of solvents.

$^1$H NMR spectra were measured on a Bruker 300 (300 MHz) or Bruker 500 (500 MHz) spectrometer. All chemical shifts are referenced to the residual solvent signals and internally referenced to TMS. The splitting patterns in the $^1$H NMR spectra are designated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). MALDI-TOF mass spectra were measured in-house using a Bruker-Daltonics Omnimflex spectrometer. Elemental analyses were performed in-house by a PerkinElmer Elemental Analyzer 2400 series II. All structural characterization spectra are presented in the Appendices.

2.2. Spectroscopic Measurements

UV-visible absorption spectra were measured on a Cary 50 Bio spectrophotometer with an accuracy of $\pm$ 2 nm. Corrected photoluminescence spectra were acquired with an analog/digital spectrophotometer from Photon Technology International equipped with a Peltier-cooled InGaAs detector for the near-IR region with emission signals collected using a lock-in amplifier (Scitek Instruments). Sample excitation was afforded by using an isolated 514.5 nm line from an argon ion laser (Coherent Innova 300) or the 442 nm laser line from a HeCd laser (Melles Griot, series 74). All solution-based photophysical measurements were taken using optically dilute (OD
solutions in spectroscopic grade solvents. The samples were contained in 1 cm$^2$ anaerobic quartz cuvettes (Starna Cells) and deoxygenated prior to all measurements. Corrected photoluminescence spectra on sensitized TiO$_2$ films were measured by an Edinburgh Instruments fluorimeter (FL 920) and excitation was afforded with a 450 W xenon lamp passed through a double monochromator.

Raman spectra were taken on a Renishaw inVia Raman Microscope equipped with a 785 nm NIR diode laser for sample excitation and an edge filter. SEM images were acquired on a carbon tape substrate by an Inspect F (FEI Company) scanning electron microscope. Thicknesses of the TiO$_2$ films were determined by a KLA-Tencor Alpha-Step IQ Surface Profiler.

2.3. Electrochemical Measurements

Electrochemical experiments were carried out at room temperature with a conventional three electrode electrochemical setup. A platinum or gold microdisk working electrode, platinum wire counter electrode and Ag/AgCl reference electrode were used for all the electrochemical experiments. Measurements were performed in anhydrous acetonitrile or dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and the ferrocinium/ferrocene (Fc$^+/Fc^0$) redox couple was used as internal reference. The potentials were measured by cyclic voltammetry and verified by differential pulse voltammetry. The potentials were thereafter converted to $E_{1/2}$ vs NHE using the appropriate Fc$^+/Fc^0$ reference potential as discussed in the relevant chapters. Typical concentration of the electroactive species used for data acquisition was 1.5 mM. The solutions were degassed with argon gas for 15 min prior to each experiment and an argon atmosphere was maintained throughout the experiment. A scan rate of 100 mV/s or 300 mV/s was typically used. All electrochemical data were acquired using either Reference 600 Potentiostat/Galvanostat/ZRA
(Gamry Instruments) or Bioanalytical Systems Epsilon electrochemical workstation interfaced with a computer and re-plotted using Origin 8.0 software.

2.4. Photovoltaic Measurements

The photovoltaic measurements were carried out on dye-sensitized solar cells with I-V and EQE measurement systems purchased from PV Measurements, Inc. All photovoltaic data were acquired by illuminating the solar cells directly through the transparent conductive glass support containing the TiO$_2$ photoanode, except where otherwise stated. All photovoltaic characteristics are reported herein as overall yields that were not corrected for losses due to light absorption and reflection by the conductive glass substrate.

A basic functional diagram of the I-V measurement system is presented in Figure 2.1. The instrument is equipped with a small area solar simulator (SASS) whose irradiance spectrum in comparison to the AM1.5 global reference spectrum is presented in Figure 2.2. It is evident from the irradiance spectra that the spectrum of the SASS closely resembles that of the AM1.5 global reference spectrum. This I-V system employs the photovoltaic out method discussed in Chapter I to acquire the current-voltage characteristics of solar cells. The SASS provides the AM1.5 G whose standard 100 mW/cm$^2$ intensity is calibrated with a NREL-certified silicon reference solar cell (PVM 274, PV Measurements, Inc.). Calibration of the light intensity involves varying the distance between the SASS light source and the reference solar cell and intermittently measuring the I-V characteristics until such a distance where the measured current is within ± 2% of value of the calibration current as provided in the calibration file. The variable electronic load is provided by the source meter during data acquisition which is fully automated using the data acquisition software (PV Measurements, Inc.).
Figure 2.1. Basic functional diagram of the solar cell I-V data acquisition system model SCD1 equipped with a small area solar simulator. This diagram was provided with copyright permission by PV Measurements, Inc.

Figure 2.2. The spectrum of the small area solar simulator compared with the AM1.5 Global reference spectrum. This graph was provided with copyright permission by PV Measurements, Inc.
A basic functional diagram of the EQE measurement system is presented in Figure 2.3. The system applies monochromatic light from a 65 W Xenon arc white light source as filtered by a monochromator and individual filters to the test device. The monochromatic beam is split by a beam splitter that diverts part of it to the monitor sensor, which corrects for fluctuations in the light intensity. The system was calibrated prior to all measurements. Calibration was performed using a reference photodiode and involves measuring the photoaction spectrum of the photodiode from which the incident photon flux for each wavelength can be calculated according to equation 1.1 using its calibration data. The photoaction spectra of test devices were then measured. Data acquisition is fully automated using the EQE data acquisition software (PV Measurements, Inc.).

**Figure 2.3.** Basic functional diagram of the EQE measurement system model IPX8 (DC only mode). This diagram was provided with copyright permission by PV Measurements, Inc.
CHAPTER III

Synthesis, Photophysical, Electrochemical, and Photovoltaic Studies of Osmium(II) Polypyridine Sensitizers
3.1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much scientific attention since the original breakthrough by Grätzel and coworkers.\(^1\)\(^2\) Amongst the merits of these cells are low production costs, high conversion efficiencies and flexibility of substrates. A typical DSSC consists of a dye-sensitized nanocrystalline TiO\(_2\) film on a transparent conducting glass substrate interpenetrated by a hole transport material, usually a liquid electrolyte containing the I\(^{-}/I_3^-\) redox mediator, and a cathode composed of a thin layer of platinum metal on transparent conducting glass. Upon photoexcitation, the sensitizer directly injects its excited-state electron into the conduction band of TiO\(_2\). This electron is transported to the conducting glass substrate from where it is relayed through an external circuit to the cathode. The oxidized sensitizer is reduced by the I\(^{-}/I_3^-\) redox mediator, which in turn recovers an electron from the cathode resulting in no net chemical change inside the device.

Historically, significant attention has focused on modification of the dye-sensitizer, with ruthenium(II) polypyridine sensitizers arguably being the most extensively studied.\(^3\)\(^-\)\(^8\) The approach of replacing the ruthenium metal center with osmium in the transition metal complexes used to sensitize nanocrystalline TiO\(_2\) has been explored by other researchers.\(^9\)\(^-\)\(^{13}\) This choice of osmium (Os) over ruthenium (Ru) is based on similarities in properties. Due to the presence of a transition-metal center in the complexes, internal heavy atom effect promotes spin-orbit interactions that enhance intersystem crossing.\(^14\) Metal – ligand bond lengths are very similar as a result of the lanthanide contraction and this minimizes differences in steric effects and solvation. The similarities that exist are accompanied by significant differences in properties of Os(II) and Ru(II) polypyridine complexes.\(^15\) For instance, it is known that Os(II) polypyridine complexes exhibit the spin-forbidden S\(_0\) – T\(_1\) absorption transition and that the first emission band of these complexes overlap with the lowest energy absorption band, features that are absent
in analogous ruthenium complexes. Comparison between the two in thermodynamic properties and reactivity can be associated with electronic factors. Differences in electron factors exist and they include: (a) a larger value of the crystal field parameter 10Dq, which leads to higher energies for d-d excited states; (b) a lower third ionization energy leading to a low redox potential for the complexes of osmium(II) and consequent stabilization of higher oxidation states; (c) greater extension of the metal d orbitals, which can enhance the metal-ligand backbonding; (d) a larger value of $\lambda$, the spin-orbit coupling constant, ($\lambda_{Ru} = 1200 \text{ cm}^{-1}, \lambda_{Os} = 3200 \text{ cm}^{-1}$)\textsuperscript{16,17} which causes extensive mixing of excited states of different spin multiplicities.$^{15,18}$ This mixing of excited states results in spin-forbidden absorption transitions in the red-to-near-infrared region of the spectrum. These lower energy transitions are expected to give additional photoconversion efficiency in the red-to-near-infrared region and ultimately result in a higher integrated photocurrent density, relative to that of ruthenium sensitizers, provided that the excited state in the osmium complex effectively injects an electron into the conduction band of TiO$_2$.\textsuperscript{9,10}

This chapter presents the syntheses, purification, photophysical, electrochemical and photovoltaic studies of the osmium(II) polypyridine sensitizers. The various synthetic pathways that were employed and the purification procedures are discussed. The photophysical and electrochemical studies are discussed and the data show that the sensitizers are well suited for exploitation in dye-sensitized solar cells. The photovoltaic characteristics of DSSCs made with the sensitizers were acquired. Further studies were carried out to study the effect of a blocking layer on the transparent conducting glass and the results indicate that the photovoltaic characteristics worsen when the blocking layer is present. A maximum power conversion efficiency of 5.03% was achieved for an osmium(II) sensitizer, TD-1, while the benchmark N3 standard sensitizer of comparison gave 7.18% under identical conditions.
3.2. Experimental Section

3.2.1. General. 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine, 4,4'-di-tert-butyl-2,2'-bipyridine (tBu2bpy), ethylene glycol, 2,2':6,2''-terpyridine-4,4',4''-tricarboxylic acid triethyl ester (Et3tctpy), 4,4',4''-tri-tert-butyl-2,2':6,2''-terpyridine (tBu3tpy), 1-butanol, DEAE Sephadex A25, ethanol, K2OsCl6, KSCN, methanol, 1-methylimidazinium iodide, 1-iodopropane, (NH4)2OsCl6, NH4PF6, N,N-dimethyl formamide (DMF), Sephadex LH-20, silver triflate, tetrabutylammonium chloride (TBACl), tetrabutylammonium hydroxide (TBAOH) and triethylamine were purchased from Aldrich Chemical Company. Deionized water was obtained using a Barnstead Nanopure System. All other reagents and solvents were reagent grade and used as received. Special thanks to Dr. Cesar Perez-Bolivar for the deposition of ca. 10 nm of molybdenum trioxide (MoO3) film and Chaiya Prasitticha (in the Hupp research group at Northwestern University) for the deposition of atomic layers of aluminium trioxide (Al2O3).

3.2.2. Synthesis and Characterization

2,2'-bipyridine-4,4'-dicarboxylic acid (dcbpyH2). The synthesis of dcbpyH2 was carried out according to a modified literature procedure.19 In a round bottom flask, 4,4'-dimethyl-2,2'-bipyridine (8.0 g) was dissolved in concentrated sulfuric acid (100 ml) while stirring at room temperature (RT). The solution was cooled to 0 °C on an ice bath and chromium trioxide (26.0 g) was added in small portions over a 1 hr period while stirring and maintaining the temperature at 0 °C. The reaction mixture turned red and then bluish green. The reaction mixture was thereafter heated at 70 °C for 4 hr on an oil bath and then stirred at RT for 10 hr. The green viscous solution was poured into a beaker of ice/water and mixed well to obtain a dark green solution containing greenish-yellow precipitate, which was allowed to settle. The precipitate was separated by centrifugation and washed multiple times with deionized water until the filtrate
became clear. The solid was then suspended in deionized water and KOH was added until solution pH became basic. The insoluble part was filtered off and the filtrate was acidified with concentrated HCl to precipitate the product. The last two steps (aq. KOH and HCl) were repeated until the product became white in color. The product was then washed with water (until neutral pH) and diethyl ether. The product was dried overnight under vacuum and used without further purification. The product is insoluble in most solvents. Yield 9.5 g (89.5%). $^1$H-NMR (300 MHz, D$_2$O/NaOD): $\delta$ ppm: 8.393 (d, 2 H), 8.015 (s, 2 H), 7.482 (d, 2 H).

2,2'-bipyridine-4,4'-dicarboxylic acid diethyl ester (deeb). The esterification of dcbpyH$_2$ was carried out according to a standard esterification procedure. Concentrated sulfuric acid (15 ml) was added to dcbpyH$_2$ (4.85 g) in a round bottom flask containing ethanol (65 ml) and refluxed overnight while stirring to obtain a clear solution. Deionized water (100 ml) was added to the cooled reaction mixture to obtain a white precipitate. Ethanol was removed by rotary evaporation. The white precipitate was filtered and washed several times with deionized water until the filtrate showed a neutral pH. The white powdery product was dried in air. The product is insoluble in methanol, but soluble in chloroform and dichloromethane. Yield 4.97 g (83%). $^1$H-NMR (300 MHz, CD$_3$Cl): $\delta$ ppm: 8.934 (s, 2 H), 8.876 (d, 2 H), 7.923 (d, 2 H), 4.785 (q, 4 H), 1.464 (t, 6 H).

1-n-propyl-3-methylimidazolium iodide (PMII). To a solution of 1-methylimidazolium iodide (10 ml) was added 1-iodopropane (20 ml) while stirring vigorously. The mixture was then heated at 50 °C for 6 hr while stirring. The ionic liquid product separated as a phase under the toluene solution. After cooling, the top phase (toluene solution) was decanted off the yellow ionic liquid product. The viscous product was then washed with ethyl acetate (4 x 20 ml) and
dried under vacuum overnight. Yield 31.3 g (98%). \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta\) ppm: 9.897 (s, 1 H), 7.695 (d, 2 H), 4.363 (t, 2 H), 4.128 (s, 3 H), 2.014 (m, 2 H), 0.995 (t, 3 H).

\([\text{Os}(\text{bpy})_2\text{Cl}_2]\). This precursor complex was synthesized according to published procedure.\(^{20}\) K\(_2\)OsCl\(_6\) (0.407 g) and bpy (0.28 g) were refluxed in anhydrous DMF (20 ml) for 1 hr. The cooled dark brown solution was filtered to remove crystals of KCl. The product was recrystallized from methanol/diethyl ether. 100 ml of saturated aqueous Na\(_2\)S\(_2\)O\(_4\) was added to a solution of the product in DMF/methanol to reduce the metal center from Os(III) to Os(II), forming a deep purple precipitate. The mixture was cooled on an ice bath. The crystals were filtered, washed with water and dried. MALDI – TOF MS: m/z: 574 (M). Yield 0.363 g (75%).

\([\text{Os}(\text{bpy})_2(\text{dcbpyH}_2)](\text{PF}_6)_2\) (AP\(_{25}\)). The synthesis of AP\(_{25}\) was carried out according to published procedure.\(^9\) NaHCO\(_3\) (0.16 g) and dcbpy\(_2\) (0.145 g) were dissolved in deionized water (15 ml) and added to [Os(bpy)_2Cl_2] (0.302 g) dissolved in ethanol (15 ml). The reaction mixture was degassed with argon for 15 min and then refluxed for 6 hr under argon atmosphere. NH\(_4\)PF\(_6\) (0.4 g) was dissolved in about 5 ml of water and added to the cooled reaction mixture. The ethanol was removed on a rotary evaporator. The product was precipitated by the addition of about 10 drops of 60% HPF\(_6\) and then diluted with about 1 ml of deionized water. The resulting mixture was left overnight in the refrigerator. The product was filtered, washed with pH 1.5 water (acidified with HPF\(_6\)) and diethyl ether. Purification was carried out by column chromatography on DEAE Sephadex-A25 using deionized water as eluent. The impure compound was dissolved in a minimal amount of aqueous 0.1 M NaHCO\(_3\) and added to the pre-packed column. The first light brownish-green band was discarded and the major green band was collected. The volume was reduced to about 10 ml by slow evaporation on the rotary evaporator.
The pure compound was then precipitated by addition of a few drops of aqueous conc. HPF₆. The dark crystals were filtered and washed with water acidified with HPF₆ and diethyl ether. The solid was then dried under vacuum overnight. Yield is 80%. MALDI – TOF MS: m/z: 748 (M²⁺-2PF₆), 891 (M²⁺-PF₆). ¹H-NMR: (300 MHz, D₂O/NaOD): δ ppm: 8.643 (s, 2 H), 8.313 (m, 4 H), 7.659 (m, 6 H), 7.481 (m, 4 H), 7.342 (d, 2 H), 7.083 (m, 4 H). Anal. Calcd for OsC₃₂H₂₄F₁₂N₆O₄P₂·3H₂O: C, 35.24; H, 2.77; N, 7.70%. Found: C, 35.23; H, 2.52; N, 7.64%.

[Os(⁴Bu₃tpy)(dc bpyH₂)(NCS)](PF₆) (TD-1). 0.5 g (1.14 mmol) of (NH₄)₂OsCl₆ and 0.463 g of 4,4',4''-tri-tert-butyl-2,2':6',2''-terpyridine (1.15 mmol) were heated in 50 ml of ethylene glycol at 120 °C for 6 hrs under argon. 0.3501 g of deeb (1.17 mmol) was then added to the reaction mixture and heated at 175 °C under argon for 12 hrs. 1.25 g of KSCN was dissolved in 1 ml of H₂O and 4 ml of ethylene glycol and added to the reaction mixture and the reaction continued for an additional 6 hrs at 175 °C under argon. The reaction mixture was cooled to RT and then aqueous NH₄PF₆ was added to the cooled mixture, precipitating the product. The dark-brown product was then filtered from the dark-green filtrate and washed with water. The product was added to 0.57 g of NaOH in 20 ml of ethanol and 80 ml of H₂O and heated at 70°C for 3 hrs to deesterify the product. The deesterified product was precipitated out by the addition of aqueous HPF₆. The product was purified on a Sephadex LH-20 column using methanol as eluent. Four successive chromatographic separations were necessary to obtain the desired purity. MALDI-TOF MS: 895.42 (M⁺-PF₆). ¹H NMR (300 MHz, CD₃OD): δ ppm 9.68 (d, 1 H), 9.19 (s, 1 H), 8.80 (s, 1 H), 8.70 (s, 2 H), 8.51 (s, 2 H), 8.16 (d, 1 H), 7.42 (d, 1 H), 7.31 (d, 2 H), 7.25 (dd, 1 H), 7.22 (dd, 2 H), 1.62 (s, 9 H), 1.30 (s, 18 H). Anal. Calcd for OsC₄₀H₄₃F₆N₆O₄PS·2H₂O: C, 44.69; H, 4.41; N, 7.82%. Found: C, 44.50; H, 4.71; N, 7.57%.
\[(C_4H_9)_4N\][Os\((Bu_3tpy)(dcbpy)(NCS)\)](PF_6) (TD-2). To a clean vial containing 59 mg of TD-1 was added one tetrabutylammonium hydroxide (0.1 M in methanol) in a 1:1 ratio. The solution was stirred overnight and the solvent was removed by rotary evaporation. The product was dried overnight under vacuum. $^1$H NMR (300 MHz, CD$_3$CN): \(\delta\) ppm 9.327 (d, 1 H), 8.891 (s, 1 H), 8.553 (s, 1 H), 8.447 (s, 2 H), 8.286 (s, 2 H), 8.185 (d, 1 H), 7.415 (d, 2 H), 7.125 (m, 3 H), 6.885 (d, 1 H), 3.056 (m, 8 H), 1.587 (s, 9 H), 1.525 (m, 8 H), 1.290 (s, 18 H), 1.275 (m, 8 H), 0.880 (t, 12 H). Anal. Calcd for OsC$_{72}$H$_{113}$F$_6$N$_8$O$_4$PS·3H$_2$O: C, 54.87; H, 7.61; N, 7.11%. Found: C, 54.58; H, 7.32; N, 7.74%.

\[Os'(Bu_3tpy)(dcbpyH_2)(Cl)](PF_6) (TD-3). This complex was prepared in a two-step synthetic procedure starting with the precursor complex, (TBA)$_2$OsCl$_6$, which was prepared from (NH$_4$)$_2$OsCl$_6$, dissolved in a minimal amount of deionized water, by addition of TBACl and formed as a yellow precipitate which was filtered and dried. In a round bottom flask was added $'Bu_3tpy$ (0.304 g), (TBA)$_2$OsCl$_6$ (0.612 g) and 1-butanol (30 ml). The mixture was degassed for 15 min with argon and thereafter refluxed for 7-8 hr under argon atmosphere while stirring. The intermediate [Os($'Bu_3tpy$)Cl$_3$] was collected by filtration of the cooled reaction mixture, washed with water and acetone and dried. The intermediate [Os($'Bu_3tpy$)Cl$_3$] complex, deeb (0.226 g) and ethylene glycol (50 ml) were mixed in a round bottom flask, degassed for 15 min and thereafter heated at 175 °C for 12 hr under argon atmosphere while stirring. Aqueous NH$_4$PF$_6$ was added to the cooled reaction mixture to precipitate the product, which was filtered and dried. The crude product was deesterified under basic conditions (0.373 g of NaOH in 50 ml of water) at 70 °C for 30 min, precipitated by the addition of aqueous HPF$_6$, filtered and dried. Purification was carried out by column chromatography on Sephadex LH-20 using methanol as eluent. Three successive chromatographic separations were necessary in order to obtain the desired purity.
MALDI-TOF MS: 872.44 (M⁺-PF₆). ¹H NMR (300 MHz, CD₃OD): δ ppm 9.874 (broad s, 1 H), 9.216 (s, 1 H), 8.958 (s, 1 H), 8.634 (s, 2 H), 8.545 (s, 2 H), 8.075 (s, 1 H), 7.275 (m, 6 H), 1.685 (s, 9 H), 1.380 (s, 18 H). Anal. Calcd for OsC₃⁹H₄₃ClF₆N₅O₄P: C, 46.08; H, 4.26; N, 6.89%. Found: C, 46.53; H, 4.80; N, 6.81%.

[Os(tctpyH₃)(Bu₂bpy)Cl](PF₆) (TD-4). The multi-step synthesis of [Os(tctpyH₃)(Bu₂bpy)Cl](PF₆) (TD-4), where tctpyH₃ = 2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid, is described as follows: In a round bottom flask was added (TBA)₂OsCl₆ (0.221 g), Et₃tctpy (0.103 g) and 1-butanol (30 ml). The mixture was degassed with argon for 15 min and then refluxed for 7 – 8 hr under argon atmosphere while stirring. The intermediate [Os(Et₃tctpy)Cl₃] was collected by filtration of the cooled reaction mixture, washed with water and acetone and dried. The intermediate [Os(Et₃tctpy)Cl₃] complex (0.150 g), (Bu₂bpy) (0.088 g), triethylamine (1.5 ml) and ethylene glycol (30 ml) were mixed in round bottom flask and degassed for 15 min. The mixture was heated at 175 °C for 12 hr under argon atmosphere while stirring. The product was precipitated by addition of aqueous HPF₆. The crude product was de-esterified under basic conditions (0.124 g of NaOH in 30 ml of water) at 70 °C for 30 min, precipitated by the addition of aqueous HPF₆, filtered and dried. Purification was carried out by column chromatography on Sephadex LH-20 using methanol as eluent. MALDI-TOF MS: 859.79 (M⁺-PF₆). ¹H NMR (500 MHz, CD₃OD): δ ppm 9.835 (broad s, 1 H), 9.046 (d, 4 H), 8.847 (s, 1 H), 8.490 (s, 1 H), 8.065 (d, 1 H), 7.749 (s, 4 H), 6.920 (d, 1 H), 6.825 (broad s, 1 H), 1.680 (s, 9 H), 1.255 (s, 9 H). Anal. Calcd for OsC₃₆H₃₅ClF₆N₅O₆P·2H₂O: C, 41.56; H, 3.78; N, 6.73%. Found: C, 41.60; H, 4.00; N, 6.91%.
[(C₄H₉)₄N]₂[Os(tctpy)(Bu₂bpy)Cl](PF₆) (TD-5). The procedure used to get [(C₄H₉)₄N]₂[Os(tctpy)(Bu₂bpy)Cl](PF₆) (TD-5), where tctpy = 2,2':6',2''-terpyridine-4,4',4''-tricarboxylate, is described as follows: To a round bottom flask was added crude TD-3 and a minimal amount of water was added to it. The pH of the solution was brought to a stable reading of 7.0 by the addition of aliquots of aqueous TBAOH (0.1 M). The water was removed on a rotary evaporator and the product was dried overnight under vacuum. The product was further purified by column chromatography on Sephadex LH-20 using methanol as eluent. ¹H NMR (300 MHz, CD₃OD): δ ppm 9.575 (d, 1 H), 9.008 (s, 2 H), 8.895 (s, 2 H), 8.785 (s, 1 H), 8.423 (s, 1 H), 8.027 (d, 1 H), 7.605 (m, 4 H), 7.928 (m, 2 H), 3.225 (m, 16 H), 1.672 (s, 9 H), 1.459 (m, 16 H), 1.397 (q, 16 H), 1.257 (s, 9 H), 1.007 (t, 24 H). Anal. Calcd for OsC₆₈H₁₀₅ClF₆N₇O₆P·4H₂O: C, 52.38; H, 7.30; N, 6.29%. Found: C, 52.36; H, 7.18; N, 7.12%.

[(C₄H₉)₄N]₂[Os(tctpy)(Bu₂bpy)NCS](PF₆) (TD-6). This complex was synthesized from crude TD-4 complex as follows: TD-4 (0.256 g), ethylene glycol, one equivalent of silver triflate and a minimal amount of methanol (to enhance solubility) were mixed in a round bottom flask and heated at 120 °C for 2 hr under argon atmosphere while stirring. Silver chloride was filtered off from the cooled reaction mixture and washed with methanol, which was thereafter removed on a rotary evaporator. Excess KNCS was dissolved in a minimal amount of water and ethylene glycol (8 ml) and added to the reaction mixture. The process was continued at 175 °C for 6 hr under argon atmosphere while stirring. MALDI-TOF MS: 883.26 (M⁺-PF₆-2TBA). ¹H NMR (300 MHz, CD₃OD): δ ppm 9.878 (d, 1 H⁰), 9.485 (d, 1 H), 9.224 (s, 2 H), 8.915 (s, 2 H), 9.785 (s, 1 H), 8.491 (s, 1 H⁰), 8.455 (s, 1 H), 8.078 (d, 1 H), 8.035 (d, 1 H⁰), 6.575 (m, 4 H), 7.045 (s, 2 H⁰), 6.975 (m, 2 H). (H⁰ stands for protonation isomer). Anal. Calcd for OsC₆₉H₁₀₅F₆N₈O₆P·2H₂O: C, 53.61; H, 7.11; N, 7.25%. Found: C, 53.65; H, 7.60; N, 7.62%.
**Chart 3.1.** Molecular structures of the osmium(II) sensitizers
Scheme 3.1. Synthetic route for TD-1

\[
\text{(NH}_4\text{)}_2\text{OsCl}_6 + \text{ethylene glycol, Ar} \rightarrow \text{TD-1}
\]
3.3. Results and Discussion

3.3.1. Synthesis

Various synthetic routes have been followed in synthesizing polypyridine complexes based on Os(II) and the synthetic approaches adopted herein reflect the usual synthetic pathways for osmium polypyridine complexes.\textsuperscript{20-22} The initial synthetic attempts in this work explored the use of microwave-assisted synthetic procedures to shorten the reaction time and increase yield. This approach stems from the fact that most of the early published works involved multi-step syntheses\textsuperscript{20,23} of heteroleptic or one-pot syntheses of homoleptic complexes, for instance, by heating reactant mixtures in glycerol\textsuperscript{24} at 240°C for one hour, refluxing in ethylene glycol\textsuperscript{25} for 12 hours, in N,N-dimethylformamide\textsuperscript{26} for three days, heating for six more hours in an aqueous solution of sodium \textit{d}-tartate\textsuperscript{27} on a steam bath after pre-heating the aqueous solution for 8 hours on a steam bath. All of these processes involved high temperature, long reaction time or both. Microwave technology offers the advantage of drastically reducing the reaction time, instantaneously reaching and maintaining reaction temperature over an extended period of time. Microwaves can transfer energy directly to reactive species by ‘molecular heating’, and therefore promote reactions that are not possible using conventional heating.\textsuperscript{28} Successful one-step syntheses of homoleptic Os(II) polypyridine complexes (\textit{bis} terpyridine, \textit{tris} bipyridine and \textit{tris} phenanthroline complexes) were achieved using microwave conditions. The use of the microwave was further explored in the synthesis of complexes bearing the 2,2\textsuperscript{'}-bipyridine-4,4\textsuperscript{'}-dicarboxylic acid anchoring group that serve as sensitizers in DSSCs. The microwave-assisted syntheses were all essentially successful but the obtained sensitizers still required extensive purification by column chromatography, a step that is desirable to avoid due to the length of time it takes. Harsh microwave conditions also have the potential of decarboxylating the carboxylic acid groups of the anchoring ligand group.\textsuperscript{29} For these reasons, the synthetic pathways were
restricted to conventional routes on a hot plate using high boiling point oil-bath as a heat transfer agent.

The adopted synthetic procedures involved one-pot and multi-step synthetic pathways which were used interchangeably in most cases and where necessary the osmium precursor was synthetically modified to suit the solubility requirements for the reaction to proceed more efficiently. The syntheses of the sensitizers were carried out mostly in ethylene glycol and occasionally in \(N, N\)-dimethylformamide. In multi-step reactions where the first step involved the coordination of a modified terpyridine ligand, this step was carried out in 1-butanol at reflux temperature. Since the product of this step is insoluble in most solvents, the reagents were chosen such that they are soluble in 1-butanol and the reaction can therefore be monitored by precipitate formation. In multi-step reactions, the less soluble (in 1-butanol) \(\text{NH}_4\text{OsCl}_6\) or \(\text{K}_2\text{OsCl}_6\) was converted to the very soluble \((\text{TBA})_2\text{OsCl}_6\) for this very reason. The coordination of the last set of ligands was carried out in ethylene glycol, which has a high boiling point and provides the necessary stability towards the harsh temperature conditions needed to overcome the huge activation energy of the reaction. The use of solvents having high boiling point, like \(N, N\)-dimethylformamide and ethylene glycol, in the synthesis of Os(II) polypyridine complexes have been reported in the literature. Since the osmium precursor is available mostly in the most stable \(+4\) oxidation state, the solvent functions as a reducing agent and also aids in the coordination of the ligands.

Purification of the sensitizers was carried out by gel-permeation chromatography and was the most time-consuming step as most sensitizers required low loading (~25 – 30 mg per column) and multiple successive chromatographic separations to achieve high purity. At high loadings of the sensitizers during chromatography, the separation between bands can be ill-defined or non-existent, affecting the effectiveness of purification. The most appalling observation is the
inability to obtain a decent $^1$H NMR spectrum of the sensitizers after a single chromatographic purification even when the MALDI-TOF mass spectrum clearly shows the presence of the compound and this was observed for almost all the complexes. For this reason, multiple successive chromatographic separations were necessary in order to obtain analytically pure samples. Apart from AP25 which was purified on Sephadex A25 using water as eluent, other sensitizers were purified on Sephadex LH-20 using methanol as eluent. This is partly because most of the sensitizers were designed to be as hydrophobic as possible (with the tert-butyl group) and partly because of the loss of solubility in simple organic solvents like methanol and acetonitrile after exposure to an aqueous solution, a phenomenon that is still not fully understood. The adsorbent was prepared by soaking overnight in the eluent and was followed by packing of the column. Since Sephadex LH-20 was recycled/purified after each purification step, its quality will ultimately affect the rate of elution. Previous attempts at recycling using dilute nitric acid solution in methanol proved destructive as the quality of the adsorbent deteriorated after such treatment. For this reason all recycling/purification of the Sephadex LH-20 was done by washing with pure methanol with or without unpacking the column. Prior to all chromatographic separations, the complex was dissolved in the appropriate solvent and filtered to remove the insoluble or less soluble impurities which can settle at the top of the column or elute more slowly, thereby affecting the effectiveness of the separation exercise.

Most of the sensitizers exhibited excellent solubility properties in methanol and for this reason, deuterated methanol was chosen as the solvent of choice for the NMR spectroscopy. The solubility properties of AP25 in basic water necessitated the use of D$_2$O/NaOD as the solution of choice. All the sensitizers have excellent NMR spectra when analytically pure and this purity was further confirmed by elemental analysis. All the sensitizers gave good $^1$H-NMR spectra after successive chromatographic separations with the proton counts corresponding to the number of
protons present in the respective sensitizer, except for TD-6 which gave excess proton peaks and higher number of protons than expected. Further chromatographic purifications of this sensitizer did not result in any separation whatsoever and the excess protons might be due to the presence of an isomer, whose retention factor is the same as that of the product. This is probably a protonation isomer as similar peaks, albeit with lower intensities, were also observed in the spectrum of TD-5. The proton spectra of TD-1, TD-2 and TD-3 are expected to show similar patterns since the sensitizers contain the same units and indeed these are observed. Each of these three sensitizers contains 14 aromatic protons of the polypyridine rings and 27 aliphatic tertiary butyl protons. The tertiary butyl protons are split into two signals containing 9 and 18 protons as a result of symmetry condition of the molecule. The proton spectra of TD-4, TD-5 and TD-6 are also expected to show similar patterns of 14 aromatic protons on the polypyridine rings and 18 aliphatic tertiary butyl protons. The two tertiary butyl protons are also split into two singlet signals containing 9 protons each because they are in different chemical environments.

All the sensitizers were subjected to elemental analysis with which their composition was confirmed. Based on the synthetic procedure, TD-2 was expected to be mono-protonated but the elemental analysis indicates that the sensitizer is fully deprotonated and the two protons replaced by two tetrabutylammonium groups. This sensitizer posed a great challenge since the titration could not be done in the aqueous phase and the associated error may have originated from the determination of the 1:1 ratio in the synthetic procedure. TD-5 and TD-6 were expected to be fully deprotonated, based on their synthetic procedures, but the elemental analysis data indicate that there are only two tetrabutylammonium groups associated with each sensitizer molecule. Since TD-5 and TD-6 were further purified by column chromatography, the third tetrabutylammonium group may have been exchanged on the Sephadex LH-20 resin.
3.3.2. Photophysical Studies

The heteroleptic Os(II) sensitizers display metal-to-ligand charge-transfer (MLCT) absorption transitions in the visible and near infra-red (IR) regions (Figures 3.1. and 3.2.) along with intense ligand-centered $\pi - \pi^*$ transitions in the ultraviolet region of the spectrum (not shown). The sensitizers possess both the spin-allowed $^1$MLCT and spin-forbidden $^3$MLCT absorption bands that are typical of Os(II) polypyridine complexes.\textsuperscript{15,21,30,31} The spin-forbidden $^3$MLCT transitions become possible due to the large spin-orbit coupling constant of osmium ($\lambda_{\text{Os}} = 3200$ cm$^{-1}$).\textsuperscript{16,17}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.1.png}
\caption{The absorption (black) and corrected photoluminescence (red) spectra of TD-1 in acetonitrile solution. Sample excitation was provided by an isolated 514.5 nm line from an argon ion laser (Coherent Innova 300).}
\end{figure}
Figure 3.2. The absorption and photoluminescence spectra of (a) AP25, TD-2 and TD-3, (b) TD-4, TD-5 and TD-6 in methanol solution. Sample excitation was provided by 442 nm laser line (Melles Griot, series 74).
Table 3.1. Summary of photophysical properties of the sensitizers with N3 included for comparison.

<table>
<thead>
<tr>
<th>Compound</th>
<th>absorption max, nm ( (\varepsilon \times 10^{-4}, \text{M}^{-1} \text{cm}^{-1}) )</th>
<th>emission max ( \text{nm} )</th>
<th>estimated ( E_{0-0} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-1 (^a)</td>
<td>397 (1.33), 513 (1.59), 711 (0.38)</td>
<td>( \sim 900 )</td>
<td>1.63</td>
</tr>
<tr>
<td>TD-2</td>
<td>377 (1.39), 509 (1.57), 723 (0.43)</td>
<td>848</td>
<td>1.66</td>
</tr>
<tr>
<td>TD-3</td>
<td>385 (1.00), 520 (1.27), 760 (0.34)</td>
<td>883</td>
<td>1.58</td>
</tr>
<tr>
<td>TD-4</td>
<td>386 (1.45), 471 (1.56), 864 (0.29)</td>
<td>978</td>
<td>1.44</td>
</tr>
<tr>
<td>TD-5</td>
<td>375 (1.28), 466 (1.34), 842 (0.28)</td>
<td>946</td>
<td>( \sim 1.54 )</td>
</tr>
<tr>
<td>TD-6</td>
<td>386 (1.54), 455 (1.60), 802 (0.33)</td>
<td>925</td>
<td>( \sim 1.59 )</td>
</tr>
<tr>
<td>AP25</td>
<td>437 (1.40), 483 (1.39), 593 (0.37)</td>
<td>748</td>
<td>1.84</td>
</tr>
<tr>
<td>N3 (^c)</td>
<td>313 (3.12), 396 (1.40), 534 (1.42)</td>
<td>755</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) measured in CH\(_3\)OH solution and excitation with an isolated 514.5 nm line from an argon ion laser (Coherent Innova); \(^b\) measured in CH\(_3\)CN solution and excitation with 442 nm line from a HeCd laser (Melles Griot). \(^c\) taken from *J. Am. Chem. Soc.* 1993, 115, 6382 – 6390.

The \(^1\)MLCT transitions of the sensitizers containing 2,2'-bipyridine-4,4'-dicarboxylic acid as the anchoring group, i.e., AP25, TD-1, TD-2 and TD-3, generally extend up to about 600 nm where they join the spin-forbidden \(^3\)MLCT transitions, which in this case may extend up to about 900 nm. The \(^1\)MLCT transitions of sensitizers containing 2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid as anchoring groups, i.e., TD-4, TD-5 and TD-6, generally extend up to about 700 nm where they join the \(^3\)MLCT transitions which may extend to approximately 1000 nm. This is consistent with increased electron density on the metal center resulting in the destabilization of the metal t\(_{2g}\) orbitals, compressing the energy gap relative to Ru(II) MLCT complexes. The low energy absorption transitions, particularly the so-called direct singlet-to-triplet transitions (\(^3\)MLCT ← \( S_0 \)) in Os(II) sensitizers, have been shown to extend to
wavelengths in the red and near infra-red regions of the spectrum,\textsuperscript{9-12} in line with an enhanced oscillator strength for an electronic transition between the ground state and the triplet excited state of the osmium complexes.\textsuperscript{15} The origin of the spin-forbidden direct singlet-to-triplet transitions is linked to the extensive mixing of excited states of different multiplicities, occasioned by the large value of the spin-orbit coupling constant for osmium ($\lambda_{\text{Os}} = 3200 \text{ cm}^{-1}$).\textsuperscript{15-18} The ground state does not couple to any of the excited states and so retains its pure singlet nature. The spin selection rule for electronic transitions ($\Delta S = 0$) still holds, but this requires only that the triplet excited states have some singlet character mixed into it for the transition to be “allowed”.\textsuperscript{16} The intensity of this “allowed” transition to an excited state will be proportional to the amount of singlet character mixed into that excited state. The lower lying MLCT states of osmium(II) are about 30% singlet in character\textsuperscript{16} and it is from these states that photoluminescence originates. A summary of the photophysical properties of the sensitizers is provided in Table 3.1. $E_{0-0}$ is the minimum energy between the ground and excited states and was estimated as 10% of the maximum of the corrected and normalized photoluminescence spectra in Figures 3.1. and 3.2., with the obtained values in nanometers (nm) converted to electron volts (eV). The photophysical properties of \textbf{AP25} and \textbf{TD-5} are in agreement with published data.\textsuperscript{22,32}

One of the requirements of an ideal sensitizer is to absorb all light in the visible region of the spectrum\textsuperscript{33} and the absorption spectrum of most of the sensitizers, except \textbf{AP25}, extend to 900 nm covering the entire visible region of the electromagnetic spectrum although the extinction coefficients across the red-absorbing $^3$MLCT region are relatively low. All the sensitizers have very weak photoluminescence in solution (Figures 3.1. and 3.2.) – a direct consequence of the energy gap law which predicts a decrease in photoluminescence intensity with red-shifting photoluminescence. \textbf{TD-1} has a quantum yield of $0.00064 \pm 0.00004$ and an excited state
lifetime of less than 15 nanoseconds which could not be resolved on our single wavelength nanosecond transient absorption system as all excited state dynamics occur within the instrument response function, < 15 nanoseconds.

3.3.3. Electrochemical Studies

Electrochemical measurements were carried out in acetonitrile solutions using a standard three-electrode apparatus. All electrochemical data were acquired using either Reference 600 Potentiostat/Galvanostat/ZRA (Gamry Instruments) or Bioanalytical Systems Epsilon electrochemical workstation interfaced with a computer and re-plotted using Origin software. Measurements were taken with a Ag/AgCl reference electrode, a platinum or gold microdisk working and platinum wire counter electrodes in deaerated acetonitrile with 0.1 M tetra-\(n\)-butylammonium hexafluorophosphate as the supporting electrolyte and ferrocene (Fc) as an internal reference. The potentials were measured by cyclic voltammetry and verified by differential pulse voltammetry. The measured potentials were converted to \(E_{1/2}\) vs. NHE using 

\[E_{1/2}(\text{Fc}^+/\text{Fc}^0) = +0.69\ \text{vs. NHE}\] 

All the sensitizers show a one electron reversible oxidation process (at positive potentials) that is attributed to the osmium metal center which is oxidized reversibly to the +3 oxidation state, and two reduction waves (at negative potentials) that are attributed to be ligand reduction processes.

The electrochemical data for TD-1 and TD-2 are presented in Figure 3.3. TD-1 shows a one electron reversible oxidation wave centered at +0.74 V vs. Ag/AgCl with the Fe\(^+\)/Fe\(^0\) wave centered at +0.51 V vs. Ag/AgCl, while TD-2 shows a similar wave at +0.50 V vs Ag/AgCl. The potentials were verified by differential pulse voltammetry where single oxidation processes were observed at +0.75 V vs. Ag/AgCl and +0.52 V vs Ag/AgCl were observed for TD-1 and TD-2, respectively, with the Fe\(^+\)/Fe\(^0\) wave at +0.53 V vs Ag/AgCl. The electrochemical data for TD-4
and TD-5 are shown in Figure 3.4. A one electron reversible oxidation wave centered at +0.70 V vs. Ag/AgCl is observed for TD-4 with the Fc+/Fc0 wave centered at +0.46 V vs. Ag/AgCl, while TD-5 shows a similar wave at +0.39 V vs Ag/AgCl. The potentials were verified by differential pulse voltammetry where single oxidation processes were observed at +0.72 V vs. Ag/AgCl and +0.39 V vs Ag/AgCl were observed for TD-4 and TD-5, respectively, with the Fc+/Fc0 wave at +0.49 V vs Ag/AgCl. The one electron reversible oxidation waves for AP25, TD-3 and TD-6 (Figures A16 and A17, Appendix A) are centered at 1.04 V vs Ag/AgCl, 0.54 V vs Ag/AgCl and 0.53 V vs Ag/AgCl, respectively, with the Fc+/Fc0 wave centered at 0.47 V vs Ag/AgCl.

The electrochemical properties of the sensitizers are summarized in Table 3.2. The excited-state oxidation potentials, \( E^{\circ \prime} (M^{3+}/M^{2+})^* \), were estimated using equation 3.1:

\[
E^{\circ \prime} = E^{\circ \prime} - E_{0-0}
\]

(3.1.)

where \( E^{\circ} \) is the oxidation potential of the ground state, \( E^{\circ \prime} \) is the oxidation potential of the excited state, and \( E_{0-0} \) is the minimum energy (in electron volts) between the ground and excited states. All the sensitizers have oxidation potentials that are more positive than that of the I-/I3- redox mediator, implying that the oxidized sensitizers can be regenerated by this redox mediator based on thermodynamics. However, the potentials are more negative than that of the N3 dye for which the I/I3- redox mediator gives the best known results for regenerative DSCs.
Figure 3.3. Electrochemistry data of (a) TD-1 and (b) TD-2 measured in acetonitrile solution. Data were acquired at a scan rate of 100 mV/s with Ag/AgCl reference electrode, 0.1 M TBAPF₆ as a supporting electrolyte and ferrocenium/ferrocene (Fc⁺/Fc) as an internal reference.
Figure 3.4. Electrochemistry data of (a) TD-4 and (b) TD-5 measured in acetonitrile solution. Data were acquired at a scan rate of 100 mV/s with Ag/AgCl reference electrode, 0.1 M TBAPF₆ as a supporting electrolyte and ferrocenium/ferrocene (Fc⁺/Fc) as an internal reference.
Table 3.2. Summary of electrochemical properties of the sensitizers with N3 and I-/I3 included for comparison.

<table>
<thead>
<tr>
<th>compound</th>
<th>E°ox (V vs. NHE)</th>
<th>E°red1 (V vs. NHE)</th>
<th>E°red2 (V vs. NHE)</th>
<th>estimated E°* (V vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-1</td>
<td>0.92</td>
<td>−1.15</td>
<td>−1.46</td>
<td>−0.71</td>
</tr>
<tr>
<td>TD-2</td>
<td>0.72</td>
<td>−1.17</td>
<td>−1.51</td>
<td>−0.94</td>
</tr>
<tr>
<td>TD-3</td>
<td>0.74</td>
<td>−1.42</td>
<td>−1.72</td>
<td>−0.84</td>
</tr>
<tr>
<td>TD-4</td>
<td>0.93</td>
<td>−1.15</td>
<td>−1.37</td>
<td>−0.51</td>
</tr>
<tr>
<td>TD-5</td>
<td>0.59</td>
<td>−1.23</td>
<td>−1.35</td>
<td>−0.95</td>
</tr>
<tr>
<td>TD-6</td>
<td>0.73</td>
<td>−1.14</td>
<td>−1.45</td>
<td>−0.86</td>
</tr>
<tr>
<td>AP25</td>
<td>1.26</td>
<td>−1.33</td>
<td>−1.55</td>
<td>−0.58</td>
</tr>
<tr>
<td>N3</td>
<td>1.09</td>
<td>1.09</td>
<td>1.09</td>
<td>—</td>
</tr>
</tbody>
</table>

Measurements were carried out in CH₃CN solution with 0.1 M TBA(PF₆) as supporting electrolyte, potentials were determined by CV and confirmed by DPV; † taken from J. Am. Chem. Soc. 1993, 115, 6382 – 6390; ‡ taken from Adv. Funct. Mater. 2008, 18, 341 – 346.

3.3.4. Photovoltaic Studies.

The procedures for the preparation of the nanocrystalline TiO₂ paste and thin film, the platinum cathode, and the fabrication of DSSC sandwich devices are described in detail in Chapter IV. The photovoltaic properties of the sensitizers are shown in Figures 3.5 and 3.6. A breakdown of the device parameters derived from the photovoltaic characterization curves is given in Table 3.3. The data presented herein represent average properties of at least three DSSCs based on each of the sensitizers, prepared and measured under identical conditions, and the values reported herein represent measured values which were not corrected for any losses whatsoever. TD-1 and TD-2 sensitizers, along with the benchmark N3 sensitizer, gave a better photovoltaic performance (Figure 3.5) compared to TD-3, TD-4, TD-5, TD-6 and AP25.
sensitizers (Figure 3.6). The photoaction spectra of **TD-1** and **TD-2** extend up to 900 nm, while that of **TD-3** extends up to about 950 nm. The substitution of the thiocyanate ligand for the chloride ligand clearly red-shifts the photoaction spectrum since the chloride is a weaker field ligand compared to the thiocyanate. This red-shift apparently does not translate to a greater value of the external quantum yield or short-circuit photocurrent for DSSCs based on **TD-3**. This is related to the regeneration of the oxidized sensitizer where the thiocyanate ligand fares better in turning over the iodide/triiodide redox mediator. For this reason, sensitizers bearing the thiocyanate ligand outperform analogous sensitizers that have the chloride ligand.\textsuperscript{35} For the sensitizers bearing 2,2':6',2"-terpyridine-4,4',4"-tricarboxylic acid anchoring group (i.e., **TD-4**, **TD-5** and **TD-6**), the photovoltaic performances were generally low despite the fact that both their ground and excited state potentials (Table 3.3) are thermodynamically well aligned with the potentials of the iodide triiodide redox mediator (\(E = 0.4 \text{ V vs NHE}\))\textsuperscript{36} and the TiO\(_2\) conduction band (\(E_{\text{CB}} = -0.5 \text{ V vs NHE at pH 7}\))\textsuperscript{37,38} respectively.
Figure 3.5. EQE (a) and I-V (b) curves of DSSCs based on N3, TD-1 and TD-2 sensitizers. The curves are average values of at least three devices prepared and measured under identical conditions.
Figure 3.6. EQE (a) and I-V (b) curves of DSSCs based on TD-3, TD-4, TD-5, TD-6 and AP25 sensitizers. The curves are average values of at least three devices prepared and measured under identical conditions.
Table 3.3. Device parameters derived from DSSCs made with the osmium(II) sensitizers with N3 included for comparison.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>EQE$_{max}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-1</td>
<td>625 ± 5.73</td>
<td>16.0 ± 1.22</td>
<td>50.3 ± 1.07</td>
<td>5.03 ± 0.44</td>
<td>57.5 ± 3.75</td>
</tr>
<tr>
<td>TD-2</td>
<td>615 ± 0.19</td>
<td>11.0 ± 0.04</td>
<td>55.7 ± 0.08</td>
<td>3.76 ± 0.01</td>
<td>39.7 ± 0.65</td>
</tr>
<tr>
<td>TD-3</td>
<td>543 ± 2.09</td>
<td>4.40 ± 0.75</td>
<td>56.8 ± 0.80</td>
<td>1.36 ± 0.21</td>
<td>16.7 ± 0.43</td>
</tr>
<tr>
<td>TD-4</td>
<td>522 ± 6.17</td>
<td>4.85 ± 0.37</td>
<td>55.4 ± 2.14</td>
<td>1.41 ± 0.17</td>
<td>20.5 ± 1.44</td>
</tr>
<tr>
<td>TD-5</td>
<td>408 ± 16.5</td>
<td>1.33 ± 0.08</td>
<td>47.4 ± 1.79</td>
<td>0.26 ± 0.02</td>
<td>7.83 ± 0.53</td>
</tr>
<tr>
<td>TD-6</td>
<td>522 ± 4.74</td>
<td>3.95 ± 0.25</td>
<td>52.8 ± 2.00</td>
<td>1.09 ± 0.02</td>
<td>15.7 ± 0.39</td>
</tr>
<tr>
<td>AP25</td>
<td>525 ± 18.3</td>
<td>4.60 ± 0.38</td>
<td>49.9 ± 1.37</td>
<td>1.21 ± 0.15</td>
<td>20.3 ± 0.87</td>
</tr>
<tr>
<td>N3</td>
<td>714 ± 5.74</td>
<td>17.9 ± 0.54</td>
<td>56.3 ± 1.60</td>
<td>7.18 ± 0.04</td>
<td>72.0 ± 0.39</td>
</tr>
</tbody>
</table>
The highest power conversion efficiency was achieved with **TD-1** sensitizer, followed closely by **TD-2** sensitizer (Table 3.3). We have earlier reported a power conversion efficiency of 4.7% for select devices based on **TD-1** sensitizer\(^ {39} \) and herein report a slight improvement in the power conversion efficiency, with the current value at 5.03% (Table 3.3). The benchmark **N3** sensitizer, under identical preparation and measurement conditions, gave a maximum power conversion efficiency of 7.18%. The redox electrolyte consisted of 0.1 M LiI, 0.05 M I\(_2\), 0.6 M PMII, 0.1 M guanidine thiocyanate, 0.5 M 4-\textit{tert}-butylpyridine in acetonitrile solution. The maximum EQE values are 57.5% and 71.0% for **TD-1** and **N3** sensitizers, respectively. It must be noted that these values represent the best values that have been achieved under our conditions and, to the best of our knowledge, these data represent the highest reported power conversion efficiency of a DSSC based on an Os(II) complex to date.\(^ {9-13} \)

Initial efforts at DSSC fabrication and measurements yielded low energy conversion efficiencies in the range of less than 1.0% for **TD-1** sensitizer. These values were achieved with commercially available DSL 18 NR-T (transparent) and DSL 18NR-AO (scattering layer) TiO\(_2\) pastes (Dyesol Company). Upon switching to the home-made paste, whose preparation procedure is described in Chapter IV, improvements were observed in the photovoltaic characteristics of the DSSCs. The earlier poor performance of the DSSCs observed with the commercially available paste may the linked to inefficient contact of the TiO\(_2\) film with the transparent conducting glass substrate. This will limit the evacuation of electrons from the conduction band of the sensitized TiO\(_2\) and result in greater losses through recombination. The current paste, prepared according to published procedures,\(^ {40} \) adheres well onto the substrate and has resulted in DSSC with better photovoltaic characteristics.\(^ {39,41} \)

DSSCs based on **TD-2** sensitizer yielded an inferior performance to **TD-1** based devices. It appears that complete deprotonation of the carboxylic acid groups leads to decrease in
photovoltaic performance of DSSCs, as has been observed earlier.\textsuperscript{42} Other sensitizers studied in this project (TD-3, TD-4, TD-5, TD-6 and AP25) exhibited poor photovoltaic characteristics and various optimization techniques may have to be employed in order to improve these characteristics. DSSCs based on TD-5 and AP25 have been reported earlier\textsuperscript{22,32} and the values that were reported are similar to the ones reported herein. It must be noted that the photovoltaic characteristics of the sensitizers will ultimately be affected by the redox electrolyte composition as will be discussed in the next chapter. Due to the fact that TD-1 sensitizer exhibited the best photovoltaic performance, this sensitizer was chosen for further studies.

The use of the scattering layer of TiO\textsubscript{2} paste was further explored with a view to enhancing the photovoltaic performance of the DSSCs. This follows reports that the use of the scattering layer enhances photovoltaic performance in the red edge of the spectrum by scattering the transmitted light for reharvesting.\textsuperscript{43,44} Various research groups that work on organometallic sensitizers have generally been using 10 – 15 µm optimum thickness, \textsuperscript{45} usually in combination with 5 µm of a scattering layer of TiO\textsubscript{2} nanoparticles. Ideally, a sensitizer with very high extinction coefficient, adsorbed on a thin film, can produce both high photocurrent and photovoltage, accompanied by a high fill factor, resulting in a higher power conversion efficiency. The scattering layer is also expected to enhance electron transport by interconnecting the semiconductor nanoparticles and filling any missing link. The DSSCs were prepared with TiO\textsubscript{2} films composed of a 13 µm transparent layer and 5 µm scattering layer. Control experiments were conducted with DSSCs made with only the transparent layer paste. The obtained data (Table 3.4, Figure 3.7) indicate that the devices made with the scattering layer films performed poorly compared to those made without the scattering layer. This attests to the fact that the transparent paste employed in this research is a good quality paste and further optimization by the use of the scattering layer might not be necessary.
Figure 3.7. EQE (a) and I-V (b) curves of DSSCs made with TiO$_2$ films containing 5 μm of a scattering layer TiO$_2$ film and sensitized with TD-1. Control experiments included for comparison.
Table 3.4. Device parameters derived from DSSCs made with TiO$_2$ films containing 5 μm of a scattering layer of TiO$_2$ film and sensitized with TD-1. Control experiments included for comparison.

<table>
<thead>
<tr>
<th>Scattering layer</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>EQE$_{max}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no</td>
<td>505 ± 7.68</td>
<td>13.9 ± 0.86</td>
<td>53.6 ± 2.21</td>
<td>3.76 ± 0.02</td>
<td>49.8 ± 3.01</td>
</tr>
<tr>
<td>yes</td>
<td>486 ± 3.16</td>
<td>12.2 ± 0.31</td>
<td>54.0 ± 0.62</td>
<td>3.19 ± 0.07</td>
<td>47.8 ± 1.11</td>
</tr>
</tbody>
</table>

The practice of minimizing losses due to unwanted processes in dye-sensitized solar cells has been explored by many researchers and includes the use of Al$_2$O$_3$ and MoO$_3$ blocking layers.$^{46-49}$ Dark reactions in this type of photovoltaic device are associated with reactions of the iodide/triiodide redox mediator with the ITO or FTO layer of the transparent conductive glass. The use of MoO$_3$ blocking layer on TCG substrates used in the preparation of SnPc/C60 bulk heterojunction solar cells (where SnPc = tin(II) phthalocyanine) significantly reduces the electron leakage current which results in a two-fold increase in $V_{OC}$ compared to cells without the blocking layers.$^{49}$ The gain in voltage was accompanied by gains in $J_{SC}$, FF and η as well as a decrease in the dark current in cells with the blocking layer compared to cells without it. The use of Al$_2$O$_3$, deposited over the TiO$_2$ film, was also shown to increase power conversion efficiency in DSSCs by reducing the recombination current, which can be determined from the dark current.$^{46,48}$
Figure 3.8. EQE (a) and I-V (b) curves of TD-1-sensitized DSSCs made with TCG substrates coated with about 10 nm of MoO$_3$. 
Figure 3.9. EQE (a) and I-V (b) curves of N3-sensitized DSSCs made with TCG substrates coated with about 10 nm of MoO3.
Table 3.5. Device parameters derived from DSSCs made with TCG substrates coated with about 10 nm of MoO₃.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>$dark\ V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>EQEmax (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-1 / MoO₃</td>
<td>548 ± 11.3</td>
<td>416 ± 53.0</td>
<td>6.28 ± 0.68</td>
<td>61.1 ± 3.10</td>
<td>2.11 ± 0.30</td>
<td>23.4 ± 1.64</td>
</tr>
<tr>
<td>TD-1 / control</td>
<td>623 ± 5.72</td>
<td>196 ± 25.0</td>
<td>15.5 ± 1.48</td>
<td>50.5 ± 0.90</td>
<td>4.89 ± 0.53</td>
<td>49.4 ± 1.57</td>
</tr>
<tr>
<td>N3 / MoO₃</td>
<td>647 ± 4.69</td>
<td>524 ± 0.02</td>
<td>11.1 ± 0.81</td>
<td>58.8 ± 6.07</td>
<td>4.20 ± 0.15</td>
<td>53.8 ± 1.88</td>
</tr>
<tr>
<td>N3 / control</td>
<td>714 ± 5.74</td>
<td>581 ± 0.01</td>
<td>17.9 ± 0.54</td>
<td>56.3 ± 1.60</td>
<td>7.18 ± 0.04</td>
<td>72.0 ± 0.39</td>
</tr>
</tbody>
</table>

Table 3.6. Device parameters derived from TD-1-sensitized DSSCs made with TCG substrates coated with layer(s) of Al₂O₃.

<table>
<thead>
<tr>
<th>Number of Al₂O₃ layers</th>
<th>$V_{oc}$ (mV)</th>
<th>$dark\ V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>EQEmax (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (control)</td>
<td>623 ± 5.72</td>
<td>196 ± 25.0</td>
<td>15.5 ± 1.48</td>
<td>50.5 ± 0.90</td>
<td>4.89 ± 0.53</td>
<td>49.4 ± 1.57</td>
</tr>
<tr>
<td>1 atomic layer</td>
<td>632 ± 6.41</td>
<td>164 ± 19.6</td>
<td>11.8 ± 1.03</td>
<td>55.3 ± 1.25</td>
<td>4.11 ± 0.37</td>
<td>41.2 ± 4.24</td>
</tr>
<tr>
<td>2 atomic layers</td>
<td>632 ± 5.56</td>
<td>94.2 ± 8.1</td>
<td>12.1 ± 0.42</td>
<td>53.7 ± 1.03</td>
<td>4.12 ± 0.16</td>
<td>43.9 ± 0.41</td>
</tr>
<tr>
<td>3 atomic layers</td>
<td>612 ± 18.3</td>
<td>105 ± 21.1</td>
<td>10.6 ± 1.22</td>
<td>53.3 ± 6.09</td>
<td>3.45 ± 0.34</td>
<td>39.6 ± 2.50</td>
</tr>
</tbody>
</table>
Surface protection of the TCG substrate was carried out using layers of MoO₃ and Al₂O₃ deposited onto the substrate prior to doctor-blading the TiO₂ paste and sintering. This study was carried out to investigate the effect, if any, of these oxide layers on the dark current and other photovoltaic characteristics of the DSSCs. For the MoO₃ study, about 10 nm of the oxide was deposited on the TCG. For the Al₂O₃ study, three sets of devices were made that contained 1, 2, and 3 atomic layers of the oxide deposited on the TCG. Control experiments were conducted with DSSCs made with no blocking layer on the TCG substrate.

The results of the MoO₃ experiments are shown in Figures 3.8 and 3.9, with the characteristics summarized in Table 3.5. For both the TD-1 and N3 sensitizers, the use of the MoO₃ blocking resulted in a worsening of the photovoltaic characteristics of the DSSCs relative to the control experiment. There decreases in the EQE, J_SC and V_OC for both sensitizers. There was an early onset of the dark current for devices based on TD-1 that employ the MoO₃ blocking layer as compared to the control devices. Early onset of the dark current decreases the value of the dark V_OC which is an indication of increased resistance to current flow. Devices based on N3 showed the opposite effect but the photovoltaic properties of the devices were still inferior to that of the control devices (Figure 3.9, Table 3.5). The overall observation is a decrease in photovoltaic performance of the DSSCs when the TCG substrate is coated with a layer of MoO₃. The results of the Al₂O₃ experiments for TD-1 sensitizer are shown in Figure 3.10. The photovoltaic properties of devices made with TCG substrates coated with one or two atomic layers of the oxide were essentially identical while devices with three atomic layers of Al₂O₃ were the worst. The photovoltaic characteristics of devices that contain the Al₂O₃ blocking layer were also generally inferior to devices without the oxide blocking layer (Figure 3.10, Table 3.6). The onset of the dark current was identical for the control devices and those containing one or two atomic layers while devices with three atomic layers have an earlier onset of the dark current.
Figure 3.10. EQE (a) and I-V (b) curves of TD-1-sensitized DSSCs made with TCG substrates coated with layer(s) of Al$_2$O$_3$. 
3.3.5. Theoretical Calculations

Density functional theory (DFT) calculations for the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals of TD-1 were performed by using the Gaussian 03 program. The B3LYP functional\textsuperscript{50,51} was employed and 6-31G(d,p) basis set for the non-metal atoms (hydrogen, carbon, oxygen and sulfur) and the LANL2DZ effective core potential (ECP) and corresponding basis set functions\textsuperscript{52} for the osmium atom. These calculations were carried out with a view to gaining more detailed insights on the ground and excited state properties and to ascertain structure/property relationships that are crucial to the photovoltaic performance of sensitizers. The profiles of the HOMO and the LUMO of TD-1 are shown in Figure 3.11.

![Graphical representation of the HOMO and LUMO of TD-1 calculated with DFT.](image)

**Figure 3.11.** Graphical representation of the HOMO and LUMO of TD-1 calculated with DFT.
From Figure 3.11 it is evident that the electron density is located primarily on the thiocyanate ligand in the HOMO with a little delocalization over the osmium metal center. This kind of HOMO character has been found for the N3 sensitizer where it was confirmed that the Ru4d and atomic orbitals centered on the thiocyanate groups, in particular S3p wave functions, contribute to the frontier orbitals of the complex. Similarly, the Os5d and the thiocyanate S3p wave functions are expected to contribute to frontier orbitals of TD-1. This observation that the outermost orbital contains a significant amount of S3p–character from the thiocyanate group suggests that this group may play a role in the sensitizer regeneration process. The thiocyanate ligand points in the direction of the redox electrolyte thereby positioning it to act as an antenna for a more effective regeneration of the oxidized sensitizer by I− moiety. The LUMO is concentrated on the π* structure of the bipyridine ligand and is shared with the carboxylic acid groups of the bpy rings. This sharing of the LUMO enhances electronic coupling to the TiO2 conduction band states for effective electron injection. Thus, the MLCT absorption transitions of TD-1 should be assigned to OsNCS → dcbpyH2 π* orbital. The calculated HOMO-LUMO energy gap is 1.95 eV which corresponds to 635 nm and this value matches the lower energy edge of the 1MLCT absorption band of TD-1 (Figure 3.1).

3.4. Conclusions

Various sensitizers bearing 2,2'-bipyridine-4,4'-dicarboxylic acid and 2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid were successfully synthesized and characterized with MALDI-TOF, 1H NMR and elemental analysis. The photophysical and electrochemical properties of the sensitizers were evaluated. The sensitizers were found to possess the necessary light-harvesting properties in the visible and near infrared region of the spectrum. The ground and excited state redox potentials are well aligned to provide the necessary thermodynamic driving force for
regeneration of the oxidized sensitizer and electron injection into the conduction band of the semiconductor TiO₂, respectively. Photovoltaic studies were carried out on DSSCs made with these sensitizers and the results indicate that there is room for further optimization of photovoltaic performance for most of the sensitizer. Further studies that employed the use of MoO₃ and Al₂O₃ blocking layers on the conducting glass substrate indicate that the photovoltaic performance worsened in the presence of these blocking layers. The best photovoltaic performance was achieved with TD-1 sensitizer which gave a 5.03% power conversion efficiency, the highest power conversion efficiency for any DSSC based on an osmium(II) sensitizer. Under identical fabrication and measurement conditions, the benchmark N3 sensitizer gave a power conversion efficiency of 7.18%. Theoretical calculations reveal that the HOMO is delocalized on the thiocyanate ligand and the osmium metal center while the LUMO is localized on the dcbpyH₂ ligand. This indicates that the sensitizer is well positioned for effective electron injection into the conduction band of TiO₂ and regeneration of the sensitizer.
3.5. References


(41) Sun, Y.; Onicha, A. C.; Myahkostupov, M. *ACS Applied Materials & Interfaces* 2010, in press.


CHAPTER IV

Electrolyte-Dependent Photovoltaic Responses in Dye-Sensitized Solar Cells Based on an Osmium(II) Sensitizer of Mixed Denticity
4.1. Introduction

The kinetics of electron transfer at the semiconductor/solution interface are critical for optimizing device performance in dye-sensitized solar cells (DSSCs). To this end, significant research has focused on iodide electron transfer kinetics in dye-sensitized solar cells,\textsuperscript{1-4} underscoring the importance of the role of this anion. Of particular interest to the present study is the role of iodide in operational DSSCs based on Os(II) complexes. It has been observed that a Ru(II) complex, \textit{cis-}Ru(dcbpyH\textsubscript{2})\textsubscript{2}(CN)\textsubscript{2}, converts photons-to-current quantitatively while the structurally analogous Os(II) complex, \textit{cis-}Os(dcbpyH\textsubscript{2})\textsubscript{2}(CN)\textsubscript{2}, does not.\textsuperscript{3} The poor performance of the Os(II) sensitizer was attributed to the ‘sluggishness’ of the iodide oxidation reaction by Os(III) which facilitates efficient recombination with e\textsuperscript{-}(TiO\textsubscript{2}) while the ruthenium analog readily oxidizes the halide with more favorable kinetics. This is readily attributed to the marked differences in oxidation potential between the two chromophores. Comparative photon-to-current conversion efficiencies have been recently obtained for select ruthenium and osmium sensitizers.\textsuperscript{5} An Os(II) sensitizer, \textit{cis-}Os(dcbpyH\textsubscript{2})\textsubscript{2}(NCS)\textsubscript{2}, has also been shown to exhibit an iodide-dependent photocurrent density, J\textsubscript{SC}, which appears to be absent in the Ru(II) structural analog, \textit{cis-}Ru(dcbpyH\textsubscript{2})\textsubscript{2}(NCS)\textsubscript{2}.\textsuperscript{5} The photocurrent was observed to increase significantly upon increasing the concentration of LiI in the redox electrolyte solution. This increase in J\textsubscript{SC} was attributed to an increase in the concentration of the iodide anion as similar increases were not obtained when the concentration of Li\textsuperscript{+} was independently increased using LiClO\textsubscript{4}. However, concerns have been raised as to the appropriateness of substituting the I\textsuperscript{-} salt for its ClO\textsubscript{4}\textsuperscript{-} analog as the latter was shown to apparently result in a change in injection dynamics in DSCs.\textsuperscript{4}

This chapter presents a detailed study of the changes in the photovoltaic performance of operational DSSCs based on an Os(II) sensitizer, \([\text{Os}('\text{Bu}_{3}\text{tpy})(\text{dcbpyH}_{2})(\text{NCS})]\text{PF}_{6} (\textbf{TD-1})\) (where 'Bu\textsubscript{3}tpy = 4,4',4''-tri-\textit{tert}-butyl-2,2':6',2''-terpyridine, dcbpyH\textsubscript{2} = 2,2'-bipyridyl-4,4'-
dicarboxylic acid), that arise as a result of variations in the concentration of Li$^+$ and I$^-$ in the redox electrolyte. The photovoltaic characteristics of TD-1 on mesoscopic titania were evaluated using external quantum efficiency (EQE) and current-voltage (I-V) measurements. We find that increasing the concentration of LiI results in an increase in the short-circuit current density ($J_{SC}$) and a decrease in the open-circuit voltage ($V_{OC}$) of the devices. The resultant changes, particularly in the photocurrent density and photon-to-current conversion efficiency, are very pronounced for the Os(II)-based devices whereas they are minimal for the Ru(II)-based devices measured in parallel. Independently increasing the concentration of the iodide anion using the ionic liquid 1-$n$-propyl-3-methylimidazolium iodide (PMII) revealed that the EQE, $J_{SC}$ and $V_{OC}$ increase, accompanied by an improvement of the fill factor. Similar experiments with TBAI demonstrate that the EQE, $J_{SC}$ and $V_{OC}$ all increase as well. These observations indicate that the increases observed in the photocurrent density and photon-to-current conversion efficiency in DSSCs based on TD-1 are not necessarily due to a higher thermodynamic driving force for electron injection, occasioned by an abundance of Li$^+$ in the redox electrolyte, but more likely due to the availability of the iodide anion which aids in more efficient regeneration (reduction) of the osmium metal center following electron injection into the conduction band of TiO$_2$. Conversely, increasing the concentration of Li$^+$ using LiClO$_4$ does not result in improved device performances.\textsuperscript{5}
4.2. Experimental Section

4.2.1. General. Guanidine thiocyanate, lithium iodide (LiI), 4-tert-butylpyridine, titanium(IV) isopropoxide, anhydrous acetonitrile, tetrabutylammonium iodide (TBAI) and hydroxypropyl cellulose were purchased from Aldrich Chemical Company and used without further purification. Iodine (I₂) was purchased from Alfa Aesar and used as received. The synthesis of 1-n-propyl-3-methylimidazolium iodide (PMII) was carried out according to published procedure⁶ and is described in detail in Chapter III. The synthesis of TD-1 is also described in detail in Chapter III. cis-Ru(dcbpyH₂)₂(NCS)₂, N₃, was synthesized and characterized in our laboratory⁷ according to the established literature procedure,⁸ as described in detail elsewhere.⁹ The chemical structures of TD-1 and N₃ sensitizers are shown in Chart 4.1 below.

Chart 4.1. Chemical structures of (a) N₃ and (b) TD-1.
4.2.2. Spectroscopic Measurements

UV – Vis absorption spectra of sensitized TiO$_2$ films were measured on a Varian Cary 50 Bio UV – Visible spectrophotometer. Corrected photoluminescence spectra on sensitized TiO$_2$ films were measured by an Edinburgh Instruments fluorimeter (FL 920) and excitation was afforded with a 450 W xenon lamp passed through a double monochromator. Thicknesses of the TiO$_2$ films were determined by a KLA-Tencor Alpha-Step IQ Surface Profiler. External quantum yield measurements were carried out using a system from PV Measurements, Inc., equipped with a xenon arc lamp and calibrated with a silicon reference photodiode. Current-voltage characteristics were measured on an I-V data acquisition system (PV Measurements, Inc.) equipped with a small area solar simulator (AM 1.5 Global) and an NREL-certified silicon reference solar cell (PVM 274, PV Measurements, Inc.) for calibrating the intensity of the simulated light to 100 mW/cm$^2$, with the measured current being within 2% of its calibration value. $J_{SC}$ values directly measured using I-V curves were typically 10-15% larger than those estimated from the integrated EQE (IPCE %) responses. Estimation of the $J_{SC}$ was performed using the I-V software provided by PV Measurements, Inc., according to ASTM standard E1021.

4.2.3. Preparation of TiO$_2$ Colloid

The TiO$_2$ paste was prepared according to the literature procedure,$^{10}$ with all important details presented as follows. Titanium(IV) isopropoxide (37 ml) in 10 ml of isopropanol was added slowly to a stirred mixture of 80 ml of glacial acetic acid and 250 ml of deionized water maintained at 0°C. The resulting colorless solution was heated at 80°C for 8 hrs while vigorously stirring. 80 ml of the resulting white colloidal solution was sonicated for 5 min with a cell disrupter. The solution was then heated at 230°C for 8 hrs while stirring in a titanium autoclave (Parr Instrument Company). The cooled colloidal solution was again sonicated with a cell
disrupter (Branson Sonifier 250) for 5 minutes. The solution was concentrated to 12 wt% with respect to the total weight of solution on a rotary evaporator (30°C, 30 torr). Hydroxypropyl cellulose (HPC), (M_n 10,000; M_w 80,000), was added over a 3-5 min period to the vigorously stirred solution. The final concentration of HPC was 6 wt% with respect to the total weight of solution. The paste was first stirred vigorously for 24 hours to dissolve the HPC and less vigorously thereafter until its use.

### 4.2.4. Preparation of Nanocrystalline TiO_2 Films

Conducting glass substrates (TEC 15, Hartford Glass) were cleaned by overnight immersion in a solution of KOH in isopropanol, washed with soap and water and dried in an oven. The TiO_2 paste was doctor-bladed onto the conducting glass substrate using scotch tape layers as spacers. The air-dried films were then sintered in a tube furnace at a heating rate of 5°C/min culminating at 500°C. The temperature was maintained at 500°C for 30 min and then reduced to 150°C. Typical film thicknesses were in the range of 12 – 16 μm. The hot slides were then slowly immersed in a 0.5 mM dye solution in a 1:1 tert-butanol: CH_3CN solvent mixture to avoid cracking the TiO_2 film and glass substrate. All samples were soaked in the dye-sensitizing solutions for 48 hr prior to further experimentation.

The scanning electron microscope (SEM) images of the as-synthesized nanocrystalline TiO_2 (prior to autoclaving) and the sintered and sensitized TiO_2 nanoparticles are shown in Appendix A (Figure A18). The SEM images were acquired on a carbon tape substrate by an Inspect F (FEI Company) scanning electron microscope. The images illustrate that the paste contains nanoparticles and that the films retain their nanocrystalline structure after autoclaving, sintering at 500°C and sensitization.
4.2.5. Preparation of the Platinum Cathode

Conducting glass substrates were cleaned precisely as described above. The slides were heated in a tube furnace at 400°C for 20 min to remove organic residues. A few drops of 5 mM PtCl₄ in anhydrous isopropanol were placed on the conducting face of the ITO-coated glass and tilted to guarantee a uniform spread, then dried in air. The coated slides were then baked in a tube furnace at 380°C for 18 min under an air atmosphere, and cooled down thereafter. Transparent platinum cathodes were readily obtained in this manner.

4.2.6. Fabrication of DSSC Sandwich Devices

The sensitized TiO₂ films were washed with acetonitrile. The active area of the sensitized films was adjusted to 0.25 cm² by removing the excess material. Stretched Parafilm-M served as spacer between the photoanode and platinum counter electrode. The typical thickness of the spacer is approximately 20 – 30 µm. The stretched parafilm was placed on top of the photoanode and the part of the Parafilm-M covering the active area of the sensitized film was removed. A few drops of the redox electrolyte were placed on top of the active electrode area and a platinized FTO-glass counter electrode was placed on top. The device was then secured together using binder clips. For these studies, the contents of the redox electrolyte solutions were varied but each solution always contained both iodine and iodide moieties producing the I⁻/I₃⁻ redox mediator.
4.3. Results and Discussion

4.3.1. Dependence of Photovoltaic Parameters on Lithium Iodide Concentration

The photocurrent action spectra of TD-1 showing its dependence on LiI concentration in the redox electrolyte are presented in Figure 4.1. Variations in the concentration of LiI in the redox electrolyte were carried out to study the photovoltaic responses of osmium sensitizers to these compositional changes. The observations reported herein are quantitatively the same across five different titania slides prepared under identical conditions that were used as photoanodes for the five different electrolyte compositions in each study. It has been reported earlier that increasing the concentration of LiI greatly increases the short-circuit photocurrent density of an osmium sensitizer while similar responses were not observed for the analogous ruthenium sensitizer.\(^5\) In the present study, we have investigated in detail how LiI concentration affects the EQE, J\(_{SC}\), \(V_{OC}\), fill factor, and overall power conversion efficiency, \(\eta\), of the devices. Initially, the electrolyte consisted of 0.05 M I\(_2\), 0.6 M PMII, 0.1 M guanidine thiocyanate, 0.5 M 4-\textit{tert}-butylpyridine and LiI in acetonitrile solution. The concentration of LiI was varied as follows: 0.1 M, 0.5 M, 1.0 M, 2.0 M and 3.0 M, as indicated in Figure 3.1. The EQE for TD-1 (Figure 4.1(a)) steadily increases with increasing LiI concentration. The overall increase in the EQE as the LiI concentration is increased can be rationalized in terms of the lowering of the conduction band potential of the TiO\(_2\) semiconductor which increases the driving force for electron injection from the excited state of the sensitizer to the conduction band of the semiconductor as has been reported earlier.\(^{12-14}\) This is linked to the effect of small cations, Li\(^+\) in this instance, which can readily adsorb on the surface of the semiconductor inducing the conduction band edge to shift to lower (more positive) potentials.\(^{12,14}\)
Figure 4.1. Influence of LiI concentration on the external quantum efficiency (a) and current-voltage curves (b) of TD-1. The concentrations of the other components of the electrolyte solution (0.05 M I₂, 0.6 M PMII, 0.1 M guanidine thiocyanate, 0.5 M 4-tert-butylpyridine) were kept constant, while the concentration of LiI was varied as shown on the graphs.
**Table 4.1.** Device parameters derived from the I-V curves illustrating the effect of LiI concentration on **TD-1**.

<table>
<thead>
<tr>
<th></th>
<th>0.1 M LiI</th>
<th>0.5 M LiI</th>
<th>1.0 M LiI</th>
<th>2.0 M LiI</th>
<th>3.0 M LiI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{SC}$, mA/cm$^2$</td>
<td>13.3</td>
<td>15.7</td>
<td>16.2</td>
<td>17.4</td>
<td>18.1</td>
</tr>
<tr>
<td>$V_{OC}$, mV</td>
<td>626</td>
<td>601</td>
<td>559</td>
<td>525</td>
<td>495</td>
</tr>
<tr>
<td>FF, %</td>
<td>52.0</td>
<td>50.1</td>
<td>49.0</td>
<td>42.6</td>
<td>36.0</td>
</tr>
<tr>
<td>$\eta$, %</td>
<td>4.34</td>
<td>4.72</td>
<td>4.45</td>
<td>3.89</td>
<td>3.23</td>
</tr>
</tbody>
</table>

**Table 4.2.** Device parameters derived from the I-V curves illustrating the effect of LiI concentration on **N3**.

<table>
<thead>
<tr>
<th></th>
<th>0.1 M LiI</th>
<th>0.5 M LiI</th>
<th>1.0 M LiI</th>
<th>2.0 M LiI</th>
<th>3.0 M LiI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{SC}$, mA/cm$^2$</td>
<td>13.8</td>
<td>14.2</td>
<td>14.6</td>
<td>14.8</td>
<td>15.0</td>
</tr>
<tr>
<td>$V_{OC}$, mV</td>
<td>664</td>
<td>630</td>
<td>611</td>
<td>571</td>
<td>553</td>
</tr>
<tr>
<td>FF, %</td>
<td>51.8</td>
<td>51.5</td>
<td>44.5</td>
<td>46.9</td>
<td>40.5</td>
</tr>
<tr>
<td>$\eta$, %</td>
<td>4.73</td>
<td>4.60</td>
<td>3.97</td>
<td>3.97</td>
<td>3.37</td>
</tr>
</tbody>
</table>
This is also reflected in the current-voltage (I-V) characteristics (Figure 4.1(b), Table 4.1), specifically in the decrease of the $V_{OC}$ values and corresponding increase in the $J_{SC}$ values with increasing LiI concentration, unfortunately accompanied by a deteriorating fill factor. The $J_{SC}$ increased from 13.3 to 18.1 mA/cm$^2$, representing a 36% enhancement, upon changing the concentration of LiI from 0.1 to 3.0 M, while the $V_{OC}$ showed a 21% decrease (from 626 to 495 mV) under the same conditions (Figure 4.1, Table 4.1). The decreasing values for the fill factor and $V_{OC}$ effectively neutralize the observed increases in the $J_{SC}$ and result in lower values for the maximum power output of the device which in turn translates into lower power conversion efficiencies as a function of LiI concentration. Parallel studies were carried out with the Ru(II)-based N3 dye. Variations in the concentration of LiI in this redox electrolyte do not significantly affect the EQE of the N3-based device (Figure 4.2(a)). The $V_{OC}$ and fill factor (Figure 4.2(b), Table 4.2) follow the same trend as observed for TD-1 which ultimately affect the power conversion efficiency in a similar adverse manner. The $J_{SC}$ increased from 13.8 to 15.0 mA/cm$^2$ across the concentration series, representing an 8.7% increase, whereas the $V_{OC}$ exhibited a net 17% decrease (from 664 to 553 mV) under the same conditions (Figure 4.2, Table 4.2). While there are slight elevations observed in the $J_{SC}$ (8.7% max.) throughout these experiments, their relative magnitudes are not at all comparable to those realized in the Os(II)-based TD-1 (36% max). These combined observations clearly demonstrate that the concentration of LiI in the redox electrolyte solution affects the osmium-based DSSC significantly whereas they have little or no influence on the corresponding N3-based device.
Figure 4.2. Influence of LiI concentration on the external quantum efficiency (a) and current-voltage curves (b) of N3. The concentrations of the other components of the electrolyte solution (0.05 M I₂, 0.6 M PMII, 0.1 M guanidine thiocyanate, 0.5 M 4-tert-butylpyridine) were maintained constant, while the concentration of LiI was varied as shown on the graphs.
4.3.2. Determination of the roles of lithium cation and iodide anion

Since LiI comprises two ions which play distinct yet essential roles in DSSCs, it is important to reveal which of these species is responsible for the observed trends in the osmium-based devices, particularly the trends in $J_{SC}$ and fill factor. Upon independently increasing the concentration of Li$^+$ using LiClO$_4$ as the lithium source, no improvement in the photovoltaic performances of these devices were obtained. Similar studies have been reported by other investigators and it was concluded that the increases in $J_{SC}$ are not due to Li$^+$ but rather due to increasing concentration of the iodide anion in the redox electrolyte.$^5$ Concerns have been raised as to the appropriateness of using a ClO$_4^-$ salt as a substitute for an I$^-$ salt as the former apparently results in a change in injection dynamics in DSSCs,$^4$ and for this reason, this alternate source of Li$^+$ was not explored any further. We therefore selectively increased the iodide concentration using PMII to assess the performances of the resultant DSSCs. These experiments were carried out using only PMII and I$_2$ in acetonitrile solution. The concentration of iodine was kept constant at 0.05 M I$_2$ while the concentration of PMII was systematically varied: 0.1 M, 0.5 M, 1.0 M, 2.0 M, and 3.0 M. The EQE steadily increases (Figure 4.3(a)) and there is an accompanying increase in $J_{SC}$ (Figure 4.3(b), Table 4.3) with increasing PMII concentration in the osmium-based devices. The $J_{SC}$ improved by 96% (3.47 to 6.79 mA/cm$^2$) while the $V_{OC}$ was correspondingly enhanced by 14% (555 to 630 mV) upon increasing the PMII concentration from 0.1 to 3.0 M. In view of the fact that both $V_{OC}$ and $J_{SC}$ values increase with increasing PMII concentration (Figure 4.3(b), Table 4.3) the improvement in $J_{SC}$ cannot simply be explained in terms of conduction band edge manipulation by adsorbed cations since PMII contains a large cation which is not expected to easily adsorb onto the TiO$_2$ surface.
Figure 4.3. Influence of PMII concentration on the external quantum efficiency (a) and current-voltage curves (b) of TD-1. The concentration of iodine in the electrolyte solution was kept constant at 0.05 M, while the concentration of PMII was varied as shown on the graphs.
Table 4.3. Device parameters derived from the I-V curves illustrating the effect of PMII concentration on TD-1.

<table>
<thead>
<tr>
<th></th>
<th>0.1 M PMII</th>
<th>0.5 M PMII</th>
<th>1.0 M PMII</th>
<th>2.0 M PMII</th>
<th>3.0 M PMII</th>
</tr>
</thead>
<tbody>
<tr>
<td>J_{SC}, mA/cm²</td>
<td>3.47</td>
<td>6.20</td>
<td>6.77</td>
<td>6.70</td>
<td>6.79</td>
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<tr>
<td>V_{OC}, mV</td>
<td>555</td>
<td>611</td>
<td>615</td>
<td>614</td>
<td>630</td>
</tr>
<tr>
<td>FF, %</td>
<td>50.7</td>
<td>51.5</td>
<td>49.3</td>
<td>52.7</td>
<td>54.8</td>
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<td>η, %</td>
<td>0.98</td>
<td>1.95</td>
<td>2.05</td>
<td>2.17</td>
<td>2.34</td>
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</tbody>
</table>

Under similar conditions, the ruthenium-based N₃ dye displayed similar increases in both J_{SC} and V_{OC} values (Figure 4.4, Table 4.4). The J_{SC} was augmented by 60% (5.08 to 8.13 mA/cm²) while the V_{OC} improved by 7% (636 to 681 mV) upon changing the PMII concentration from 0.1 to 3.0 M. Importantly, the fill factor is not negatively impacted with increasing PMII concentration in both the Os(II)- and Ru(II)-based devices. It is clear from the above experiments that independently varying the concentration of PMII improves the EQE, J_{SC}, V_{OC}, fill factor and device efficiency values in both classes of devices with those based on TD-1 being more significantly influenced. The low values of the EQE and J_{SC} observed while using PMII in these experiments might be associated with the viscosity of this ionic liquid which limits mass transport within the device. Visual comparison of 3.0 M solutions of LiI and PMII reveals that the PMII solution is indeed much more viscous. To counter this effect, we performed similar experiments using tetrabutylammonium iodide (TBAI) as the iodide source.
Figure 4.4. Influence of PMII concentration on the external quantum efficiency (a) and current-voltage curves (b) of N3. The concentration of iodine in the electrolyte solution was kept constant at 0.05 M, while the concentration of PMII was varied as shown on the graphs.
Table 4.4. Device parameters derived from the I-V curves illustrating the effect of PMII concentration on N3.

<table>
<thead>
<tr>
<th>PMII Concentration</th>
<th>J_{SC}, mA/cm^2</th>
<th>V_{OC}, mV</th>
<th>FF, %</th>
<th>η, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M PMII</td>
<td>5.08</td>
<td>636</td>
<td>58.3</td>
<td>1.88</td>
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<td>672</td>
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<td>3.11</td>
</tr>
<tr>
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<td>7.92</td>
<td>674</td>
<td>56.6</td>
<td>3.02</td>
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<tr>
<td>2.0 M PMII</td>
<td>8.22</td>
<td>668</td>
<td>58.3</td>
<td>3.20</td>
</tr>
<tr>
<td>3.0 M PMII</td>
<td>8.13</td>
<td>681</td>
<td>62.8</td>
<td>3.47</td>
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</tbody>
</table>

Table 4.5. Device parameters derived from the I-V curves illustrating the effect of TBAI concentration on TD-1.

<table>
<thead>
<tr>
<th>TBAI Concentration</th>
<th>J_{SC}, mA/cm^2</th>
<th>V_{OC}, mV</th>
<th>FF, %</th>
<th>η, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M TBAI</td>
<td>4.67</td>
<td>456</td>
<td>53.5</td>
<td>1.14</td>
</tr>
<tr>
<td>0.5 M TBAI</td>
<td>11.7</td>
<td>453</td>
<td>41.6</td>
<td>2.21</td>
</tr>
<tr>
<td>1.0 M TBAI</td>
<td>13.5</td>
<td>451</td>
<td>38.9</td>
<td>2.37</td>
</tr>
<tr>
<td>2.0 M TBAI</td>
<td>14.9</td>
<td>458</td>
<td>34.1</td>
<td>2.32</td>
</tr>
</tbody>
</table>
The concentration of iodine was maintained at 0.05 M I₂ while the concentration of TBAI was systematically varied: 0.1 M, 0.5 M, 1.0 M and 2.0 M; the latter was the highest possible concentration that could be obtained in acetonitrile. For devices based on **TD-1**, the EQE and J_{SC} enhancements were rather substantial (Figure 4.5, Table 4.5). The J_{SC} is amplified by 219% (4.67 to 14.9 mA/cm²) while the V_{OC} remains relatively constant and is unfortunately accompanied by a decline in fill factor. We believe that these studies confirm that iodide alone is responsible for the marked increases observed in the photocurrent density. Under identical conditions, **N3**-based devices reveal improvement in both the J_{SC} and V_{OC} (Figure 4.6, Table 4.6). The J_{SC} improved by 77% (7.22 to 12.8 mA/cm²) while the V_{OC} increased by 17% (526 to 614 mV), accompanied by an attenuation in fill factor across the TBAI concentration series. The magnitude of the enlargement in J_{SC}, as also observed in earlier experiments, is not comparable to that observed for devices based on **TD-1**. Assuming that not all of the four carboxylic acid groups present in the N3-sensitizer are anchored onto nanocrystalline TiO₂ in these devices, the observed increases in V_{OC} may be attributed to in-situ deprotonation of some of these carboxylic acid groups leading to the formation of negatively charged carboxylate moieties in close proximity to the semiconductor nanoparticles which shifts the TiO₂ band edge to more negative values, thereby resulting in the observed increases in V_{OC}. This was confirmed by steady-state absorption measurements on dye-sensitized TiO₂ films in the presence and absence of TBAI. TiO₂ films sensitized with N3 display a blue-shift of the MLCT absorption band in the presence of 0.1 M TBAI, relative to the absorption spectrum measured in neat acetonitrile solvent, whereas the absorption spectra of films sensitized with **TD-1** were superimposable under similar experimental conditions (Figure 4.7). This indicates that there is likely no in-situ deprotonation of **TD-1** as both of the two carboxylic acid groups are anchored on TiO₂, while the reverse case is likely operable for **N3**.
Figure 4.5. Influence of TBAI concentration on the external quantum efficiency (a) and current-voltage curves (b) of TD-1. The concentration of iodine in the electrolyte solution was kept constant at 0.05 M, while the concentration of TBAI was varied as shown on the graphs.
Figure 4.6. Influence of TBAI concentration on the external quantum efficiency (a) and current-voltage curves (b) of N3. The concentration of iodine in the electrolyte solution was kept constant at 0.05 M, while the concentration of TBAI was varied as shown on the graphs.
Table 4.6. Device parameters derived from the I-V curves illustrating the effect of TBAI concentration on N3.

<table>
<thead>
<tr>
<th></th>
<th>0.1 M TBAI</th>
<th>0.5 M TBAI</th>
<th>1.0 M TBAI</th>
<th>2.0 M TBAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{SC}$, mA/cm²</td>
<td>7.22</td>
<td>11.3</td>
<td>12.7</td>
<td>12.8</td>
</tr>
<tr>
<td>$V_{OC}$, mV</td>
<td>526</td>
<td>589</td>
<td>602</td>
<td>614</td>
</tr>
<tr>
<td>FF, %</td>
<td>55.8</td>
<td>52.2</td>
<td>51.9</td>
<td>48.5</td>
</tr>
<tr>
<td>$\eta$, %</td>
<td>2.12</td>
<td>3.49</td>
<td>3.97</td>
<td>3.80</td>
</tr>
</tbody>
</table>

Figure 4.7. Absorption spectra of TiO₂ films sensitized with either TD-1 or N3 in acetonitrile solvent. Spectra were first taken in neat solvent and then in 0.1 M TBAI solution for each sensitizer. Corrections were made for TBAI absorption in acetonitrile.
To further understand the role of LiI in the redox electrolyte solution, similar experiments were carried out using only LiI and I₂ as the primary components of the acetonitrile solution. The concentration of I₂ was maintained constant at 0.05 M while the concentration of LiI was varied as follows: 0.1 M, 0.5 M, 1.0 M, 2.0 M and 3.0 M. As anticipated, there is a general increase in the EQE and JSC values for devices based on TD-1 (Figure 4.8, Table 4.7). The JSC increased by 181% (4.17 to 11.7 mA/cm²) while the V_OC declined by 30% (305 to 213 mV), accompanied by a deterioration in fill factor across the LiI concentration series. Under identical conditions, N3-based devices exhibited increases in both the JSC and V_OC (Figure 4.9, Table 4.8). The JSC increased by 106% (7.73 to 16.0 mA/cm²) while the V_OC decreased by 21% (457 to 361 mV) with a concomitant decrease in fill factor. The changes in the JSC, V_OC, fill factor and power conversion efficiency as a function of LiI concentration in both the osmium (Figure 4.8(b), Table 4.7) and ruthenium (Figure 4.9(b), Table 4.8) devices using this two component (LiI & I₂ only) electrolyte follow the same trend as observed when using the complete electrolyte composition (LiI, I₂, PMII, guanidine thiocyanate and 4-tert-butylpyridine).

It is important to note that the fill factor sharply attenuates with LiI concentration, suggesting that an abundance of LiI in the redox electrolyte solution leads to greater internal resistance in the present DSCs. Internal resistance elements in DSCs are related to the charge transfer processes at the platinum counter electrode, the charge transport at the TiO₂/dye/electrolyte interface, Nernstian diffusion in the electrolyte, and sheet resistance of the transparent conducting glass (TCG) substrate. The concentration of iodide species has almost no influence on the charge transfer resistance and since the same TCG was used in all the experiments, these components can be excluded as the origin of the experimental observations.
Figure 4.8. Influence of LiI concentration on the external quantum efficiency (a), current-voltage curves (b) and normalized EQE (c) of TD-I. The concentration of iodine in the electrolyte solution was kept constant at 0.05 M, while the concentration of LiI was varied as shown on the graphs.
Figure 4.9. Influence of LiI concentration on the external quantum efficiency (a) and current-voltage curves (b) of N3. The concentration of iodine in the electrolyte solution was kept constant at 0.05 M, while the concentration of LiI was varied as shown on the graphs.
Table 4.7. Device parameters derived from the I-V curves illustrating the effect of LiI concentration on TD-1.

<table>
<thead>
<tr>
<th>LiI Concentration</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt;, mA/cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt;, mV</th>
<th>FF, %</th>
<th>η, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M LiI</td>
<td>4.17</td>
<td>305</td>
<td>42.0</td>
<td>0.54</td>
</tr>
<tr>
<td>0.5 M LiI</td>
<td>10.1</td>
<td>256</td>
<td>33.0</td>
<td>0.85</td>
</tr>
<tr>
<td>1.0 M LiI</td>
<td>11.2</td>
<td>229</td>
<td>28.1</td>
<td>0.72</td>
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<tr>
<td>2.0 M LiI</td>
<td>11.8</td>
<td>218</td>
<td>27.3</td>
<td>0.70</td>
</tr>
<tr>
<td>3.0 M LiI</td>
<td>11.7</td>
<td>213</td>
<td>27.0</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 4.8. Device parameters derived from the I-V curves illustrating the effect of LiI concentration on N3.

<table>
<thead>
<tr>
<th>LiI Concentration</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt;, mA/cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt;, mV</th>
<th>FF, %</th>
<th>η, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M LiI</td>
<td>7.73</td>
<td>457</td>
<td>52.3</td>
<td>1.85</td>
</tr>
<tr>
<td>0.5 M LiI</td>
<td>15.3</td>
<td>432</td>
<td>41.7</td>
<td>2.75</td>
</tr>
<tr>
<td>1.0 M LiI</td>
<td>16.1</td>
<td>422</td>
<td>37.5</td>
<td>2.55</td>
</tr>
<tr>
<td>2.0 M LiI</td>
<td>16.1</td>
<td>383</td>
<td>35.9</td>
<td>2.21</td>
</tr>
<tr>
<td>3.0 M LiI</td>
<td>16.0</td>
<td>361</td>
<td>31.3</td>
<td>1.81</td>
</tr>
</tbody>
</table>
Therefore, we conclude that the enhanced internal resistance likely emanates from a combination of the remaining processes which are beyond the scope of this study.

Interestingly, the EQEs for the $^1$MLCT and $^3$MLCT transitions in the osmium-based device (Figure 4.8(c)) increase at different rates when compared to their values at the initial concentration of 0.1 M LiI. The values for the EQEs over the $^3$MLCT transitions tend towards the values at the $^1$MLCT transitions with increasing LiI concentration. This was also observed in the experiments presented earlier (Figure 4.1(a)). Photoluminescence measurements of TD-1 while adsorbed onto the TiO$_2$ thin film reveal a quenching of the sensitizer’s already weak photoluminescence in the presence of 0.1 M LiI in acetonitrile solution (Figure 4.10). Similar observations have been reported earlier.\textsuperscript{18} This quenching was readily observed at excitation wavelengths of 514 (Figure 4.10(a)) and 700 nm (Figure 4.10(b)), corresponding to peak wavelengths in the $^1$MLCT and $^3$MLCT transitions of TD-1, respectively, and is reversible upon washing the sensitized film. The absorption spectrum (Figure 4.10(c)) exhibits a red-shift and an increase in intensity in the presence of 0.1 M LiI, compared to the spectrum in neat acetonitrile.
Figure 4.10. Photoluminescence (a, b) and absorption spectra (c) of FTO/TiO₂/TD-I thin film immersed in 0.1M LiI/CH₃CN solution (red); and in neat CH₃CN after removal of the LiI/CH₃CN by multiple washing (black). Quenching was observed at excitation wavelengths of 514 nm (a) and 700 nm (b), corresponding to wavelengths in the ¹MLCT and ³MLCT transitions, respectively.
The observed spectral effects are associated with electron transfer from the excited state of the sensitizer to the conduction band of the semiconductor. The presence of Li$^+$ induces a shift in the energetics of the TiO$_2$ acceptor states and makes them more accessible to electron transfer from the sensitizer excited states, resulting in photoluminescence quenching. Electrons, injected into the conduction band of metal-oxide semiconductors, create an electric field which induces a Stark-like effect on the absorption spectrum of the surface-anchored sensitizer.$^{19}$ Stark effects can be manifested as growths or losses in absorbance intensity and energetic shifts in the position of the absorption maxima.$^{19,20}$ The observed photoluminescence quenching suggests that excited-state electrons, arising from the spin-forbidden direct singlet-to-triplet transitions ($^3$MLCT $\leftarrow$ S$_0$) of TD-1, are capable of direct (hot) injection into the conduction band of TiO$_2$. This might be due to injection from upper vibrational levels, wherein vibrational relaxation processes, intersystem crossing, and electron injection are competing with each other.$^{21,22}$ Positive shifts in the TiO$_2$ acceptor states redox potential as a result of enhanced interfacial cation concentration results in more significant overlap of the sensitizer excited states with the density of the semiconductor acceptor states.$^{14}$ Increased contributions from the $^3$MLCT transitions to the generated photocurrent may therefore be due to more favorable thermodynamics of electron injection from the $^3$MLCT transitions to the TiO$_2$ acceptor states. Electrons injected upon photoexcitation with low energy photons might end up at trap sites within the TiO$_2$ density of states. The electron occupancy of the trap/conduction band states of the TiO$_2$ film strongly influence the electron transfer dynamics between trap sites within the TiO$_2$ nanoparticles, which results in a strong dependence of charge recombination kinetics upon variations in the light intensity, applied electrical potential and electrolyte composition, but largely independent of the sensitizer.$^{23,24}$ This apparent wavelength-dependent injection, observed when the redox electrolyte composition is varied, may then be rationalized as arising
from either decreased recombination losses of electrons injected into the TiO₂ density of states with the oxidized sensitizer cation or more favorable thermodynamics of electron injection from the ³MLCT transitions to the TiO₂ acceptor states as discussed earlier. Both cases are expected to increase the external quantum yield of photon to electron conversion. The exact origin of this feature will be the subject of further investigation. This observation suggests that the ¹MLCT/³MLCT ratio of the EQEs of TD-I can be experimentally tuned to approach unity by making variations in the composition of the redox electrolyte. This particular experimental facet is important as it can be used to increase the external quantum yield in the low energy spectral region without resorting to the use of a scattering layer of larger-sized TiO₂ nanoparticles.²⁵,²⁶

Further investigations were carried out to ascertain if there are contributions from competitive triiodide absorption to the observed enhancements in the photocurrent density as a function of the concentration of the iodide source; the results are shown in Figure 4.11. It was observed that there is no significant input from this phenomenon. The photovoltaic measurements were taken with back-irradiation of the DSSCs from the cathode side. There was minimal photoaction in the region of the spectrum where the triiodide species absorb, indicating that there are no contributions from absorption transitions of the triiodide species to the observed increments in the EQE. Other regions of the spectrum showed the expected photoaction as a function of the concentration of the iodide source, albeit with slightly lower external quantum efficiencies. This decrease in EQE is due to the transmittance of the cathode which reduces the intensity of light reaching the dye-sensitized photoanode.
Figure 4.11. Competitive triiodide absorption studies of DSSCs based on TD-1. The DSSCs were illuminated from the backside (cathode side) and the redox electrolyte consisted of LiI and 0.05 M I₂ in CH₃CN solution. The concentration LiI was varied as shown on the graph.
4.3.3. Towards an Optimized Redox Electrolyte Composition.

The significance of the role of the iodide anion in the photovoltaic performance of Os(II)-based DSSCs necessitates alternate I− sources that will yield high photocurrents and EQEs without sacrificing the photovoltage that is required for efficient power conversion. We have shown (Figure 4.5, Table 4.5) that using TBAI as the iodide source affords high photocurrents without any loss in photovoltage while using I2 and TBAI as the main contents of the redox electrolyte. To understand how the photovoltaic performance will change upon using a full-component electrolyte, experiments were conducted using a more conventional mixture (0.05 M I2, 0.6 M PMII, 0.1 M guanidine thiocyanate, 0.5 M 4-tert-butylpyridine, and TBAI instead of LiI) that systematically varies the TBAI component (0.1 M, 0.5 M, 1.0 M and 2.0 M) in acetonitrile solution. In these experiments, both J_sc (25%, 8.83 to 11.0 mA/cm²) and V_oc (8.5%, 600 to 651 mV) of devices based on TD-1 displayed small enhancements with increasing TBAI concentration (Figure 4.12, Table 4.9). The augmentation in the J_sc and V_oc along with a stable fill factor importantly leads to a net gain in power conversion efficiency. This indicates that TBAI should serve as a viable alternative to LiI towards achieving high current and voltage values in Os(II)-based dye-sensitized solar cells. Control experiments were conducted with DSSCs based on N3 as the sensitizer (Figure 4.13, Table 4.10). Under identical conditions, the J_sc (11.8 to 12.6 mA/cm²) and V_oc (659 to 700 mV) both displayed improvements upon increasing the TBAI concentration in these Ru(II)-based devices.
Figure 4.12. Influence of TBAI concentration on the external quantum efficiency (a) and current-voltage curves (b) of TD-1. The concentrations of the other components of the electrolyte solution (0.05 M I₂, 0.6 M PMII, 0.1 M guanidine thiocyanate, 0.5 M 4-tert-butylpyridine) were kept constant, while the concentration of TBAI was varied as shown on the graphs.
Figure 4.13. Influence of TBAI concentration on the external quantum efficiency (a) and current-voltage curves (b) of N3. The concentrations of the other components of the electrolyte solution (0.05 M I₂, 0.6 M PMII, 0.1 M guanidine thiocyanate, 0.5 M 4-tert-butylpyridine) were kept constant, while the concentration of TBAI was varied as shown on the graphs.
Table 4.9. Device parameters derived from the I-V curves illustrating the effect of TBAI concentration on TD-1.

<table>
<thead>
<tr>
<th></th>
<th>0.1 M TBAI</th>
<th>0.5 M TBAI</th>
<th>1.0 M TBAI</th>
<th>2.0 M TBAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{sc}$, mA/cm²</td>
<td>8.83</td>
<td>9.91</td>
<td>10.8</td>
<td>11.0</td>
</tr>
<tr>
<td>$V_{oc}$, mV</td>
<td>600</td>
<td>632</td>
<td>646</td>
<td>651</td>
</tr>
<tr>
<td>FF, %</td>
<td>56.9</td>
<td>58.7</td>
<td>58.3</td>
<td>56.6</td>
</tr>
<tr>
<td>$\eta$, %</td>
<td>3.01</td>
<td>3.67</td>
<td>4.05</td>
<td>4.07</td>
</tr>
</tbody>
</table>

Table 4.10. Device parameters derived from the I-V curves illustrating the effect of TBAI concentration on N3.

<table>
<thead>
<tr>
<th></th>
<th>0.1 M TBAI</th>
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<th>1.0 M TBAI</th>
<th>2.0 M TBAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{sc}$, mA/cm²</td>
<td>11.8</td>
<td>12.4</td>
<td>12.7</td>
<td>12.6</td>
</tr>
<tr>
<td>$V_{oc}$, mV</td>
<td>659</td>
<td>679</td>
<td>694</td>
<td>700</td>
</tr>
<tr>
<td>FF, %</td>
<td>57.8</td>
<td>59.0</td>
<td>56.6</td>
<td>52.4</td>
</tr>
<tr>
<td>$\eta$, %</td>
<td>4.48</td>
<td>4.97</td>
<td>5.01</td>
<td>4.63</td>
</tr>
</tbody>
</table>
The various loss pathways that are possible for the dye-sensitized solar cell are presented in Scheme 4.1 and include the quenching of the sensitizer excited state by the iodide/triiodide redox mediator, $k_{bm}$, trapping of the conduction band electrons, $e^-(\text{TiO}_2)$, by the iodide/triiodide redox mediator, $k_{br}$, charge recombination of the $e^-(\text{TiO}_2)$ with the oxidized sensitizer, $k_{cr}$, and nonradiative decay of the sensitizer excited state, $k_d$. On the basis of the short-lived nature of the excited state of TD-1 ($\tau < 15$ nanoseconds) and the ultrafast nature of electron injection$^{1,24,28,29}$ to TiO$_2$, losses from the bimolecular, $k_{bm}$, and nonradiative decay, $k_d$, pathways are expected to be minimal for DSSCs based on TD-1. The reduction of $\text{I}_3^-$ by $e^-(\text{TiO}_2)$, $k_{br}$, and the recombination of injected electrons with the oxidized sensitizer, $k_{cr}$, are kinetically slow processes$^{30}$ and may become the dominant loss pathways if the regeneration of the oxidized sensitizer, $k_{reg}$, is inefficient.

\textbf{SCHEME 4.1:} Energy level diagram and associated interfacial electron transfer pathways at the dye-sensitized nanocrystalline TiO$_2$/electrolyte interface
Values for $k_{\text{reg}}$ are generally lower for Os(III) than for the analogous Ru(III) metal centers.$^{3,31}$ The reaction of the Os(III) metal center with iodide anion has been investigated in aqueous solution and equations 4.1 and 4.2 below show the proposed mechanism of reduction (regeneration).$^{32}$ It was shown that the forward reaction ($k_1 = 3.3 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$) is four orders of magnitude slower than the reverse reaction ($k_{-1} = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and constitutes the limiting stage of the reduction process ($k_2 = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) at 22 ºC and an ionic strength of 0.1 M.

\[
2I^- + \text{Os(bpy)}_3^{3+} \rightleftharpoons \frac{k_1}{k_{-1}} \text{Os(bpy)}_3^{2+} + I_2^- \quad (4.1)
\]

\[
I_2^- + \text{Os(bpy)}_3^{3+} \rightarrow \frac{k_2}{k_3} \text{Os(bpy)}_3^{2+} + I_2 \quad (4.2)
\]

\[
I_2 + I^- \rightarrow \frac{k_3}{k_3} I_3^- \quad (4.3)
\]

The produced iodine is instantaneously converted, according to equation 3.3, to the triiodide species ($k_3 = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-3} = 8.5 \times 10^6 \text{ s}^{-1}$ in 50% D$_2$O-H$_2$O).$^{33}$ From equations 4.1, 4.2 and 4.3, it is evident that an abundance of $I^-$ will shift the equilibrium to the right and facilitate a more efficient regeneration (reduction) of the oxidized metal center. In DSSCs, the triiodide species diffuses to the cathode where it is reduced back to iodide.

The observed increases in the EQEs and $J_{\text{SC}}$ of osmium-based devices arise primarily as a result of an abundance of the iodide anion. This relates to an inefficient regeneration of the oxidized osmium sensitizer$^{3,31}$ due to a relatively unfavorable thermodynamic driving force which can be compensated for by an abundance of this anion in the electrolyte. An abundance of Li$^+$ is expected to strongly affect semiconductor energetics by positively shifting the TiO$_2$ acceptor state potentials due to increased positive charges at the TiO$_2$ surface. This increases the
thermodynamic driving force for electron injection to the conduction band of the TiO$_2$
semiconductor but decreases $V_{oc}$ and leads to greater loss of injected electrons by recombination
with the oxidized sensitizer.$^{14,34}$ Substituting TBAI for LiI leads to net gains in current and
voltage with increasing concentration of the iodide source. We have shown that the percentage
increases in $J_{SC}$ values were greater in all cases for devices based on TD-1 as compared to
devices based on N3.
4.4. Conclusions

The influence of variations in the concentration of Li$^+$ and I$^-$ ions in the redox electrolyte solution of TD-1- and N3-based DSSCs on the photovoltaic performances of such devices was evaluated. Increases in the LiI concentration were found to result in increased $J_{SC}$ in an osmium-based device and decreased $V_{OC}$ in both osmium- and ruthenium-based devices. The fill factor was found to deteriorate with increasing LiI concentration, independent of the dye-sensitizer. Increases in the concentration of the iodide anion using PMII or TBAI resulted in increases in both the $J_{SC}$ and $V_{OC}$ of the devices. This suggests that increases in the iodide concentration results in a more efficient regeneration of the oxidized osmium sensitizer in the operational DSSC, a decrease in electron losses through recombination with the oxidized sensitizer, and as such, larger values for the $J_{SC}$. Variations in the composition of the redox electrolyte appears to be crucial for optimizing the photovoltaic performance of osmium-based DSSCs as we have shown that osmium- and ruthenium-based devices respond distinctively differently to changes in the electrolyte composition. Our results suggest that TBAI might be a viable alternative to LiI towards achieving high photocurrent and photovoltage values, and ultimately higher photoconversion efficiencies in Os(II)-based dye-sensitized solar cells.
4.5. References


Chapter V

Organic Sensitizers Based on a Carbazole Donor Moiety for Dye-Sensitized Solar Cells
5.1. Introduction

Limitations in the availability of rare transition metals have triggered a search for metal-free organic sensitizers that may play a role in the impending large-scale application of dye-sensitized solar cells, provided that their photostability and efficiency can be considerably improved upon. Although metal-complexed sensitizers exhibit higher efficiency and photostability, they incorporate rare transition metals which are expensive, toxic and the organometallic complexes are also difficult to purify compared to the metal-free organic sensitizers. Ruthenium polypyridyl complexes are widely used as sensitizers in DSSCs,\textsuperscript{1-4} and the highest reported NREL-certified power conversion efficiency of 11.18 % has been obtained for the N719 sensitizer, a derivative of \textit{cis}-Ru(dcbpyH\textsubscript{2})(NCS)\textsubscript{2} (the N3 sensitizer).\textsuperscript{5} Recently, an unprecedented power conversion efficiency of 10.3 % has been achieved for an organic sensitizer\textsuperscript{6} thus indicating that with further strategic optimization metal-free organic sensitizers may overtake their organometallic counterparts in photovoltaic performance. An ideal sensitizer, whether metal-based or metal-free, for application in single junction photovoltaic cells that converts standard AM1.5 global sunlight to electricity should (a) absorb all light below a threshold wavelength of 900 nm, (b) be firmly anchored to the semiconductor surface, (c) inject electrons with a quantum yield of unity upon photoexcitation, (d) have a redox potential that is sufficiently high to enable regeneration of the oxidized sensitizer via electron transfer by the redox electrolyte or hole conductor, (e) be stable enough to survive at least $10^8$ turnovers corresponding to about 20 years of irradiation under natural sunlight.\textsuperscript{7,8} Metal-free organic sensitizers have unique advantages over organometallic sensitizers. These include the absence of the usually expensive transition metal center which significantly reduces cost, relative ease of synthesis and purification, and higher molar extinction coefficients, amongst others. The limitations in the photovoltaic performance of organic sensitizers are associated with, for
instance, narrow absorption bands that rarely extend into the red region of the spectrum, and formation of aggregates due to intermolecular interactions between π-electrons which result in dissipative energy loss. Coadsorption of sensitizers with organic acids, like 3R,7R-dihydroxy-5β-cholic acid\textsuperscript{6} and deoxycholic acid,\textsuperscript{9} and structural modification of sensitizer molecules\textsuperscript{6,10} have been explored to improve device performance by breaking up π-stacked aggregates. Many attempts have been made by researchers in the design and construction of organic sensitizer molecules with broader spectral responses and higher molar extinction coefficients.\textsuperscript{9,11-14} Various classes of organic compounds such as coumarin,\textsuperscript{9,15,16} cyanine,\textsuperscript{17,18} hemicyanine,\textsuperscript{19,20} indoline,\textsuperscript{21,22} merocyanine,\textsuperscript{23,24} phenothiazine,\textsuperscript{25} tetrahydroquinoline,\textsuperscript{26,27} and triphenylamine,\textsuperscript{18,28,29} have been used as sensitizers in DSSCs with promising results. Very few organic sensitizers that bear the carbazole donor unit\textsuperscript{30-32} have been used in DSSCs with promising results. Few reports show the use of thiophene-based linkers in organic sensitizers exhibiting good device efficiencies.\textsuperscript{12} There are no reports to date related to metal-free organic sensitizers bearing carbazole units as both donor and linker moieties.

In this chapter, the electrochemical and photovoltaic studies of three new organic sensitizers, 2-cyano-3-[4-((3',6'-di-tert-butyl-9-(4-(trifluoromethyl)phenyl)-9H-carbazol-7yl)ethynyl)phenyl]acrylic acid (\textbf{Kr-1}), 2-cyano-3-(4-(2-(7-(2-((4-(4,9-di-tert-butyl-9H-carbazolol-9-yl)phenyl)ethynyl)-9-(4-(trifluoromethyl)phenyl)-9H-carbazol-2-yl)ethynyl)phenyl)acrylic acid (\textbf{Kr-2}) and 2-cyano-3-(4-(2-(5-(2-(4-(3,6-di-tert-butyl-9H-carbazolyl)phenyl)ethynyl)-2,2’-bithiophene) ethynyl)phenyl)acrylic acid (\textbf{Kr-3}), that show promise for incorporation in dye-sensitized solar cells were investigated and are reported herein. The molecular structures of these sensitizers are shown in Chart 5.1. All sensitizers have the same acceptor cyanoacrylic acid, which incorporates the carboxylic acid anchoring group, and the identical carbazole donor but differ in the linker. \textbf{Kr-1} and \textbf{Kr-2} sensitizers have 2-, 7-substituted carbazole linker and \textbf{Kr-3}
sensitizer has bithiophene group as a linker. Cyanoacrylic acid has evolved as the acceptor group of choice since it functions both as an electron acceptor and as an anchoring group and has been shown to outperform the carboxylic acid group in these roles in dye-sensitized solar cells.²⁸

**Chart 5.1.** The molecular structures of **Kr-1**, **Kr-2** and **Kr-3** sensitizers.

- **Kr-1**
- **Kr-2**
- **Kr-3**
5.2. Experimental Section

5.2.1. General. Krishna Panthi is graciously acknowledged for providing Kr-1, Kr-2 and Kr-3 sensitizers. Lithium iodide, 4-tert-butylpyridine (4-tBupy), iodide and 1-n-propyl-3-methylimidazolium iodide (PMII) were available from our previous study.\textsuperscript{33}

5.2.2. Characterization, Physical Measurements and Instrumentation.

Electrochemical data were obtained using a BAS Epsilon electrochemistry workstation with a conventional three-electrode arrangement. Cyclic voltammetry measurements were carried out in either anhydrous acetonitrile or dichloromethane solution containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, a gold microdisk (1.6 mm dia.) working electrode (BAS model MF-2014), a platinum wire auxiliary electrode (BAS model MW-4130) and a Ag/AgCl (3 M NaCl) reference electrode (BAS model MF-2079), respectively. Measurements were conducted in ca. 1 mM electroactive substrate in an argon atmosphere with a scan rate of 300 mV/s and ferrocene was used as internal standard. For all measurements, potentials were recorded \textit{vs} the ferrocenium/ferrocene (Fc\textsuperscript{+}/Fc\textsuperscript{0}) internal standard, and finally were converted to \(E_{1/2}\) \textit{vs} the normal hydrogen electrode (NHE) using \(E_{1/2}(Fc^+/Fc^0) = +0.69\ \text{V vs. NHE}\).\textsuperscript{34} Incident photon-to-current conversion efficiency (IPCE) measurements were carried out using a system from PV Measurements, Inc., equipped with a Xenon arc lamp and calibrated with a silicon reference photodiode. Current-voltage characteristics were measured on an I-V data acquisition system (PV Measurements, Inc.) equipped with a small area solar simulator (AM 1.5 Global) and an NREL-certified silicon reference solar cell (PVM 274, PV Measurements, Inc.) for calibrating the intensity of the simulated sunlight to 100 mW/cm\textsuperscript{2}, with the measured photocurrent being within 2% of its calibration value. Photocurrent density (\(J_{SC}\)) values directly measured using I-V curves were typically 10-15% larger than those estimated.
from the integrated EQE (IPCE) spectra. Estimation of $J_{SC}$ was performed by the I-V software (PV Measurements Inc.) according to the ASTM standard E1021. The sandwiched solar cells were illuminated directly through the transparent conductive glass support containing the TiO$_2$ photoanode. The photovoltaic characteristics are reported herein as overall yields that were not corrected for losses due to light absorption and reflection by the conductive glass substrate.

5.2.3. Preparation of Nanocrystalline TiO$_2$ Electrode and Transparent Platinum Cathode

The sol-gel synthesis of the colloidal TiO$_2$ paste was described in detail elsewhere.$^{33,35}$ The prepared TiO$_2$ paste was doctor-bladed onto the conductive glass substrate (Hartford Glass, TEC-15) to give the transparent layer of TiO$_2$ film with a typical thickness of 13 μm. The obtained nanoparticle film was then dried at 125 °C for 6 minutes and a 5 μm thick scattering layer of mesoscopic TiO$_2$ (Solaronix, Ti-Nanoxide 300) was doctor-bladed on top of it. The resulting TiO$_2$ films were subsequently annealed for 30 minutes at 500 °C under oxygen flow in a tube furnace with ramped heating control of 5 °C per minute. Upon cooling to 100 °C, TiO$_2$ electrodes were immersed in 0.5 mM sensitizer solution in acetonitrile/tert-butanol (50 : 50 v/v%) for 48 hours at RT. Due to solubility limitations, sensitization of sensitizer 3 was carried out in THF solution. Transparent platinum-coated FTO cathodes were prepared as described elsewhere.$^{33}$

5.2.4. Sandwiched Solar Cell Assembly

The active device area of the sensitized TiO$_2$ photoanode was adjusted to 0.25 cm$^2$. Stretched Parafilm-M was used as a spacer between the photoanode and the platinum counter electrode. The typical thickness of the spacer was 20 - 30 μm. A few drops of the redox electrolyte were placed on top of the active electrode area and a platinized FTO-glass counter electrode was
placed on top. The electrodes were then sealed together using binder clips. For these studies, the redox electrolyte solution consisted of 0.2 M LiI, 0.05 M I₂, 0.7 M PMII and 0.5 M 4-\textit{t}Bupy in anhydrous acetonitrile.³⁶
5.3. Results and Discussion

5.3.1 Electrochemistry

The cyclic voltammogram of Kr-1 in acetonitrile solution (Figure 5.1a) shows a quasi-reversible oxidation process centered at 1178 mV vs Ag/AgCl with the Fc⁺/Fc⁰ wave centered at 443 mV vs Ag/AgCl. The cyclic voltammogram of Kr-2 in dichloromethane solution (Figure 5.1b) shows a quasi-reversible oxidation process centered at 1191 mV vs Ag/AgCl with the Fc⁺/Fc⁰ wave centered at 428 mV vs Ag/AgCl. Due to solubility limitations, the electrochemical properties of Kr-3 could not be measured as no oxidation waves were observed either by cyclic voltammetry or differential pulse voltammetry measurements. Although Kr-3 sensitizer has high solubility in tetrahydrofuran (THF), no oxidation waves were observed in THF solution within the solvent potential window. The oxidation potentials were further converted to E₁/₂ vs NHE using E₁/₂(Fc⁺/Fc⁰) = +0.69 vs. NHE yielding E₁/₂(Kr-1) = 1.43 V vs NHE and E₁/₂(Kr-2) = 1.45 V vs NHE. The sensitizers have oxidation potentials that are more positive than that of the I⁻/I₃⁻ redox mediator (0.4 V vs NHE) which implies that they can be effectively regenerated by the redox mediator based on thermodynamics.
**Figure 5.1.** Cyclic voltametry of (a) Kr-1 sensitizer in CH$_3$CN solution and (b) Kr-2 sensitizer in CH$_2$Cl$_2$ solution.

- **(a)**
  - $E_{1/2}(1) = 1178$ mV vs Ag/AgCl
  - $E_{1/2}(Fc) = 443$ mV vs Ag/AgCl
  - $=> E_{1/2}(783) = 735$ mV vs Fc

- **(b)**
  - $E_{1/2}(2) = 1191$ mV vs Ag/AgCl
  - $E_{1/2}(Fc) = 428$ mV vs Ag/AgCl
  - $=> E_{1/2}(883) = 763$ mV vs Fc
5.3.2. Photovoltaic Measurements

The photoaction spectra and I-V curves were measured under identical conditions for all the sensitizers investigated herein. Four independent DSSCs were assembled and measured in parallel and the results reported herein are the average of the four cells, represented as overall yields that were not corrected for any kind of losses. All devices have an active area of 0.25 cm². Preliminary photovoltaic studies were undertaken with DSSCs made with 13 µm of transparent TiO₂ film overcoated with a 5 µm of a scattering layer of TiO₂ film and sensitized with Kr-2. The DSSCs display an average maximum IPCE of 75.1%, a power conversion efficiency of 2.24 ± 0.25%, a VOC of 664 ± 9.03 mV, a JSC of 4.72 ± 0.39 mA/cm² and a fill factor of 71.5% (Table 5.1). Due to concerns about the photostability of organic sensitizers in DSSCs, light-soaking tests were performed for about an hour with sandwich DSSCs based on Kr-2 sensitizer and the results (Figure 5.2) indicate a stable photovoltaic performance of the solar cells within the period under review. Apart from an initial decrease in all the photovoltaic parameters in the first ca. 7 min, the performance indicators exhibited stable values and indicate that these sensitizers may withstand prolonged light-soaking. Prolonged light-soaking is usually accompanied by temperature increases which result in a faster rate of redox electrolyte diffusion and a downward shift in the conduction band edge potential relative to I⁻/I₃⁻. The former results in improvements in fill factor and the latter in decreases in open-circuit voltage, while observed increases in the short-circuit current are a combination of both effects. Similar experiments, performed at 50 – 55 °C over a 1000 hr period, have been reported by Wang et al. and it was shown that the power conversion efficiency and other photovoltaic properties stabilized over the period of the test, indicating that metal-free organic sensitizers could have a good photostability, similar to the more frequently used coordination complex sensitizers.
Figure 5.2. Preliminary light-soaking test results for DSSCs based on Kr-2 showing (a) current-voltage curves and (b) properties of the current-voltage curves as a function of irradiation time.
The best photoaction spectra that were obtained for dye-sensitized solar cells incorporating **Kr-1**, **Kr-2** and **Kr-3** sensitizers, along with that of the **N3** sensitizer, are presented in Figure 5.3. The carbazole-based sensitizers convert visible light to photocurrent efficiently over the wavelength range of 350 to 550 nm. A maximum photon-to-current conversion efficiency of about 75% at 450 nm was realized for **Kr-1** and **Kr-2** sensitizers, while **Kr-3** sensitizer has a maximum EQE of 66% at 440 nm whereas the **N3** sensitizer produces a maximum EQE of 71.5% (Figure 5.3, Table 5.1). The current-voltage properties of the DSSCs based on **Kr-1**, **Kr-2** and **Kr-3** sensitizers, as well as the **N3** sensitizer, measured under standard one-sun conditions (AM 1.5G, 100 mW/cm²) are shown in Figure 5.4. Devices based on the carbazole-linked **Kr-1** and **Kr-2** sensitizers displayed the highest power conversion efficiency of 2.7%, those based on the thiophene-linked sensitizer **Kr-3** displayed a power conversion efficiency of 2.23%, while devices based on **N3** sensitizer achieved a power conversion efficiency of 6.04% under identical device fabrication and measurement conditions. Importantly, DSSCs based on the sensitizers display excellent fill factors, which suggest that there is reduced contribution to the internal resistance within these devices, especially from the charge transport at the TiO₂/dye/electrolyte interface.⁴⁰,⁴¹ Compared with **Kr-1** and **Kr-2** sensitizers, **Kr-3** sensitizer possesses a higher short-circuit current despite having a lower value for the maximum EQE. This is probably due to the fact that the sensitizer has a much broader absorption spectrum, which is reflected in the photoaction spectrum, whose contributions are expected to enhance the value of the photogenerated current. **Kr-1** and **Kr-2** sensitizers are structurally similar, except for the inclusion of an extra phenylacetylene group in the motif of **Kr-2** sensitizer, and as such should display similar properties which are reflected in the photophysical, electrochemical and photovoltaic properties of these sensitizers. The photogenerated short-circuit current and the values of the EQE maxima are identical, within experimental error, for both sensitizers and the
observed differences are revealed in the open-circuit voltage. **Kr-2** sensitizer shows a ~ 25 mV increase in the value of the $V_{OC}$, relative to sensitizer **Kr-1**. This difference in open-circuit voltage can be attributed to the effects of an extended π-conjugated backbone in **Kr-2** which promotes charge separation between the carbazole donor and cyanoacrylic acceptor moieties, enhances electron injection and occupancy of the conduction band which, in turn, raises the Fermi level and ultimately results in a greater open-circuit voltage.
Figure 5.3. Photoaction spectra of Kr-1, Kr-2 and Kr-3 sensitizers (a) and N3 sensitizer (b). TiO2 films consisted of a 16 µm transparent layer and a scattering layer is 5 µm thick. The redox electrolyte consisted of 0.2 M LiI, 0.05 M I2, 0.7 M PMII and 0.5 M tbutpy in acetonitrile solution.
Figure 5.4. Current-voltage curves of Kr-1, Kr-2 and Kr-3 sensitizers (a) and N3 sensitizer (b). TiO$_2$ films consisted of a 16 µm transparent layer and a scattering layer is 5 µm thick. The redox electrolyte consisted of 0.2 M LiI, 0.05 M I$_2$, 0.7 M PMII and 0.5 M $^t$bupy in acetonitrile solution.
All photovoltaic performances were obtained with TiO$_2$ photoanodes incorporating TiO$_2$ nanoparticle films that are made up of a 16 µm transparent layer and a 5 µm layer of scattering particles to yield the best photovoltaic performance (Table 5.1). Optimization of the TiO$_2$ film thickness is necessary in order to ascertain the optimum range that would yield the best photovoltaic performance and in this case involved the use of transparent layer of TiO$_2$ film (13 and 16 µm thickness) with or without a second layer of a 5 µm scattering layer on top of it (Table 5.1). Thicker films are expected to give better light absorption from an optical point of view since the films will adsorb more sensitizer molecules whose combined absorption properties will increase the light-harvesting property of the sensitized film. The thickness of a film affects its mechanical strength, adherence onto substrates and the interconnectivity between particles and these pose a challenge when making thicker films. Interconnectivity between particles will ultimately affect electron transport and resistance within the bulk semiconductor. Inefficient charge transport through the substrates results in losses through various recombination pathways. The optimal thickness of any given photoelectrode, on the other hand, depends on the extinction coefficient of the adsorbed sensitizer as well as on the semiconductor particle properties$^{42}$ and these conditions need to be optimized to realize the best performance of any combination of semiconductor and sensitizer.
Table 5.1. Summary of the photovoltaic properties of **Kr-1**, **Kr-2** and **Kr-3** sensitizers with **N3** sensitizer included for comparison.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>TiO₂ Film Thickness&lt;sup&gt;a&lt;/sup&gt; (µm)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF(%)</th>
<th>η(%)</th>
<th>IPCE&lt;sub&gt;max&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr-1</td>
<td>13 + 5</td>
<td>649 ± 4.83</td>
<td>5.60 ± 0.10</td>
<td>67.4 ± 2.89</td>
<td>2.45 ± 0.04</td>
<td>74.0 ± 0.39</td>
</tr>
<tr>
<td>Kr-1</td>
<td>16</td>
<td>615 ± 11.7</td>
<td>5.77 ± 0.07</td>
<td>68.7 ± 0.50</td>
<td>2.44 ± 0.00</td>
<td>74.4 ± 0.68</td>
</tr>
<tr>
<td>Kr-1</td>
<td>16 + 5</td>
<td>617 ± 1.80</td>
<td>6.24 ± 0.30</td>
<td>70.2 ± 1.77</td>
<td>2.70 ± 1.77</td>
<td>75.3 ± 0.36</td>
</tr>
<tr>
<td>Kr-2</td>
<td>13 + 5</td>
<td>664 ± 9.03</td>
<td>4.72 ± 0.39</td>
<td>71.5 ± 1.00</td>
<td>2.24 ± 0.25</td>
<td>75.1 ± 0.18</td>
</tr>
<tr>
<td>Kr-2</td>
<td>16</td>
<td>636 ± 4.41</td>
<td>5.73 ± 0.39</td>
<td>67.4 ± 6.11</td>
<td>2.44 ± 0.07</td>
<td>74.0 ± 0.75</td>
</tr>
<tr>
<td>Kr-2</td>
<td>16 + 5</td>
<td>642 ± 6.59</td>
<td>5.96 ± 0.20</td>
<td>70.5 ± 1.23</td>
<td>2.70 ± 0.05</td>
<td>75.9 ± 0.57</td>
</tr>
<tr>
<td>Kr-3</td>
<td>16 + 5</td>
<td>523 ± 10.1</td>
<td>7.03 ± 0.28</td>
<td>60.5 ± 0.30</td>
<td>2.23 ± 0.04</td>
<td>66.5 ± 0.64</td>
</tr>
<tr>
<td>N3</td>
<td>16 + 5</td>
<td>683 ± 4.09</td>
<td>15.9 ± 1.01</td>
<td>55.9 ± 1.58</td>
<td>6.04 ± 0.31</td>
<td>71.5 ± 0.80</td>
</tr>
</tbody>
</table>

<sup>a</sup> Thickness of the transparent layer was either 13 or 16 µm while the scattering layer is 5 µm thick. Four identical solar cells were prepared and evaluated in each case. The redox electrolyte consisted of 0.2 M LiI, 0.05 M I₂, 0.7 M PMII and 0.5 M tbupy in acetonitrile solution.

The overall photovoltaic performance of the sensitizers may have been affected by π-stacking as we did not use any coadsorbents while sensitizing the semiconductor nanocrystals. In planar sensitizers, the effect of pi-stacking may be reflected in a dissipative intermolecular energy transfer which could have adverse effects on the cell photovoltaic performance. Various approaches, such as the coadsorption of organic acids such as 3R,7R-dihydroxy-5β-cholic acid and deoxycholic acid, have been explored with the aim of improving device performance by breaking up of π-stacked aggregates. In view of the excessive driving force for regeneration of the sensitizers (ca. 1.0 V vs NHE) by the iodide/triiodide redox mediator, the use of an alternate redox mediator with a more positive oxidation potential might yield a greater photovoltaic performance by decreasing the thermodynamic driving force and loss of the excess energy in the
form of heat. Wang et al.\textsuperscript{45} have shown that Br\textsuperscript{-}/Br\textsubscript{3}\textsuperscript{-} redox mediator, $E(\text{Br}^-/\text{Br}_3^-) = 1.09$ V vs NHE, is more suitable than the I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-} (0.4 V vs NHE)\textsuperscript{38} if the sensitizer has a significantly more positive oxidation potential that that of Br\textsuperscript{-}/Br\textsubscript{3}\textsuperscript{-}. This substitution is expected to alter the energetics of the DSSC by reducing the driving force for charge regeneration while increasing the potential difference between the Fermi level of the sensitized semiconductor and the redox electrolyte, both of which will affect the $V_{OC}$ and $J_{SC}$ to some extent.

5.4. Conclusions

The electrochemical and photovoltaic properties of organic sensitizers that incorporate a carbazole unit as a donor, carbazole or bithiophene as a $\pi$-conjugated linker and a cyanoacrylic acid group as an acceptor were evaluated. The sensitizers containing carbazole as the linker exhibited higher power conversion efficiency compared to the sensitizer having bithiophene as the linker. Kr-1 and Kr-2 sensitizers produced a power conversion efficiency of 2.70% with a maximum EQE of 75% at 450 nm, while Kr-3 sensitizer had a power conversion efficiency of 2.23% with a maximum EQE of 66 % at 440 nm. Under identical conditions, the benchmark N3 sensitizer produced a power conversion efficiency of 6.04 % with a maximum EQE of 71 % at 550 nm. Short term light-soaking indicated the potential stability of these organic sensitizers towards prolonged exposure to solar irradiation. All the results indicate that these organic compounds are promising candidates in the development and further optimization of metal-free organic sensitizers for application in the growing field of organic-based dye-sensitized solar cells.
5.5. References


(38) Zhang, Z.; Zhang, Z.; Chen, P.; Murakami, T. N.; Zakeeruddin, S. M.; Grätzel, M.


APPENDIX A. $^1$H-NMR, MALDI-TOF and some Electrochemical Characterization

Figure A1. $^1$H-NMR spectrum of 2,2'-bipyridine-4,4'-dicarboxylic acid (dcbpyH$_2$) in D$_2$O/NaOD.

Figure A2. $^1$H-NMR spectrum of 2,2'-bipyridine-4,4'-dicarboxylic acid diethyl ester (deeb) in CD$_3$Cl.
**Figure A3.** $^1$H-NMR spectrum of 1-$n$-propyl-3-methylimidazolium iodide (PMII) in CD$_3$Cl.
Figure A4. MALDI-TOF spectrum of [Os(bpy)$_2$Cl$_2$].

Figure A5. MALDI-TOF spectrum of [Os(bpy)$_2$(dcbpyH$_2$)](PF$_6$)$_2$ (AP25).
Figure A6. $^1$H-NMR spectrum of [Os(bpy)$_2$(dcbpyH$_2$)](PF$_6$)$_2$ (AP25) in D$_2$O/NaOD.
Figure A7. MALDI-TOF spectrum of [Os(tBu3tpy)(dcbpyH2)(NCS)](PF6) (TD-1).

Figure A8. $^1$H-NMR spectrum of [Os(tBu3tpy)(dcbpyH2)(NCS)](PF6) (TD-1) in CD$_3$OD.
Figure A9. $^1$H-NMR spectrum of [(C$_4$H$_9$)$_4$N][Os('Bu$_3$tpy)(dcbpyH$_2$)(NCS)](PF$_6$) (TD-2) in CD$_3$OD.

Figure A10. MALDI-TOF spectrum of [Os('Bu$_3$tpy)(dcbpyH$_2$)(Cl)](PF$_6$) (TD-3).
Figure A11. $^1$H-NMR spectrum of [Os($^t$Bu$_3$tpy)(dcbpyH$_2$)(Cl)](PF$_6$) (TD-3).
Figure A12. MALDI-TOF spectrum of [Os(tctpyH₃)(tBu₂bpy)Cl](PF₆) (TD-4).

Figure A13. $^1$H-NMR spectrum of [Os(tctpyH₃)(tBu₂bpy)Cl](PF₆) (TD-4) in CD₃OD.
Figure A14. $^1$H-NMR spectrum of $[(C_4H_9)_4N]_3[Os(tctpy)('Bu_2bpy)Cl](PF_6)$ (TD-5) in CD$_3$OD.
Figure A15. MALDI-TOF spectrum of \([(C_4H_9)_3N]_3[Os(tctpy)(tBu_2bpy)NCS](PF_6) \ (TD-6)\) in CD$_2$OD.

Figure A15. $^1$H-NMR spectrum of \([(C_4H_9)_3N]_3[Os(tctpy)(tBu_2bpy)NCS](PF_6) \ (TD-6)\) in CD$_2$OD.
Figure A16. Electrochemistry data of (a) AP25 and (b) TD-3 measured in acetonitrile solution at a scan rate of 100 mV/s with Ag/AgCl reference electrode, 0.1 M TBAPF$_6$ as a supporting electrolyte and ferrocenium/ferrocene (Fc$^+$/Fc) as an internal reference.
Figure A17. Electrochemistry data of TD-6 measured in acetonitrile solution at a scan rate of 100 mV/s with Ag/AgCl reference electrode, 0.1 M TBAPF₆ as a supporting electrolyte and ferrocenium/ferrocene (Fc⁺/Fc) as an internal reference.

Figure A18. SEM images of as-synthesized nanocrystalline TiO₂ (left) and TiO₂ nanoparticles after autoclaving, sintering and sensitization (right).
Appendix B. Preparation and Study of [(C₄H₉)₄N][Ru(EtCO₂tpy)(NCS)₃] sensitizer

The synthesis of this sensitizer starting with the synthesis of monocarboxylate terpyridine ligand is described below:

**Ethyl 2,2′:6′,2′′-terpyridine-4′-carboxylate (1).** The synthesis of 1 was carried out starting from citrazinic acid according to literature procedure¹ as follows:

2,6-dibromopyridine-4-carboxylic acid (2). Citrazinic acid (25 g, 0.16 mol) and POBR (75 g, 0.26 mol) were mixed and heated in an autoclave at 175 °C for 5 h. The reaction mixture was cooled down overnight. 500 ml of H₂O was cautiously added to the dark product and filtered. The aqueous filtrate was extracted with CH₂Cl₂ (5 x 40 ml). The dark precipitate was continuously extracted in a Soxhlet extractor with CH₂Cl₂ for 24 h and the brown extract was combined with the extract from the aqueous phase. The organic phase was dried over MgSO₄ and the solvent removed. The brown solid was recrystallized from boiling water to obtain an off-white solid; yield: 25 g (55%). MALDI-TOF MS: 280.27 (M). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.08 (s, 2 H).

Ethyl 2,6-dibromopyridine-4-carboxylate (3). A mixture of 4.0025 g of 2 and concentrated H₂SO₄ (1.0 mL) in ethanol (30 mL) was heated at 78 °C for 4 h. Ethanol was removed by rotary evaporation. 50 mL of H₂O was added to the off-white solid and extracted with CH₂Cl₂. The solvent was removed from the organic phase and the product was recrystallized from 5 ml of ethanol; yield 4.0022 g (91%). ¹H NMR (300 MHz, CDCl₃): δ ppm 8.08 (s, 2 H), 4.41 (q, 2H), 1.35 (t, 3H).
Ethyl 2,2′:6′,2″-terpyridine-4′-carboxylate (1). A mixture of 3 (2.0 g), tributyl(pyridine-2-yl) stannane (5.0 g) and tetrakis(triphenyl phosphine) palladium(0) (0.168 g) in 50 ml of toluene was degassed for 15 min and thereafter refluxed for 16 hr under argon atmosphere. Saturated NH$_4$Cl (aq.) (20 ml) was added to the cooled reaction mixture and stirred overnight. The mixture was filtered over celite on a glass frit. The celite was washed with CH$_2$Cl$_2$ (~ 150 ml). The filtrate (from celite filtration) was extracted (top layer) with toluene (4 x 30 ml). The organic phases (in toluene and CH$_2$Cl$_2$) were combined and dried over magnesium sulfate. The magnesium sulfate was filtered off and the solvents removed on a rotary evaporator. Concentrated HCl (40 ml) was added to the solid and shaken vigorously to dissolve. The stannate-byproducts were extracted with CH$_2$Cl$_2$ (4 x 30 ml) The aqueous phase was then neutralized with sodium carbonate (~ 25 g) to form a dirty white precipitate, which was extracted with CH$_2$Cl$_2$ (4 x 50 ml) from the purple aqueous phase. The brownish-yellow organic phase was dried over magnesium sulfate to give a yellow solution. The CH$_2$Cl$_2$ was removed on a rotary evaporator. Yield: 1.1719 g (60%). $^1$H NMR (300 MHz, CD$_3$OD): δ ppm 8.985 (s, 2 H), 8.754 (d, 2 H), 8.621 (d, 2 H), 7.895 (dt, 2 H), 7.387 (dd, 2 H), 4.485 (q, 2 H), 1.465 (t, 3 H).

$[(C_4H_9)_4N][Ru(EtCO_2tpy)(NCS)_3]$ (4). Complex 4 was synthesized according to modified published procedure for an analogous complex.$^2$ RuCl$_3$ (0.27 g) and ethanol (40 ml) were stirred under argon for about 5 min. A solution of 1 (0.38 g) in dichloromethane (40 ml) was then added and the mixture was refluxed for 2 hr under argon atmosphere. The cooled reaction mixture was concentrated to about 20 ml on a rotary evaporator and the precipitated intermediate complex was collected on a filter paper and washed thoroughly with ethanol to remove the unreacted RuCl$_3$, followed by drying in air. The intermediate complex was dissolved in DMF (40 ml) and tetrabutylammonium thiocyanate (10 g in 20 ml of water) was added to it. The mixture was
degassed for 15 min and the reaction was carried out at 130 °C for 4 hr under argon atmosphere. The dark blue reaction mixture was cooled and the solvent volume was reduced to about 10 ml, forming an oily mixture. The volume was further reduced and conc. HCl was added to the product and left in the refrigerator overnight. The product was further dissolved in acetone and precipitated by the addition of water. This step was repeated until all the DMF was removed and the product became solid. The product was added to a conc. NaOH (aq) solution and heated at 70 °C for 3 hrs. To the cooled reaction mixture was added drops of HPF₆ (aq) to precipitate the pure product which was filtered and dried in air. MALDI – TOF MS: m/z: 580.10 (M–TBA), ¹H-NMR: (300 MHz, CD₃CN): δ ppm: 8.857 (d, 2 H), 8.8645 (s, 2 H), 8.391 (d, 2 H), 7.944 (t, 2 H), 7.657 (t, 2 H), 4.412 (q, 2 H), 2.975 (m, 8 H), 1.495 (m, 8 H), 1.401 (t, 3 H), 1.237 (m, 8 H), 0.878 (t, 12 H). Anal. Calcd for RuC₃₇H₅₁N₇O₂S₃·3C₂H₅OH: C, 53.72; H, 7.23; N, 10.20%. Found: C, 53.62; H, 6.95; N, 10.19%.
Figure B1. $^1$H NMR spectrum of 2,6-dibromopyridine-4-carboxylic acid (2) in CD$_3$Cl.

Figure B2. $^1$H NMR spectrum of Ethyl 2,6-dibromopyridine-4-carboxylate (3) in CD$_3$Cl.
Figure B3. $^1$H NMR spectrum of Ethyl 2,2':6',2''-terpyridine-4'-carboxylate (1) in CD$_3$Cl.

Figure B4. MALDI-TOF spectrum of [(C$_4$H$_9$)$_4$N][Ru(EtCO$_2$tpy)(NCS)$_3$] (4). in CD$_3$CN.
Figure B5. $^1$H NMR spectrum of [(C$_4$H$_9$)$_4$N][Ru(EtCO$_2$tpy)(NCS)$_3$] (4). in CD$_3$CN.
Figure B6. Absorption and photoluminescence spectra of [(C₄H₉)₄N][Ru(EtCO₂tpy)(NCS)₃] (4) in CH₃CN. Excitation was afforded by using an isolated 514.5 nm line from an argon ion laser (Coherent Innova 300).

Figure B6. Electrochemistry data of [(C₄H₉)₄N][Ru(EtCO₂tpy)(NCS)₃] (4). measured in acetonitrile solution at a scan rate of 100 mV/s with Ag/AgCl reference electrode, 0.1 M TBAPF₆ as a supporting electrolyte and ferrocenium/ferrocene (Fc⁺/Fc) as an internal reference.
The photophysical and electrochemical properties of 4 are presented in Figures B5 and B6. Sensitizer 4 is the monocarboxylic acid analog of the black dye which has one of the highest reported power conversion efficiencies. As a result, the properties of 4 are expected to mirror that of the black dye. The sensitizer displays ¹MLCT absorption transitions in the visible and near infrared regions with a maximum centered at 560 nm (Figure B5) along with ligand-centered π-π* transitions in the ultraviolet region of the spectrum (not shown). The absorption spectrum extends up to 900 nm and covers the entire visible region with the photoluminescence maximum centered at 934 nm (Figure B5). Excitation into the ¹MLCT absorption manifold leads rapidly to photoluminescence from the ³MLCT excited states. The photophysical properties indicate that the sensitizer is well suited to application in DSSC as it can harvest solar photons over a broad range of the spectrum.

The sensitizer has a one electron reversible oxidation potential centered at +0.65 V vs Ag/AgCl with the Fc⁺/Fc⁰ wave centered at +0.46 V vs Ag/AgCl. The oxidation wave is assigned to the reversible oxidation of the ruthenium(II) metal center in the sensitizer. The sensitizer also has a reversible reduction wave centered at -1.26 V vs Ag/AgCl which is assigned to the reduction of the modified terpyridine ligand. The measured potentials were converted to E₁/₂ vs. NHE using E₁/₂(Fc⁺/Fc⁰) = +0.69 vs. NHE.³ Thus, the oxidation potential of the sensitizer is E_ox = 0.88 V vs NHE and the reduction potential is E_red = -1.03 V vs NHE. The minimum energy between the ground and excited states is estimated to be E₀₀ = 1.53 eV. The excited state oxidation potential is estimated to be E° r* = -0.65 V vs NHE. The electrochemical properties of 4 indicate that the sensitizer is well positioned to inject electrons in the conduction band of TiO₂ and to be regenerated by the I⁻/I₃⁻ redox mediator based on thermodynamic considerations.

Despite these potentials, the photovoltaic properties of sensitizer 4 could not be obtained as the sensitizer was found to exhibit poor binding properties on TiO₂ films during sensitization.
References

