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Synthesis and Characterization of a Ruthenium(II) Complex for Photovoltaic Cells

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We have designed and synthesized a new ruthenium complex, [(5-amino-1,10-phenanthroline)bis(4,4′-dicarboxylic acid-2,2′-bipyridine)] ruthenium(II) by introducing two types of ligands, 5-amino-1,10-phenanthroline and 4,4′-dicarboxylic acid-2,2′-bipyridine. We investigated the electronic, spectroscopic, electrochemical, and photovoltaic properties of the Ru(II) complex. The short-circuit current density and overall solar-to-electric energy conversion efficiency of photovoltaic cells made with this Ru(II) complex were found to be 8.9 mA/cm^2 and 2.1%, respectively. A series of analogous Ru(II) complexes have also been synthesized and investigated to compare the effects of functional groups on various ligands. HOMO-LUMO energies and molecular orbital surfaces have been investigated using semiempirical quantum chemical methods.

Keywords: ruthenium complex; TiO$_2$; solar cells; photoluminescence

1 Introduction

Dye sensitized solar cells based on ruthenium complexes have been extensively investigated due to their high potential for the fabrication of light weight, flexible, and low cost photovoltaic (PV) devices (1–3). Grätzel and his coworkers triggered the development of these types of solar cells. Ruthenium complexes such as [cis-di(cyanato)-N,N-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium(II)dehydrate] (N3) and [tri(cya-nato)-2,2′,2″-terpyridyl-4,4′,4″-tricarboxylate)ruthenium(II)] (Black Dye) were used for the photoinduced sensitization of nanocrystalline TiO$_2$. The solar cells fabricated using these dyes have been reported to have 7∼12% solar-to-electric energy conversion efficiency (4, 5). Based on these original ruthenium complexes, similar ruthenium complexes have since been investigated in order to enhance solar-to-electric energy conversion efficiency and to understand the photophysical processes (6–8).

The general photophysical processes of photoinduced regenerative electro-chemical cells are as follows: 1) Absorption of photons and oxidation of sensitizer, 2) Fast charge transfer (sub-pico second) from sensitizer to the conduction band of the nanocrystalline semiconductor, 3) Charge transfer to the redox electrolyte from the counter electrode, and 4) Reduction of sensitizer due to supply of charge from the electrolyte. The requirements for being an efficient sensitizer in nanocrystalline TiO$_2$ PV cells include absorption of incident light over a broad spectral range (9), efficient and fast conversion of the light energy into photoinduced electrons (oxidation) (10), and well matched electronic energy levels for transport of charge (11). One approach towards improving conversion efficiency has been to use different ligands for enhancing the absorption of incident light (12) and the photoinduced charge transfer between dye and TiO$_2$ (13). These modifications are also designed to improve the dye adsorption onto the surface of the TiO$_2$ (14). It has been reported that one of the representative ligands, 2,2′-bipydine 4,4′-dicarboxylic acid, can be anchored on the surface of TiO$_2$ through the formation of covalent Ti-O-C linkages (15, 16). The formations of covalent Ti-O-C linkages between the ligand and nanocrystalline TiO$_2$ may

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Dedicated to Professor Sukant K. Tripathy (deceased).

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contribute to efficient and fast photo induced charge transfer (17). Other classes of ligands such as carboxylated terpyridine and phenanthroline showed enhanced UV-vis absorption over a broad range due to their large conjugated backbone structure. These ligands can be utilized as efficient light harvesting sensitizers as well (18).

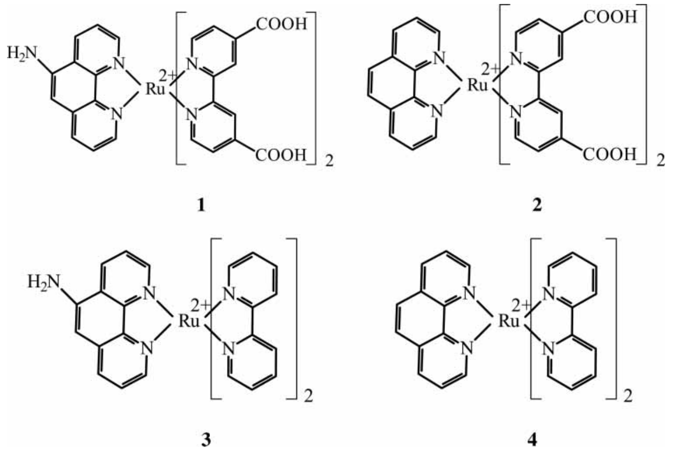
Precise matching of electronic energy levels among the components in the PV cells is a critical factor towards the resulting PV performances of the cells. Däubler and his coworkers extensively investigated the relationship of electronic energy levels among the components such as N3 and conjugated polymers that are sensitizer and hole transporting materials, respectively (19).

In this paper, the design and synthesis of new Ru(II) complexes introducing two types of ligands, 5-amino-1,10-phenanthroline(ap) and 4,4′-dicarboxylic acid-2,2′-bipyridine(dcbpy) (Scheme 1, complex **1**) are discussed. This Ru(II) complex has the functionality to graft onto nanocrystalline TiO_2 as well as to be incorporated into a conjugated polymer. The advantage of designing a Ru(II) dye-polymer complex is to facilitate photo-induced electron transfer for the fabrication of solid state PV cells. A series of analogous ruthenium complexes (Scheme 1, complex **2**–**4**) have also been synthesized and investigated to compare the effects of functional groups on various ligands by measuring UV-vis absorption spectra and photovoltaic properties. Theoretical calculations provide some explanation for the electronic properties of these ruthenium complexes.

2 Experimental

2.1 *Materials*

All reactions were performed under argon and in a low light environment using Al foil. Ruthenium chloride hydrate (Fluka), 4,4′-dicarboxylic acid-2,2′-bipyridine (Alfa Aesar), cis-bis-(2,2′-bipyridine) dichloro ruthenium(II) (Alfa Aesar), and 5-amino-1,10 phenanthroline (Polyscience) were used without any further purification.



Sch. 1. Structures of ruthenium complexes considered in the study.

2.1.1 *Synthesis of (4,4′-dicarboxylic acid-2,2′-bipyridine)ruthenium(II)*

This complex was synthesized and purified as described earlier (4). Anal. Calcd. for $C_{24}H_{16}N_4O_8RuCl_2 \cdot 2H_2O$: C, 41.38; H, 2.87; N, 8.05. Found: C, 40.89; H, 3.28; N, 8.27.

2.1.2 *Synthesis of [(5-amino-1,10-phenanthroline)bis (4,4′-dicarboxylic acid-2,2′-bipyridine)]ruthenium(II) (complex **1**)*

149 mg of the (4,4′-dicarboxylic acid-2,2′-bipyridine) ruthenium(II) and 42 mg of 5-amino-1,10-phenanthroline(Polyscience) were dissolved in 15 ml of DMF and refluxed for 6 hrs. After cooling, a dark red powder was filtered off and then dried under vacuum at room temperature for 3 days to obtain complex **1** in 43% yield. Anal. Calcd for $C_{36}H_{25}N_7O_8Ru \cdot 2Cl$: C, 52.68; H, 3.54; N, 11.95. Found: C, 53.10; H, 3.29; N, 11.87.

2.1.3 *Synthesis of [bis(4,4′-dicarboxylic acid-2,2′-bipyridine)(2,2′-bipyridine)] ruthenium (II) (complex **2**) (20)*

149 mg of (4,4′-dicarboxylic acid-2,2′-bipyridine) ruthenium(II) and 39 mg of 1,10-phenanthroline were dissolved in 15 ml of DMF and refluxed for 12 h. After cooling, a dark red powder was filtered off and dried under vacuum at room temperature for 3 days to obtain complex 2 in 49% yield. Anal. Calcd for $C_{36}H_{24}N_6O_8Ru \cdot 2Cl$: C, 53.66; H, 3.48; N, 10.43. Found: C, 52.15; H, 3.22; N, 10.19.

2.1.4 *Synthesis of [(5-amino-1,10-phenanthroline)bis(2,2′-bipyridine)]ruthenium(II) (complex **3**)*

This complex was synthesized and purified as described earlier (21). Anal. Calcd. for $C_{32}H_{26}N_7Ru \cdot 2PF_6$: C, 42.76; H, 2.78; N, 10.91. Found: C, 41.96; H, 2.86; N, 10.52.

2.1.5 *Synthesis of [(1,10-phenanthroline)bis(2,2′-bipyridine)]ruthenium(II) (complex **4**)*

This complex was synthesized and purified as described earlier (22). Anal. Calcd. for $C_{32}H_{24}N_6Ru \cdot 2PF_6$: C, 43.49; H, 2.72; N, 9.51. Found: C, 43.55; H, 2.72; N, 9.55.

2.2 *Measurements*

UV-vis spectra were recorded using a GBC UV-vis 916 spectrometer. Emission and excitation characteristics of the samples were measured with a SLM-Aminco Model 8100 spectrofluorometer. Electrochemical measurements were performed using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat. A platinum button working electrode, platinum wire auxiliary electrode, and an Ag reference electrode were used in a single-compartment cell configuration. Complexes **1** and **2** had been measured on Pt disk and complexes **3** and **4** in solution due to the difference of solubility. In both cases, 0.1 M of supporting electrolyte, $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) was used in dried acetonitrile at the scan rates of 100 mV/sec.

2.3 Fabrication of Photovoltaic Cells and Measurements

All PV cells were fabricated on fluorine doped tin oxide (SnO_2: F) covered glass substrates with an active area of 0.25 cm^2. Films of nanocrystalline TiO_2 (P25, Degussa) on SnO_2: F coated glass substrates (TEC 15, sheet resistance of 15 Ω/sq) were prepared by spin coating a TiO_2 paste which was made according to a reference (4). Sintering was carried out at 450°C for 30 min., followed by cooling to 120°C and then dipping into the dye solution (10^{-3} M) for 1 day. The dye solution was prepared using ethanol for the complexes **1** and **2** and acetone for complexes **3** and **4**. Dye coated TiO_2 films were rinsed in ethanol and then dried under argon flow. Platinum coated (thickness of 50 nm) TEC 15 glass substrates were used as the counter electrode. Iodine (0.05 M) and lithium iodide (0.5 M) in acetonitrile were used as electrolytes.

The current-voltage $(I - V)$ characteristics were measured with a Keithley SMU 2400 source measurement unit under AM 1.5 illumination (100 mW/cm^2) using a 1000 SW Xe arc lamp (Oriel instruments, Model 68921) and a set of air mass filters. The incident monochromatic photon-to-current conversion efficiency (IPCE) was obtained with a Keithley 169 multimeter unit coupled with a monochromator (Digicrom 240, CVI Co.) under illumination from a 150 W Xe arc lamp (LPS 220B, Photon Tech. International).

2.4 Theoretical Methodology

Semi-empirical quantum chemical calculations were performed on various ruthenium complexes using a computational program (Cerius^2 version 4.6 from Accelrys Inc.). The information of geometrically optimized structures and HOMO (The Highest Occupied Molecular Orbitals) − LUMO (The Lowest Unoccupied Molecular Orbitals) energies were obtained by using DMol 3 and ZINDO 1.0, respectively.

3 Results and Discussion

3.1 Spectroscopic Study

Figure 1 shows the UV-vis absorption spectra of a series of the Ru(II) complexes. The low-energy metal-to-ligand charge transfer (MLCT) absorption band of complex **1** is 467 nm, which is red shifted by 11 nm compared to the band of complex **3** (456 nm) due to the presence of carboxylic groups. A similar red shift (12 nm) was also observed in the low-energy MLCT bands of complexes **2** and **4** (MLCT bands at 462 nm and 459 nm, respectively). The carboxylic acids in the Ru(II) complexes contributed to the shift to lower energy in the UV-vis absorption. The low-energy MLCT band absorptions of complexes that contain amine groups (complexes **1** and **3**) shift to longer wavelength (~6 nm) compared to the complexes without an amine group (complexes **2** and **4**). From these results, it is concluded that amine and carboxylic groups in the bipyridyl ligand are playing a role in shifting the absorption wavelengths towards the red region. Consequently, the complexes that possess amine and carboxylic groups are more efficient broad band absorbers for producing photoinduced charge transfer even at lower photon energy. Table 1 summarizes the absorption properties of the Ru (II) complexes.

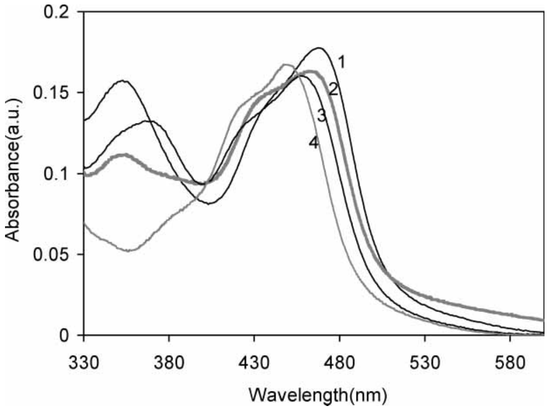


Fig. 1. UV-vis absorption spectra of complexes **1–4**; Solvents: 0.1 N NaOH solution for complexes **1** and **2**, acetone for complexes 3 and 4; Concentration: 10^{-5} mol/L.

The fluorescence peaks of the ruthenium complexes that contain carboxylic groups (complexes **1** and **2**) showed a red shift (~23 nm) compared to the complexes that don't contain the carboxylic groups (complexes **3** and **4**). This is similar to that seen in the UV-vis absorption spectra. Interestingly, as shown in Figure 2, the emission spectrum of complex 2 shows strong fluorescence compared to those of the other complexes (**1**, **3**, and **4**). The fluorescence results of the Ru(II) complexes are summarized in Table 1.

3.2 Photovoltaic Performances

The overall solar-to-electric energy conversion efficiencies and the short circuit currents of PV cells made with complexes **1**, **2**, **3**, and **4** were found to be 2.1%, 2.6%, 0.9% and 0.3% and of 8.9, 10.4, 4.3, and 1.5 mA/cm^2, respectively (as shown in Figure 3). The fill factors of the PV cells with complexes **1**, **2** and **3** are 0.53~0.54. Complexes

Table 1. Absorption and fluorescence maxima for the complexes **1–4** in solution[a]

Complex	Abs λ_{max} (nm)	Em λ^b_{max} (nm)
1	350, 467	634
2	354, 462	629
3	368, 456	615
4	450	608

[a] Solvents: 0.1 N NaOH solution for complexes **1** and **2**, acetone for complexes **3** and **4**, 10^{-5} mol/L.

[b] Measured under the excitation at abs λ_{max} of each complex.

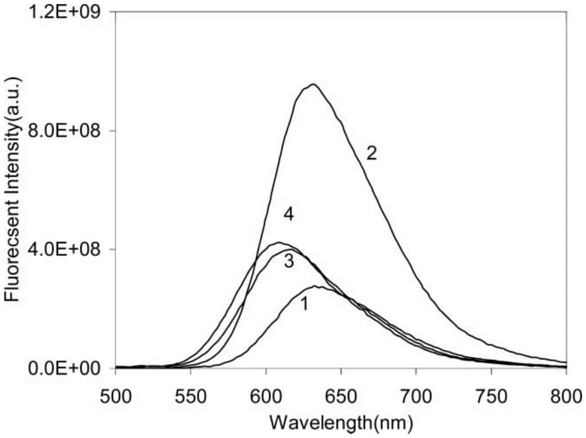


Fig. 2. Fluorescence spectra of the ruthenium complexes; Solvents: 0.1 N NaOH solution for complexes **1** and **2**, acetone for complexes **3** and **4**; Concentration: 10^{-5} mol/L. Excited at MLCT absorption maximum wavelength.

1 and **2** (with the ligand dcbpy) show much higher solar-to-electric energy conversion efficiencies due to the presence of the carboxylic groups compared with complexes **3** and **4**. The PV properties of complex **4** are inconsistent due to its poor adsorption on the surface of TiO_2, for which the possible interfacial discretion between the complex and TiO_2 seems to induce limited charge injection to TiO_2 from the complex in the PV cells as seen in Figure 3 (device of complex **4**). Figure 4 shows the IPCE of complex 1 based PV cells for which IPCE was found to be 31% at MLCT band.

3.3 *Electrochemical Study*

Table 2 shows the ground state redox potentials of the complexes. At different scan rates, the oxidation potentials of complexes **1** and **2** were changed by about 0.08 V *vs*. Fc/Fc$^+$ while reduction potentials showed no significant changes. Interestingly, the potentials of the complexes **1** and **2** are similar to those of N3, which is already known to have a well matched electronic energy level for efficient charge transfer to the conduction band of TiO_2. At the same scan rate of 100 mV/s, however, in the case of complexes **3** and **4**, the oxidation potentials (0.67∼0.68 V *vs*. Fc/Fc$^+$) are too biased to efficiently transfer photoinduced charge to the conduction band of nanocrystalline TiO_2. The large energy gap between the conduction band of TiO_2 and oxidation potentials of the complexes may hamper efficient charge injection resulting in low PV performances.

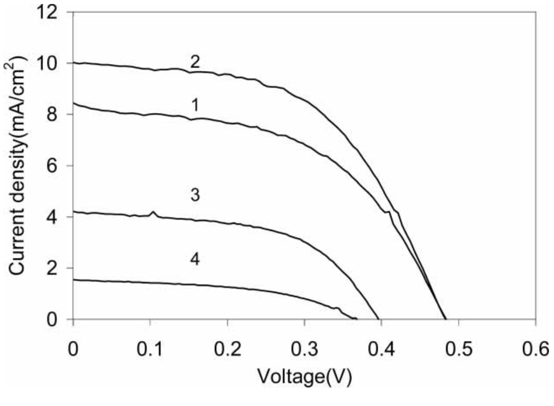


Fig. 3. I-V curves of PV cells made with the ruthenium complexes.

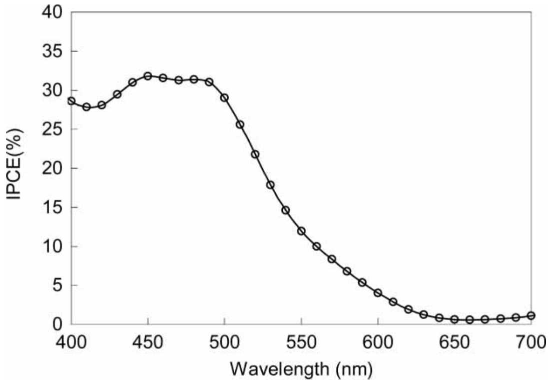


Fig. 4. IPCE of complex **1**.

3.4 *Quantum Chemical Calculations*

Optimized geometry and HOMO − LUMO of complex 1 are shown in Figures 5 and 6. In the HOMO (Figure 6a), most π^* electrons dwell in the ligand dcbpy due to the electron withdrawing property of carboxylic acids in the ligand dcbpy and the electron donating property of the amine group in the ligand ap (23). In the LUMO (Figure 6b), photoinduced electron density is present on the metal (ruthenium) and the ligand dcbpy so that the electrons are conveyed to the nanocrystalline TiO_2 through dicarboxilic bipyridines due to the metal-ligand charge transfer (MLCT). In the LUMOs of complexes **2**, **3**, and **4**, π^* electrons are scattered over the ligands (bipyridine and phenanthroline) including the metal. This shows that in the ruthenium complexes, carboxylic acids can act as strong electron withdrawing groups when an

Table 2. Redox potentials of ruthenium complexes measured at a scan rate (100 mV/s)[a]

Complex	Oxidation (V *vs*. Fc/Fc$^+$)	Reduction (V *vs*. Fc/Fc$^+$)
1[b]	0.24	−1.18
2[b]	0.32	−1.2
3	0.68	−1.26
4	0.67	−1.27

[a] At the scan rate of 100 mV/sec. Ox./Red. Potentials (V *vs*. FC/FC+): 0.33/−1.33 for N3.

[b] Tested on a Pt disk in CH_3CN with 0.1 M $TBAPF_6$.

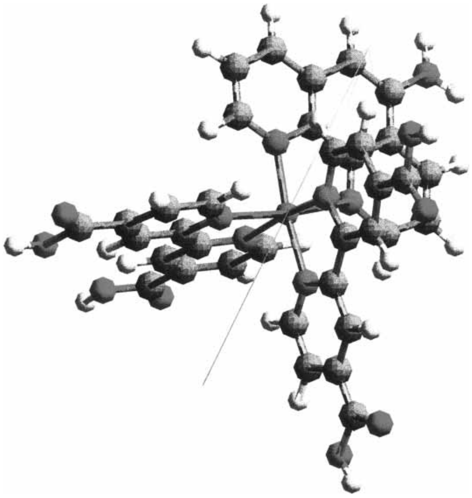
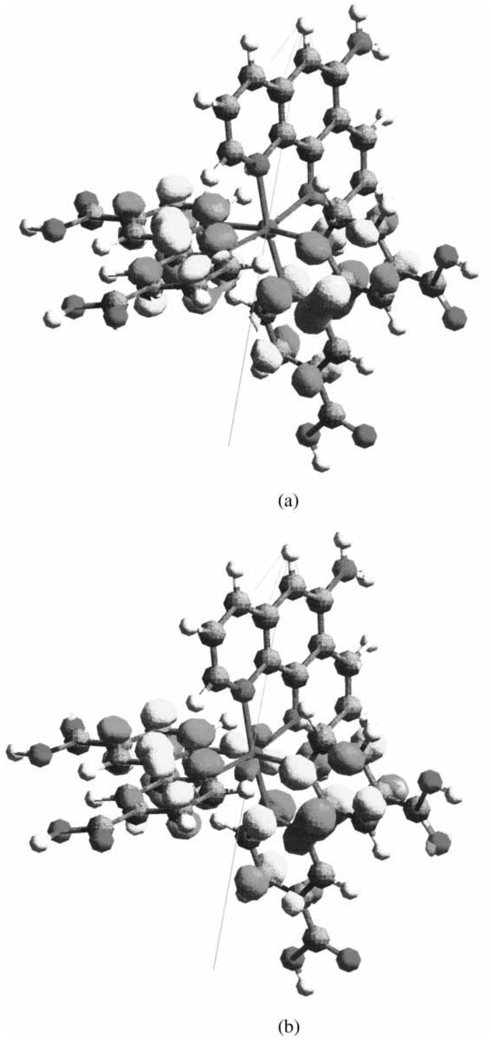


Fig. 5. Optimized geometry of complex **1**.


(a)

(b)

Fig. 6. (a) HOMO and (b) LUMO surfaces of complex **1**.

Table 3. HOMO-LUMO energies and band ΔE obtained from semiempirical quantum chemical calculations

Complex[a]	HOMO (eV)	LUMO (eV)	ΔE (eV)
N3[b]	−6.7	−1.9	4.8
1	−4.3	−1.5	2.8
2	−4.5	−1.6	2.9
3	−4.0	−1.0	3.0
4	−3.9	−1.1	2.8

[a] Cerius^2 version 4.6 (DMol 3 for geometry optimization, Zindo 1.0 for HOMO-LUMO calculation).

[b] Ref. (24).

electron-donating group such as the amino group is present. The role of dicarboxylic bipyridine is to collect π^* electrons which can be transferred efficiently via the route of metal-to-ligand-to-semiconductor through the carboxylic acid group.

Table 3 shows the electronic energy levels of the ruthenium complexes **1**–**4** for which the energy levels have been estimated by the semi-empirical quantum chemical calculations. The HOMO (−6.7 eV) and LUMO (−1.9 eV) levels of the standard dye, N3 are reported elsewhere (24). LUMOs of complexes **1** and **2** have values close to that of N3 compared to those of complexes **3** and **4**. Large differences between the conduction band of TiO_2 and LUMO of the sensitizer can deter efficient charge transfer and result in efficient charge in the reverse direction. The calculated energy levels show a consistent trend compared to the electrochemical data. The combination of all the studies including quantum chemical calculations, electrochemistry, and spectroscopy have improved our understanding of the PV performance of the Ru(II) bifunctional complex.

4 Conclusions

We synthesized a new ruthenium complex which contains two ligands, 5-amino-1, 10-phenanthroline and 4,4′-dicarboxylic-2,2′-bipyridine. The functional groups (amine and carboxylic acid) in ligands phenanthroline and bipyridine of the ruthenium complex are playing a role in showing promising spectroscopic properties and photovoltaic performances. The semi-empirical quantum chemical calculations and ground state redox potentials help to explain and support these properties of the ruthenium complexes. Further experiments to incorporate this ruthenium complex into polythiophene based conjugated polymers are underway in our laboratory.

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