Synthesis and characterization of a [Ru(bpy)2(NCS)2] derivative for use as a dye-sensitizer in nanocrystalline solar cells

Joel Thomas Kirner
University of Northern Iowa

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SYNTHESIS AND CHARACTERIZATION OF A [Ru(bpy)$_2$(NCS)$_2$]
DERIVATIVE FOR USE AS A DYE-SENSITIZER IN NANOCRYSTALLINE
SOLAR CELLS

A Thesis Submitted

in Partial Fulfillment

of the Requirements for the Designation

University Honors with Distinction

Joel Thomas Kirner

University of Northern Iowa

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This Study by: Joel Thomas Kirner

Entitled: SYNTHESIS AND CHARACTERIZATION OF A [Ru(bpy)$_2$(NCS)$_2$] DERIVATIVE FOR USE AS A DYE-SENSITIZER IN NANOCRYSTALLINE SOLAR CELLS

has been approved as meeting the thesis requirement for the Designation University Honors with Distinction.

Date

Dr. Jeffrey Elbert, Honors Thesis Advisor, Department of Chemistry and Biochemistry

Date

Jessica Moon, Director, University Honors Program
ABSTRACT

After extensive review of the field of dye-sensitized solar cells, the molecule [Ru(4,4’-dicarboxy-2,2’-bipyridine)(4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine)(NCS)₂] has been designed as an original contribution to the field. This dye sensitizer was chosen by derivatizing upon the structure of the standard sensitizer, cis-diisothiocyanato(4,4’-dicarboxylic acid-2,2’-bipyridine)ruthenium(II) (N3), by extending the conjugation of one bipyridine ligand. This structural derivatization should enhance light harvesting by red-shifting the dye’s absorbance and increasing the dye’s molar absorptivity, which should result in a dye-sensitized solar cell with higher efficiency. The Density Functional Theory (DFT) molecular orbital calculations of the new dye complex indicate that the HOMO is highly localized around the NCS ligands, while the LUMO is shifted toward the anchoring 4,4’-dicarboxylic acid-2,2’-bipyridine ligand. The final dye complex has not been completed, but the synthesis of the previously unpublished 4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine ligand is described. The product was characterized by ¹H-NMR and LC/MS.
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CHAPTER 1
INTRODUCTION

Overview

The rise in global energy consumption, combined with rising energy costs and the steady depletion of fossil fuels, have served as strong incentives for the research and development of new and improved forms of renewable energy. One such development in solar technology has been the invention of a new class of solar devices called dye-sensitized solar cells (DSCs). These cells have the potential for low production and materials costs, great flexibility, and aesthetically pleasing designs. One important factor in the development of DSCs is the engineering of new dye molecules in order to fine-tune their desirable properties. The goal of this thesis project has been to synthesize and characterize a new dye molecule with the formula: [Ru(4,4’-dicarboxy-2,2’-bipyridine)(4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine)(NCS)₂], from here on referred to as (K2). A structural representation is given in Figure 1. This structure was chosen because it is an original molecule that has not been previously studied, and it can be conveniently synthesized from commercial starting materials. It was designed with the intention of enhancing light absorbance when used in a DSC, increasing the potential for photon-to-electrical conversion efficiency.

Figure 1: Structural representation of [Ru(4,4’-dicarboxy-2,2’-bipyridine)(4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine)(NCS)₂].
Background

Global electrical energy consumption was 18.0 trillion kilowatt hours in 2006, and is predicted to rise by 77% by the year 2030.\textsuperscript{1a} Coal and natural gas are currently the top fuels used for electricity generation.\textsuperscript{1a} Rising concern about the environmental impacts of pollution and greenhouse gasses produced from the burning of these fossil fuels stirs motivation for the development of alternative energy methods. A recent conspectus\textsuperscript{2} warns that “the quality of human life to a large degree depends upon the availability of clean energy sources.” As energy consumption grows, the demand for electricity will further deplete the slowly vanishing fossil fuels, creating an energy deficit that will need to be filled by renewable resources.\textsuperscript{2}

Solar energy is one of the fastest growing sources of clean, renewable energy worldwide, and is sure to be a major contributor to total energy production in the future.\textsuperscript{1b,2} In fact, the solar energy that reaches earth’s surface is about 6,000 times greater than the current rate of global energy consumption.\textsuperscript{2} Devices that harvest this light energy to create electrical power are often called photovoltaic cells. However, the current cost for electricity from photovoltaics is not yet competitive with conventional methods of electricity generation.

Solar technologies have benefitted from much attention over the last two decades,\textsuperscript{1b} resulting in improved efficiencies and the development of new types of devices photovoltaics can be made from materials that are abundantly available and less expensive to manufacture.\textsuperscript{2} These gradual improvements constantly help to bridge the cost gap between photovoltaics and conventional power plants, making them very attractive for power generation in the near future.\textsuperscript{1b}
Dye Sensitized Solar Cells (DSCs)

Dye sensitized solar cells (DSCs) are a type of thin-film photovoltaic devices that have been receiving a great deal of attention from the scientific community. The DSC was discovered in 1985 by the Swiss scientist Michael Grätzel.\(^3\) A basic DSC consists of three major parts: a mesoscopic thin film of semiconducting metal oxide, a molecular dye sensitizer, and a regenerative electrolyte.\(^6\) A schematic representation of the operating principle of a DSC is provided in Figure 2.

The system is built around a mesoscopic semiconducting metal oxide film, traditionally anatase (TiO\(_2\)), due to its wide conduction band and cheap availability. The film is made by spreading a colloid of the nanocrystalline anatase particles into a thin layer on a piece of conductive glass. The glass is usually made conductive by pre-coating one side with a transparent layer of fluorine-doped tin dioxide (FTO). The film is then sintered at high temperature. Upon sintering, the nanocrystalline semiconductor particles are fused together to form a 3D porous structure similar to that of a sponge. Like a sponge, these porous films have a very large surface area.

This film is then soaked in a solution containing the molecular dye of choice. The dye spontaneously adsorbs to the surface of the film in a monolayer. When light hits the dye molecule, a photon of sufficient wavelength can be absorbed by donating its energy to an electron, promoting the electron from its ground state (low energy) to an excited state (higher energy). Since excited electron states are less stable, the process of light absorption is usually followed by a relaxation process. If the energy of the dye’s excited electron is well-matched with the energy of the conduction band in the semiconductor film, the electron can relax by intersystem crossing. Therefore, it is quickly injected into the semiconductor layer and can flow
Figure 2: Principle of operation of a dye-sensitized solar cell. Photoexcitation of the ground state sensitizer ($S^0$) to an excited electronic state ($S^*$) is followed by electron injection into the conduction band of the semiconducting metal oxide film. The oxidized dye molecule ($S^+$) is regenerated by the red/ox system, which itself is regenerated at the counter electrode by electrons passed through the load.²

Through to the anode (conducting glass) to enter a circuit.

By this process of electron injection, the dye is left oxidized. Oxidized dyes are often unstable and can lead to photodegradation, but the dye is quickly reduced by an electron donated from an electrolyte, commonly an organic solvent containing a reduction/oxidation system of iodide/triiodide. The electrolyte is subsequently regenerated at the cathode (a second piece of conducting glass) by electrons passing through the external load, thus completing the circuit. The net result is electric power without any permanent chemical transformation.⁶

The functioning principal behind these cells is different from conventional solid state cells in that the roles of light absorber (dye) and charge carrier (semiconductor) are separated. This opens up many new options for absorbing materials, because they do not also have to be conductive.² DSCs are also promising because they may be made from widely available materials such as TiO₂ of low to medium purity.⁵ As a result, the production costs and low
energy consumption of manufacturing the cells can be much lower than the silicon solar cells currently used. Small improvements in the light harvesting efficiency achieved by DSCs will bridge the efficiency gap between them and solid-state silicon cells, bringing them closer to being a cost-effective alternative. Therefore, significant amounts of research continues to be done in attempt to optimize the cell performance.

**DSC Performance Parameters**

There are many factors that determine the efficiency of a DSC. In order to gain an understanding for these factors, one can study the parameters that are used to measure and calculate the performance of state of the art DSCs. To start with the big picture, the overall conversion efficiency ($\eta_{global}$) of a cell depends on the short-circuit photocurrent density ($J_{sc}$), the open-circuit photovoltage ($V_{oc}$), the fill factor of the cell ($FF$), and the intensity of incident light ($I_s$), following the equation below.

$$\eta_{global} = \frac{J_{sc}V_{oc}FF}{I_s}$$

(1)

The fill factor is effectively a measure of the quality of the cell. It can assume values between 1 and 0 and is defined as the ratio of the maximum power ($P_{max}$) of the cell divided by the theoretical maximum power, which is the product of the short-circuit current ($I_{sc}$) and the open-circuit voltage ($V_{oc}$).

$$FF = \frac{P_{max}}{I_{sc}V_{oc}}$$

(2)

The maximum power $P_{max}$ is the product of the empirical photocurrent and photovoltage values where the cell power is maximal. These values are measured by illuminating cell and measuring the variability in current and voltage while increasing resistance. The fill factor gives an idea as
to the extent of electrical (Ohmic) and electrochemical (overvoltage) losses occurring during DSC operation. These issues are discussed below.

Significant overvoltage losses can occur from the regeneration of the oxidized dye if there is an energy mismatch between the electrolyte’s red/ox potential and that of the oxidized dye. Ohmic losses result from low shunt resistance or from high series resistance. Low shunt resistance can be caused by manufacturing defects such as cracks in the semiconductor film, which provides alternate paths for light-harvested current to travel, and thus creates a short-circuit and reduces the current that travels through the load to do work. Series resistance involves resistance to electron flow between different cell boundaries, and has the effect of lowering the voltage. One cause of series resistance in DSCs is the random path that an electron must take to migrate through the porous semiconductor film.

It is clear from Equation 2 that the efficiency of a DSC can be improved by increasing the photocurrent density ($J_{sc}$), the open-circuit voltage ($V_{oc}$), or the fill factor. Attempts in modern research to improve the fill factor will be discussed below. Open-circuit voltage is a measure of the amount of charge recombination that occurs within a cell. This can be improved by reducing film thickness or using more viscous electrolyte solutions. On the other hand, photocurrent density ($J_{sc}$) is directly related to the dye used. As shown in Equation 3, it is derived by integrating the wavelength-dependent incident photon to current conversion efficiency (IPCE) over the spectral distribution of Air Mass (AM) 1.5 solar photon flux:

$$J_{sc} = \int eI\text{PCE}(\lambda)I_s(\lambda)d\lambda$$

(3)

where $e$ is the elementary charge of an electron and $I_s$ is solar photon flux.

In order to understand how the dye affects the DSC’s efficiency, it is important to understand how the IPCE is calculated. First, it is dependent on the light harvesting efficiency
(LHE) of the dye adsorbed on the cell. Second, it depends on the quantum yield of electron injection from the excited sensitizer into the conduction band of the semiconductor film ($\phi_{inj}$). This depends on the quality of electronic coupling between the dye and semiconductor film. Lastly, the IPCE is dependent on the electron collection efficiency ($\eta_{coll}$) of the semiconductor film. The overall formula is given by Equation 4.²

$$IPCE(\lambda) = LHE(\lambda) \phi_{inj} \eta_{coll}$$  \hspace{1cm} (4)

Finally, Equation 5 shows that the light harvesting efficiency is directly dependent on the dye:

$$LHE(\lambda) = 1 - 10^{-ad} \hspace{0.5cm} (\alpha = 1000 \times \varepsilon c)$$  \hspace{1cm} (5)

where $d$ is the film thickness, $\alpha$ is the reciprocal absorption length, $\varepsilon$ is the molar absorptivity of the dye, and $c$ is the concentration of the dye in the film.

Molar absorptivity, $\varepsilon$, is a measure of how strongly a molecule absorbs light. Therefore, it is clear from Equation 5 that a dye with higher absorptivity will result in higher light harvesting efficiency. To summarize, if it were possible to increase the molar absorptivity of a dye while keeping all other factors constant, the dye would result in a greater current conversion efficiency, a greater photocurrent density, and finally a greater overall cell efficiency.

**Modern Research**

Much research has been done in the areas of the semiconductor thin film and the electrolyte, which can improve a cell’s fill factor. As described above, series resistance in the film is caused by the random path that an electron must take through the sponge-like semiconductor film to reach the anode. Several research teams have tried to reduce this effect by creating more ordered TiO$_2$ films consisting of nanotubes$^8$ or nanowires$^9$. These structures allow a more direct path for electron injection, and therefore decrease the resistance to electron flow.
Unfortunately, a problem arises when using nanotubes or nanowires: these structures have less surface area than a porous, sponge-like film. As a result, such structures cannot absorb as much dye, resulting in lower light absorbance.

Shunt resistance can be increased by improving manufacturing technique. Significant improvements in cell assembly and materials development have afforded cells that are more stable, reproducible, and have efficient charge collection properties ($\eta_{col}$). In fact, a description of manufacturing techniques has been published which can be used to create reproducible, high-quality DSCs with high fill factor values. Such techniques usually require a screen printer to deposit the TiO$_2$ film uniformly.

While the above developments have improved cell fill factors, it is still up to the dye molecule to efficiently collect light. First and foremost, the function of the dye is to collect the energy from incident photons to excite an electron and inject it into the semiconductor. The dye’s ability to do this effectively is highly dependent upon its structure. Changes in structure can change the dye’s electronic properties, its red/ox properties, and absorption properties (the range and quantity of light energy that it can absorb). Therefore, extensive research continues to focus on the molecular engineering of dye molecules in order to improve upon a number of desirable properties. A recent DSC review listed the properties that a perfect dye sensitizer should possess. These properties are listed below.

The ideal dye should absorb all light between 300 and 920 nm when adsorbed on the semiconducting film. Solar radiation that reaches the planet’s surface has low intensity outside this region due to absorbance from the atmosphere. The energy level of the excited state of the dye should be well-matched with the lower-region of the conduction band of the metal oxide film. This helps to minimize energy losses during electron transfer and reduces the likelihood of
electron recombination. The dye must possess functional groups to anchor the dye to the semiconductor surface. These groups ensure the spontaneous assembly of a dye monolayer on the film, and ensure the spatial overlap of electronic orbitals between the dye and semiconductor. This allows for rapid charge injection upon excitation. The perfect dye should have a high enough red/ox potential so that the electrolyte system can quickly reduce it from its oxidized state, preventing decomposition of the dye. Lastly, the dye should be stable enough to endure approximately 20 years of exposure to natural light without experiencing significant losses in performance.

While it is highly unlikely that any molecule could achieve all of the above characteristics, new dyes can certainly be engineered in order to make small improvements in at least a few of these areas. In fact, a large amount of research in DSCs is devoted to the synthesis of new dyes and the characterization of their properties. Dyes can have a wide variety of structures. Organometallic complexes based on a ruthenium metal center have become standard dyes for use in DSCs.\textsuperscript{11} These complexes are effective dyes because they absorb light in the visible region due to their metal-to-ligand charge transfer (MLCT) character, they show rapid charge injection into TiO\textsubscript{2} from the excited state, and they exhibit superior stability in the excited state.\textsuperscript{11}

Organic dyes without metals are also receiving significant attention because they have the prospect of being less expensive.\textsuperscript{2} While rare earth metals such as ruthenium can be expensive, organic materials are abundantly available, so the cost of organic dyes is mostly dependent on the number of synthesis steps. However, these dyes are generally less stable than the organometallic complexes, and have not yet reached comparable efficiencies.\textsuperscript{2} Although there is
room for improvement in the synthesis of purely organic dyes, organometallic dyes were chosen as the focus of this project because of their extensive background.

**Computational Studies**

When considering new structures for dye molecules, it is often desirable to be able to predict the molecule’s electronic characteristics. Molecules are held together by chemical bonds, which are actually attractive forces between nuclei and their electrons. These electrons are often described by orbitals. An orbital is a model that describes the probability of finding an electron in a certain location relative to the nuclei. Orbitals have different energies associated with them. Orbitals are well understood and predictable in atoms, but when the atoms are arranged into molecules, the electron orbital structures become very complicated. In order to model molecular orbitals, chemists must use computer programs that applying quantum mechanical models to calculate the shapes and energies of these orbitals. One of the most popular and versatile methods in computational chemistry is the use of the quantum mechanical density functional theory (DFT) to perform these calculations. Using such models, chemists can predict the effectiveness of prospective dyes or explain the observed properties for dyes already made.

**Dye Design Strategies**

A common strategy for creating new molecules is simply to use a parent structure with favorable properties, then derivatize upon it in an attempt to improve one or more of the desirable characteristics. This strategy has been used abundantly on polypyridyl ruthenium dyes. One of the earliest ruthenium dyes to be used in DSCs has become the golden standard to which many new dyes are compared. This dye, with the formula [Ru(4,4’-dicarboxy-2,2’-bipyridine)₂(NCS)₂], was discovered in 1993 and was named N3 after M. K. Nazeeruddin, a member of
Michael Grätzel’s research team. The use of N3 in a DSC with an iodide/triiodide electrolyte system reached conversion efficiencies of 10% under AM 1.5 simulated solar radiation. This was a promising result because a small amount of improvement in efficiency could make such DSCs cost effective competitors for traditional silicon-based solar cells. Therefore, many research teams have used N3 as a reference and derivatized its structure in order to tune its electronic and optical properties. The structure of N3 and its structural skeleton are shown in Figure 3.

![Figure 3](image)

**Figure 3**: N3 and its structural skeleton.

In organometallic chemistry, a ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. Ligands can have a huge variety of structures, so they become an easy focus for structural derivatization. Several strategies for ligand derivatization in RuII complexes are discussed below.

**Ligand Substitution**. There are several options to consider when derivatizing upon a dye structure. One approach is to systematically substitute the chromophore of the dye (positions $R_5$ and $R_6$ in Figure 3) with a different ligand and to test the change in performance. This is how the N3 dye was initially discovered: several ligands were tried, including thiocyanate, cyanide,
halogen anions, and water. Of these ligands, thiocyanate (NCS) was found to show the best performance. Further ligand substitutions have succeeded in broadening absorbance, but have resulted in cells with lower overall efficiencies.

Computational studies of the N3 dye using DFT have calculated the appearance of the molecule’s electronic orbitals in the ground and excited states. In the ground state, electrons in the dye’s highest occupied molecular orbital (HOMO) are highly localized around the NCS ligands. Once an electron is excited by solar radiation, it enters the lowest unoccupied molecular orbital (LUMO), which is localized on the anchor-containing ligand, where it can easily be injected into the semiconductor film. Therefore, it becomes apparent that the NCS ligands are highly responsible for the inversion of electron density upon excitation, which may be required for optimal charge injection.

Anchor Substitution. Another strategy is to change the position or functionality of the anchor groups (positions R1 and R2 in Figure 3) in attempt to improve either the adsorption stability or the electronic coupling between the dye and the semiconductor film surface. Studies have shown that bipyridine ligands substituted with anchor groups in the 4,4’ position show better results than the 5,5’ positions (See Figure 4). This may be due to superior electronic coupling between the dye and the semiconductor when anchor groups are in the 4,4’ positions, perhaps because the 4,4’ position of pyridine is more electron withdrawing, and helps direct the charge transfer through the anchor group and into the semiconductor.

Figure 4: Position assignments for substituted bipyridine.
A wide variety of anchor groups have been researched, resulting in a range of adsorption strengths and cell efficiencies. Typically the strongest anchor groups for binding to metal oxides (such as TiO$_2$) are as follows: phosphonic acids > carboxylic acids > esters > acid chlorides > carboxylic salts > amides.$^{17}$ While the stronger bonding of phosphonate groups improves the stability of the dye adsorbed on the film, it does not always correlate to better charge injection efficiency. For example, in the case of the N3 dye, substituting the carboxylate anchoring groups for phosphonic acid groups resulted in a blue shift in light absorbance and a subsequent 30% decrease in DSC efficiency.$^{18}$

This drop in efficiency is likely due to the lack of conjugation in the phosphonic acid group.$^{13}$ Conjugation is a property in organic compounds resulting from alternating multiple bonds. Electrons in conjugated systems are understood to move freely throughout the conjugated region because of resonance structures—a stabilizing effect. The more conjugation a molecule has, the lower the gap between molecular orbitals, thus increasing the wavelength of the lowest energy excitation. In short, extending conjugation red-shifts light absorbance, as shown in Figure 5. Because the phosphonate anchor group is sp$^3$ hybridized, instead of sp$^2$ hybridized like the carboxylate group, there is poor overlap between the conjugated $\pi$ system from the planar pyridine group and the anchor.$^{13}$ This accounts for the blue shift in light absorbance. Also, because the conjugation in the pyridine does not extend into the phosphonate ligand electrons would not be delocalized into the anchor, so they would not migrate as freely into the semiconductor film.$^{18}$

When carboxylate groups are used as the anchor, conjugation is extended from the pyridine into the anchor group, resulting in a stronger molecular overlap of the electron orbitals from the dye and the TiO$_2$. This accounts for the ultrafast (<25 fs) charge injection rates that
have been measured for N3. Such a fast injection rate improves the cell efficiency by essentially making impossible the slower, unproductive process of electron recombination.

![Diagram](image)

**Figure 5**: Red shift of light absorbance as a result of extending conjugation.

**Anchor Protonation.** An additional aspect of research has been the protonation level of the dye’s anchor groups. It was found that removing such protons before adsorption onto the TiO$_2$ surface could significantly affect the cell efficiency. In the N3 dye, there are four anchor groups, meaning four anchor protons. By sequentially removing the protons with a base, a maximum cell performance was found for the monoprotonated form of N3, resulting in a DSC efficiency of 11.18\%. One possible explanation is that the remaining protons on the dye are transferred to the TiO$_2$ surface, where they effect the electronic coupling between the dye and the film. It is likely that each new dye structure will have a different optimum protonation level, which would need to be empirically determined after the dye has been synthesized.

**Ligand Modification.** The anchor linkage of the dye to TiO$_2$ is susceptible to breakage if water molecules leak into the cell and absorb on the surface. This is a large barrier to be crossed if DSCs are to be scaled up for mass production, as water vapor from the air is likely to seep into the cells. One strategy taken to increase dye stability is to modify one of the bipyridine...
ligands by replacing the anchor ligands with alkyl chains\textsuperscript{20} or with extended conjugated systems.\textsuperscript{21,22} Both of these groups are hydrophobic groups that would repel water, protecting the bond at the film surface. Using conjugated systems instead of alkyl chains also has the desirable effect of shifting light absorbance to longer wavelengths and increasing the area of the chromophore.\textsuperscript{13} This, in turn, raises the molar absorptivity of the dye because a greater area of the dye can collect photons. As a result, less dye is needed to collect the same number of photons, so the semiconductor film thickness can be reduced. Thinner films mean a higher $V_{oc}$ and higher fill factors due to decreased interaction between the film and the electrolyte.\textsuperscript{2} It is important to note that if conjugation is greatly extended, dye molecules become bulky, and fewer molecules can absorb on the film, meaning less light can be absorbed.

There has been one reported Ru\textsuperscript{II} complex with a structure that deviates from basic parent structure of the N3 dye. This dye is known simply as “black dye” or N749, and recently achieved a certified efficiency of 11.1\%.\textsuperscript{23} Structures of both N3 and N749 are shown in Figure 6, along with their corresponding IPCE spectra. The N749 dye has a lower molar absorptivity than N3, and when it adsorbs on a film surface, it is 30\% less concentrated.\textsuperscript{24} Despite this, the N749 dye can achieve superior performance in a DSC because of its superior absorption properties. As mentioned above, a perfect dye would absorb all light within the wavelength range of 300 to 920 nm; this would allow it to harvest all of the available light at the earth’s surface to potentially to convert it into electrical current. Looking at Figure 6, it is clear that the spectral response of N749 extends farther into the near IR range than N3. This response is enough to overcome worse molar absorptivity and film adsorptivity to result in cells with higher efficiencies.
It is also important to notice that the IPCE curves for both dyes only rise gradually from their absorption onset in the longer wavelengths. As a result, much of the power from the sun within the near IR region is not collected by these dyes, and according to Michael Grätzel, “improving the light harvesting in the 650-900 nm domain is therefore one of the greatest challenges faced by present day research in the DSC field.”

Figure 6: Incident photon to current conversion efficiency as a function of the wavelength for the standard ruthenium sensitizers N3 (red curve), the black dye N749 (black curve), and the blank nanocrystalline TiO$_2$ film (blue curve). The chemical structure of the sensitizers are shown as insets.®
Objective

The goal of this project was to synthesize a new dye molecule that would be an original contribution to the field of dye-sensitized solar cells. Such a molecule should be designed in an attempt to improve the light harvesting efficiency by shifting absorbance further into the near-IR region. After collecting the above information, it was determined that the most promising approach to creating a new dye molecule was to use Michael Grätzel’s N3 dye as a starting point and to create a derivative by using the strategy of ligand modification, as other strategies have experienced limited success. The dye designed has the formula: [Ru(4,4’-dicarboxy-2,2’-bipyridine)(4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine)(NCS)₂], referred to as (K2). This dye has extended conjugation of one bipyridine ligand, which should have the effect of red-shifting the dye’s absorbance, and increasing the dye’s molar absorptivity.
CHAPTER 2
MATERIALS AND METHODS

Materials

All chemical reagents used in the synthesis of K2 were purchased commercially from Sigma-Aldrich, Fisher Scientific, or Acros Organics and used without further purification. Solvents were Certified ACS grade (Fisher Scientific) and were used without further purification. Deuterated chloroform was purchased from Cambridge Isotope Laboratories, Inc. and sealed with Parafilm when not in use. When dry solvents or chemicals were required, they were stored under nitrogen atmosphere in a glove box (THF, LDA) or dried statically over 4 Å molecular sieves (CH₂Cl₂).

Methods

Computational Study

In order to gain insight into the structure of the electronic orbitals in K2, the molecule was modeled using the GaussView 4.1 computer program, following commonly used parameters. An initial geometry optimization calculation was run using the Hartree-Fock method with a 3-21G basis set. The output was re-submitted for a density functional theory (DFT) geometry optimization calculation using the B3LYP/3-21G basis set. The results were used to model the HOMO and LUMO of the dye in order to estimate if the desired charge transfer would occur upon excitation. Calculations were repeated for a previously synthesized dye (N945) which has been successfully used in a DSC to reach efficiencies of 10.82 % under AM 1.5 sunlight. The N945 dye has a very similar structure to K2, so it is interesting to discover if K2 would show such a favorable performance.
Instruments

$^{1}$H-NMR spectroscopy. Nuclear magnetic resonance spectroscopy is a useful tool in product characterization. It uses the unique magnetic properties of different nuclei in order to determine the structure of a molecule. The most common technique uses $^{1}$H nuclei, which are found in practically all organic compounds. Each proton within a molecule will have a unique oscillation frequency within an external magnetic field, as a result of its unique chemical environment. This information can be used to determine the structure of the molecule. $^{1}$H-NMR spectra were recorded on an OXFORD 400 MHz NMR equipped with V-NMR software package. Samples were dissolved in CDCl$_3$.

Liquid chromatography/mass spectrometry (LC/MS). Chromatography is an analytical technique used to separate a mixture of chemicals into its individual components. Liquid chromatography works by dissolving a mixture of chemicals in liquid solvents (the mobile phase), and pumping the solution through a column packed with a solid material (the stationary phase). Each molecule within the mixture will have a different affinity for both the mobile phase and the stationary phase. As a result, different molecules will spend different amounts of time in the column as the solvent is pumped through. The time it takes for a specific chemical to come through the column is called the retention time, and will be uniquely characteristic of each molecule.

Mass spectroscopy is coupled with liquid chromatography in order to determine the molecular weight of each chemical band as it comes through the column. This helps to determine the identity of each band. Mass spectra were acquired on an Agilent 1100 HPLC/ESI TOF MS. The LC column used was a 4.6 x 150 mm ZORBAX Eclipse XDB-C8 reverse phase column made by Agilent Technologies. The packing material had a 5 μm particle size. Samples
dissolved in CDCl$_3$ for NMR testing were added to Snap-Its™ 1.5 mL microsampling vials purchased from National Scientific, and used to acquire mass spectra. Mixtures of HPLC-grade water/acetonitrile in varying ratios were used as the LC eluent.

**Synthesis**

Synthesis methods for K2 were modified from a published reaction scheme for a similar dye.$^{22}$ The first two steps involve the synthesis of the new ligand, 4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine.

4,4’-di-(2-hydroxy-2-(2-pyridyl)ethyl)-2,2’-bipyridine (1). In a glove box under nitrogen atmosphere, 4,4’-dimethyl-2,2’-bipyridine (184.4 mg, 1.000 mmol) was added to a two-neck round bottom flask and dissolved in 10 mL of dry THF while stirring. Lithium diisopropylamine (LDA, 1.1 mL of 2 M solution in THF) was added to an addition funnel and assembled with the above flask. The vessels were sealed with rubber septa, removed from the glove box, and set up under nitrogen flow in a fume hood. While stirring, the flask was cooled to -40 °C on a bath of acetone and dry ice, and the LDA was added slowly, instantly turning the solution black. The solution was warmed to room temperature and stirred for one hour, after which 2-pyridine carboxaldehyde (230 μL, 2.41 mmol) was added dropwise by glass syringe. Stirring was continued for one hour, during which time the solution changed from black to orange to blood red. The reaction was quenched with 2 mL of water and extracted with 40 mL of CH$_2$Cl$_2$. The organic layer was washed with 40 mL of brine solution, dried over MgSO$_4$, vacuum filtered, and evaporated to dryness, yielding a bright yellow powder. The product was characterized by $^1$H-NMR and LC/MS and used in the next step without purification.
4,4'-di-(2-(2-pyridyl)ethenyl)-2,2'-bipyridine (2). The above product was dissolved in 10 mL of concentrated acetic acid (excess). The flask was fitted with a condenser and drying column and heated to reflux for 18 hours. After cooling to room temperature, the black solution was poured into 100 mL of saturated NaHCO₃ solution to neutralize the acid. The product was extracted with 250 mL of CH₂Cl₂, dried over MgSO₄, vacuum filtered, and evaporated to dryness, yielding 356 mg of a black residue. Testing by LC/MS indicated a mixture of byproducts.
CHAPTER 3
RESULTS AND DISCUSSION

Computational Study Results

Calculated molecular orbitals for K2 and a previously studied dye, N945, are shown in Figure 7. The appearance of the orbitals calculated for N945 in this study are very similar to those previously published, indicating that calculations were consistent. It was discussed above that past studies indicate that the NCS ligands are responsible for the shift in charge localization following excitation. The results in Figure 7 show this to be true for both K2 and N945. The HOMOs of both dyes show ruthenium t2g character with a dominating contribution from the NCS ligands, along with minor contributions from the bipyridine ligands.

If a photon were to excite an electron from the HOMO to the LUMO, Figure 7 indicates that the charge would shift from the NCS ligands towards the anchor ligand, as is theoretically desired. While the HOMOs for both dyes are quite similar, the LUMOs appearances slightly different. In N945, the LUMO is a π* orbital strongly localized on the 4,4’-dicarboxy-2,2’-bipyridine ligand, which would allow for rapid charge injection due to strong overlap with the semiconductor. This effect is also present in K2, although its LUMO orbital shows significant contribution from the 4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine ligand as well.

This has a possible implication that the K2 dye will have slightly less efficient charge injection from the excited state into the semiconductor film than N945, or that charge recombination could be slightly more likely. These could negatively affect the efficiency of a DSC employing K2, but other factors would have to come into play as well, such as the rate of regeneration from the electrolyte, or the protonation level of the dye. Furthermore, these
calculations are merely approximations, so no definitive conclusions can be drawn. It is encouraging, however, to see approximately the same behavior in both dyes.

Figure 7: Calculated molecular orbitals of K2 and N945.
Synthesis Results

Proton NMR and LC/MS experiments provide the evidence that 4,4'-di-(2-hydroxy-2-(2-pyridyl)ethyl)-2,2'-bipyridine and 4,4'-di-(2-hydroxy-2-(2-pyridyl)ethyl)-2,2'-bipyridine were successfully synthesized.

Characterization of 4,4'-di-(2-hydroxy-2-(2-pyridyl)ethyl)-2,2'-bipyridine (1). Scheme 1 represents the synthesis of (1).

Scheme 1: Synthesis of 4,4'-di-(2-hydroxy-2-(2-pyridyl)ethyl)-2,2'-bipyridine.

The $^1$H-NMR spectrum of the above reaction product dissolved in CDCl$_3$ is provided in Figure 8. Proton signals have been assigned to the structure by letters A through G. The most important proton signals to indicate a successful reaction have been labeled signals E and F. Signal E is a doublet of doublets at a shift of 5.08 ppm, indicative of the benzylic CH(OH) proton. Signal F is a doublet of quartets at a shift of 3.13 ppm, indicative of the benzylic CH$_2$ protons. Signals A, B, C, and D are all indicative of aromatic protons. Signal D is actually many overlapping proton signals with similar shift values. The signal labeled G with a shift of 2.44 ppm is characteristic of the benzylic CH$_3$ group in the starting material, 4,4’-dimethyl-2,2’-
bipyridine. This peak indicates that the reaction was incomplete; the product mixture contains either starting material or the mono-substituted byproduct 4-(2-hydroxy-2-(2-pyridyl)ethyl)-4’-methyl-2,2’-bipyridine. All remaining unlabeled peaks are of unknown origin, but would be removed in subsequent reactions and purification steps.

Figure 8: $^1$H-NMR spectrum of Scheme 1 reaction products.
Further analysis of the reaction product was done by LC/MS using a mixture of water/acetonitrile (60%/40%) as the eluent. The resulting spectra are shown above in Figure 9. The poor resolution in the LC spectrum is likely a result of a racemic mixture of product enantiomers, due to the possible stereochemistry of the hydroxyl group. Each enantiomer would have a slightly different retention time on the column, resulting in broader peaks for each byproduct and extensive peak overlap. The mass spectrum for each major LC peak is included in Figure 9. It is clear that each LC peak contains many compounds, as a result of the poor resolution. An analysis of major mass peaks has been included below in Table 1.
Table 1: Mass analysis of Scheme 1 reaction products.

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</table>

The peak at 399 m/z proves that the intended product (1) was successfully synthesized. The presence of mono- and tri-substituted byproducts are indicated by MS peaks at 292 (mono-) and 506 (tri-) m/z. It is likely that the tri-substituted product would still yield the desired final product in the next reaction step. The presence of unreacted starting material is indicated by peaks at 185 and 108 m/z. Despite this evidence of being an incomplete reaction, the desired product was clearly present, so the product mixture was used in the next step without further purification, assuming that impurities and byproducts could be removed in later steps.
Characterization of 4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine (2). Scheme 2 represents the synthesis of (2).

Scheme 2: Synthesis of 4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine.

Analysis of the black product dissolved in CH$_2$Cl$_2$ was done by LC/MS using a mixture of water/acetonitrile (75%/20%) as the eluent. The resulting spectra are shown in Figure 10. Note that the LC spectrum shows three clearly resolved bands. This can be explained by the absence of product enantiomers. After the reaction, any stereochemistry was eliminated with the removal of the hydroxyl groups, leaving behind alkenes in the trans configuration (the cis configuration would be far too sterically hindered to occur). Included in Figure 10 are the mass spectra for each of the three LC bands, and the mass analysis is provided in Table 2. It appears each band is highly pure, indicating that the extraction step was adequate purification. The mass peak of 108 m/z indicates 2-pyridine carboxaldehyde starting material, but is present as a background signal throughout the whole spectrum. The mass peak at 185 m/z indicated the presence of 4,4’-dimethyl-2,2’-bipyridine starting material. Still, the data indicates that the acid-
Figure 10: LC/MS spectrum of Scheme 2 reaction products.

Table 2: Mass analysis of Scheme 2 reaction products.

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catalyzed dehydration reaction was successful. The peaks at 363 ([M+H]+) and 182 ([M+2H]++) m/z indicate the desired di-substituted product. The peaks at 274 ([M+H]+) and 137 ([M+2H]++) m/z indicate a mono-substituted byproduct.
CHAPTER 4.

CONCLUSION AND FUTURE WORK

Computational Study

The calculated molecular orbital densities indicate that K2 exhibits directionality toward the anchoring bipyridine ligand in the excited state, which has been linked with efficient dye sensitizers in past studies. This characteristic is likely to enable rapid charge injection into the TiO$_2$ conduction band, which is an encouraging result.

Synthesis

Product analysis by $^1$H-NMR and LC/MS indicate that the product 4,4’-di-(2-hydroxy-2-(2-pyridyl)ethyl)-2,2’-bipyridine was successfully synthesized by the reaction of dimethyl-2,2’-bipyridine with LDA and the subsequent addition of 2-pyridine carboxaldehyde, though the reaction was incomplete and undesired mono- and tri-substituted byproducts were also formed. Attempts to alter reaction conditions to eliminate these byproducts were unsuccessful.

LC/MS analysis indicates that the original molecule, 4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine, was successfully synthesized by the acid-catalyzed hydrolysis of the above unpurified products. The neutralization and extraction steps significantly purified the final product, though starting material and a mono-substituted byproduct were present. Though the ligand was successfully synthesized, time limitations did not allow for the isolation of the product, not the completion of the final K2 dye complex.

Future Work

The synthesized ligand 4,4’-di-(2-(2-pyridyl)ethenyl)-2,2’-bipyridine must be isolated and purified. This would be done by testing the product mixture by thin-layer chromatography (TLC) to determine an appropriate solvent to give good product separation. Once a good solvent
is found, the ligand can be purified by column chromatography. The pure product should be characterized by \(^{1}\text{H}\)- and \(^{13}\text{C}\)-NMR, UV-Vis spectroscopy, and IR spectroscopy.

Once the ligand product has been purified and characterized, it can be used in the synthesis of the final K2 dye, shown in Scheme 3. The use of the dichloro(p-cymene) ruthenium(II) dimer (shown on the left in Scheme 3) as a starting material has been shown to improve yields and reduce reaction time.\(^{26}\) This compound is dissolved in dimethylformamide (DMF), and each ligand is added separately and allowed to mix at high temperatures to allow the complex to form. The product will need to be isolated, purified, and characterized.

![Scheme 3: Synthesis of K2.](image)

Similar dye complexes are often precipitated by adjusting solvent polarity or pH. Subsequent purification can be attempted by washing, recrystallization, or column chromatography. The purified product should be characterized by \(^{1}\text{H}\)- and \(^{13}\text{C}\)-NMR and UV-Vis spectroscopy. Further testing of the dye should be done after it is adsorbed to a TiO\(_2\) thin film. This should alter its absorption spectrum, so another UV-Vis absorption experiment should be conducted. These tests should confirm that the K2 dye absorbs farther into the IR region than the N3 dye, which could likely improve the efficiency of a DSC.
Finally, the K2-dyed film should be assembled into a functioning DSC in order to test its photovoltaic properties. It is common to take measurements of the photocurrent at short-circuit ($I_{sc}$), the voltage at open circuit ($V_{oc}$), and the maximum power. It is also common to plot these photocurrent-voltage characteristics at varying light intensities. Finally, it would be necessary to measure the wavelength-dependent IPCE over the range of visible light. These parameters could then be used to calculate the cell’s overall efficiency ($\eta_{global}$), as discussed above. The results should be compared to similar dyes, such as N3 and N945, in order to determine if the structural differences found in K2 were ultimately beneficial or detrimental to DSC efficiency.
LITERATURE CITED


