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Mono- and Dinuclear Ruthenium Complexes for Nanocrystalline TiO_2 Based Dye-Sensitized Photovoltaics[#]

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ABSTRACT

We have carried out synthesis, characterization, and theoretical modeling of a rigid, rod-like homometallic dinuclear ruthenium complex and an analogous mononuclear ruthenium complex using terpyridine and bipyridine ligands. The photophysical and photovoltaic properties have been investigated. We compared the results to understand the charge transfer processes in these complexes. The dinuclear complex showed overall photoelectric conversion efficiency of 1.9% in dye-sensitized nanocrystalline TiO_2 based photovoltaic cells under simulated AM1.5 solar irradiation and is found to be an efficient photosensitizer compared to the mononuclear complex.

Key Words: Ruthenium complexes; Terpyridyl bridging ligand; Dye-sensitization; Photovoltaic cell.

[#]Dedicated to the memory of Professor Sukant K. Tripathy.

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INTRODUCTION

There has been tremendous interest in the design and synthesis of novel photosentizers for their use in dye sensitized photovoltaic (DSPV) cells. Presently the most efficient and stable sensitizers are carboxylated polypyridyl complexes. Among them, $[Ru(dcbpy)_2(NCS)_2]$ where dcbpy = 4,4′-dicarboxylic-2,2′-bipyridine, well known as N3, shows overall photoelectric conversion efficiency of 7%–10% when a liquid electrolyte containing I_3^-/I^- solution is used.[1] The high efficiency in these DSPV cells is partly attributed to the nanoporous high surface area of TiO_2.[2] Though N_3 dye has been the most efficient dye candidate, there is a need for developing more inexpensive dyes with panchromatic absorption with high extinction coefficients beyond 650 nm to utilize full solar radiation for better conversion efficiencies. Structural variations of Ru(II) complexes containing various polypyridyl ligands have been carried out by Gratzel et al.[3]

From earlier studies, dinuclear complexes, well known as “dyads,” were found to be advantageous over mononuclear complexes due to the following reasons: (i) multinuclear systems can be easily synthesized with well-defined molecular lengths; (ii) they may provide fundamental insight into the interfacial electron transfer processes; and (iii) they provide stabilization of photo-induced charge separation, multi-electron collection, and antenna effects.[4,5] Homometallic dinuclear complexes using Ru and heterometallic complexes using Ru(II)/Rh(III) and other metals have been reported with strong internal energy and electron transfer processes.[6] Recently, Kleverlaan et al. studied stepwise charge separation in a multinuclear system containing Ru(II)/Rh(III) using bipyridyl ligands on nanocrystalline TiO_2 films.[7] In our recent study, we found that dinuclear Ruthenium complexes with bridging ligands containing two terpyridine fragments linked by a phenylene ring and dcbpy ligands are promising candidates for DSPV cells.[8] In the present study, we report the synthesis and photophysical properties of a dinuclear complex and an anologous mononuclear Ru(II) complex. The photovoltaic properties measured in a nanocrystalline TiO_2 based DSPV cell sensitized by these complexes are presented and are compared with each other to understand the advantage of multi metallic centers in complexes over mono metallic complexes on photovoltaic properties. Theoretical HOMO–LUMO energies calculated for both complexes and a standard dye, N3 using semi empirical ZINDO method are also discussed.

EXPERIMENTAL

Materials and Measurements

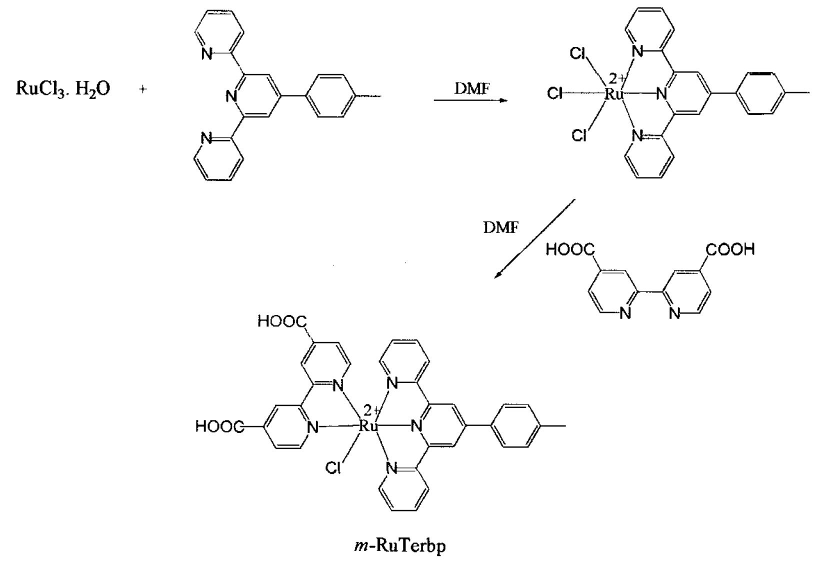
(4-methylphenyl)-2,2′:6′,2″2,2′-terpyridine, 2,2′;6′,6″-terpyridine, $RuCl_3 \cdot 3H_2O$ and 4,4′-dicarboxylic acid-2,2′-bipyridine were purchased from Aldrich Chemical Co. and were used as received. N3 was purchased from Solaronix. The infrared spectra were measured on a Perkin-Elmer 1720 FT-IR spectrometer. The UV-VIS absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer. Fluorescence spectra were measured on a Perkin-Elmer LS-55. ^1H NMR spectra were obtained on a Bruker ARX-500 MHz FT-NMR spectrometer.

TiO_2 films were prepared by the spin coating method onto $SnO_2:F$ coated glass plates. The TiO_2 films were then sintered at 500°C for 1 h. Adsorption of the dye was carried out by placing the sintered hot (about 80°C) TiO_2 film into the dye solution (10^{-4} M) in an ethanol/water mixture and soaking overnight. After completion of the dye adsorption the film was rinsed with ethanol and dried for 4 h at 60° under vacuum to remove any trapped water and ethanol. The PV measurements were performed immediately after the preparation of the dye-adsorbed films. Dye sensitized photovoltaic cells were assembled by clamping the platinum coated SnO_2 counter electrode and the dye adsorbed TiO_2 working electrode which had an active area of 0.25 cm^2. A liquid electrolyte consisting of 1.0 M LiI, 0.1 M I_2, and 2.0 M 4-*tert*-butylpyridine (tbp) in acetonitrile was introduced between the two plates. The DSPV cells were exposed to simulated AM1.5 solar light at 1 sun of 100 mW/cm^2 light intensity using an Oriel 1000-W xenon lamp and appropriate filters. Photo-currents and photovoltages were measured using a Keithley 2400 source meter in conjunction with a personal computer.

Synthesis Procedures

Synthesis of Mononuclear Complex (*m*-RuTerbp)

The *m*-RuTerbp complex was synthesized using the following procedure (Sch. 1). 0.31 g (0.95 mmol) of 4′-(4-methylphenyl)-2,2′; 6′,2″2,2′-terpyridine and 0.25 g (1.2 mmol) of ruthenium chloride hydrate were dissolved in 90 mL of *N,N*′-dimethylformamide (DMF) and refluxed for 12 h. After cooling, dark red powder was filtered off and washed several times with diethylether/acetone and dried under vacuum to obtain RuTerpy in 54% yield. RuTerpy (0.25 g) and 0.12 g of 4,4′-dicarboxylic acid-2,2′-bipyridine in a 1 : 1 ratio were then dissolved in 60 mL of DMF and refluxed for 8 h under N_2 atmosphere. After cooling, a dark brown powder was filtered off and washed several times with

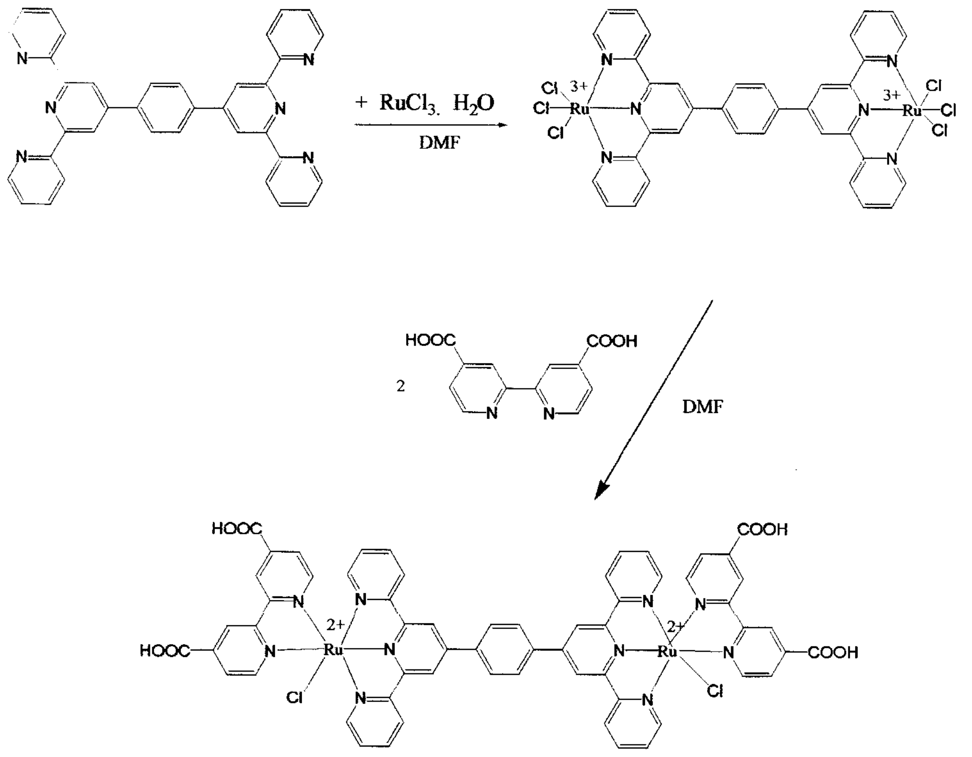


Scheme 1. Synthesis of mononuclear complex, *m*-RuTerbp.

diethylether/acetone and dried under vacuum to obtain *m*-Ruterbp with a 45% yield. FTIR (KBr pellet): 1460, 1500, 1600 cm^{-1} (C=C and C—N stretchings), 1720 cm^{-1} (C=O stretching); UV/VIS absorption maximum is 488 nm in dilute NaOH. CHN Anal. Calcd. for $C_{34}H_{25}N_5O_4Cl$ Ru 2Cl$^-$: C, 52.68; H, 3.23; N, 9.04. Found: C, 52.83; H, 3.18; N, 8.48.

Synthesis of Dinuclear Complex (*di*-Ruterbp)

RuTerbp complex was synthesized using the following procedure (Sch. 2): 0.18 g (0.87 mmol) of $RuCl_3$, H_2O and 0.2 g (0.37 mmol) of terpyridyl ligand (2,2′; 6′,6″-terpyridine) were refluxed for 8 h in *N*,*N*-dimethylformamide under N_2. The resultant precipitate was allowed to cool to room temperature and filtered and washed several times with diethylether/acetone to obtain RuTerCl. To this complex (0.15 g) added 1 : 2 ratio of dcbpy (0.08 g) in DMF and refluxed for 6 h under N_2. After standing overnight, the reaction mixture was filtered to give a dark colored precipitate, which was washed several times with diethylether/acetone to obtain 0.163 g of *di*-RuTerbp. UV-VIS (dilute NaOH) λ_{max} 519 nm; FTIR (KBr), 1600 cm^{-1} (C=C and C=N stretchings), 1720 cm^{-1} (C=O



RuTerbp

Scheme 2. Synthesis of dinuclear complex, *d*-RuTerbp.

stretching); CHN Anal. calcd. for $C_{60}H_{40}Cl_2N_{10}O_8Ru_2 \cdot 2Cl^- \cdot H_2O$: C, 51.76; H, 3.02; N, 10.06. Found: C, 52.05; H, 3.94; N, 9.34.

RESULTS AND DISCUSSION

Photocurrent–voltage (*I–V*) curves measured from sandwich type dye sensitized TiO_2 solar cells for the complexes, N3, *m*-RuTerbp and *di*-RuTerbp are shown in Fig. 1. The open circuit voltages (V_{oc}), short circuit currents (I_{sc}), fill factors (ff), and overall efficiencies (η_{eff}) are presented in Table 1. From the data, it is clear that there is considerable improvement in efficiency from the mono complex to the dinuclear complex. The overall efficiency of *m*-RuTerbp and *di*-RuTerbp in DSPV cells were found to be 1.1% and 1.9% respectively compared to 4.7% which was measured for N3 using the same conditions.

The UV-VIS absorption spectrum of the complexes *m*-RuTerbp and *di*-RuTerbp were measured in dilute NaOH (10^{-4} M) due to their poor solubility in organic solvents. As shown in Fig. 2, the absorption maxima of *m*-RuTerbp is found to be 488 nm with an extinction coefficient of $4.2 \times 10^3 M^{-1} cm^{-1}$. As expected, the absorption maxima in *di*-RuTerbp is red shifted (35 nm). The extinction coefficient of the dinuclear complex is $3.8 \times 10^3 M^{-1} cm^{-1}$. The absorption cutoff wavelengths of these complexes are around 650–750 nm, which makes them potential candidates for light harvesting properties. The absorption band in the visible region is characterized by metal-to-ligand charge transfer (MLCT). *m*-RuTerbp and *di*-RuTerbp show very weak fluorescence bands at 672 and 642 nm, respectively, when excited at the lowest energy MLCT absorption band and measured in dilute NaOH solutions. However the weak fluorescence does not affect the photovoltaic properties as was observed in the case of N3.[1,2]

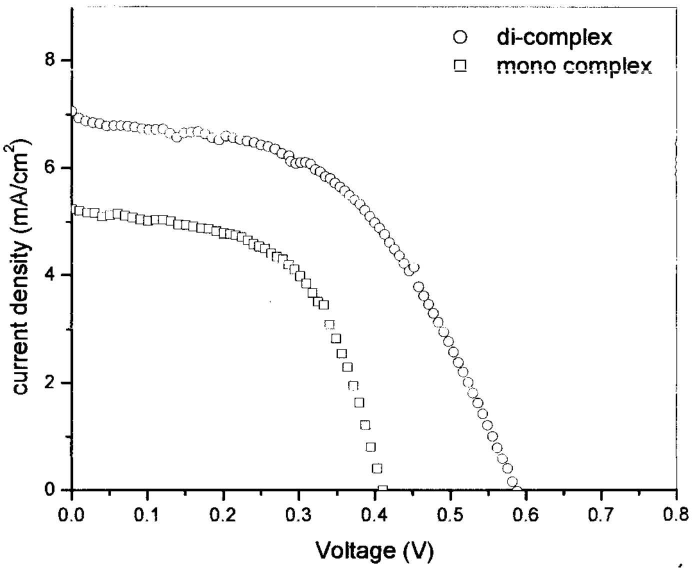


Figure 1. Photocurrent–voltage (*I–V*) curves of *m*-RuTerbp and *di*-RuTerbp.

Table 1. Short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (ff), and overall efficiency (η_{eff}) of *m*-RuTerbp and *di*-RuTerbp.

Dye	I_{sc} (mA/cm^2)	V_{oc} (mV)	ff	η_{eff} (%)
m-RuTerbp	5.2	410	0.48	1.1
di-RuTerbp	6.4	570	0.53	1.9
N3	18.7	592	0.43	4.7

Earlier theoretical investigation shows that the calculated HOMO–LUMO energies of Ruthenium complexes are well correlated with their experimental redox potentials and thus theoretical modeling can be a useful tool for designing efficient dyes for photosensitization.[9] We carried out theoretical calculations on mono and dinuclear complexes and the standard dye, N3. All the geometries were optimized using Dmol^3 in Cerius^2 modeling software and then these geometries were used to run ZINDO,[10] calculations to obtain HOMO–LUMO energies.

The optimized geometries of *m*-RuTerbp and *di*-RuTerbp are shown in Figs. 3 (a) and (b). In Fig. 3(b), it is clearly seen that, the introduction of a phenylene spacer between the terpyridine units leads to a decrease of the delocalization of the π^* orbitals, due to a non-coplanar arrangement of the terpyridine moieties and the inserted phenylene unit. Similar to the mono complex, the average dihedral angles between the tpy units and phenylene unit at both ends in *di*-RuTerbp are found to be 45 and 38 degrees. The metal-to-metal distance in this complex is 14 Å.

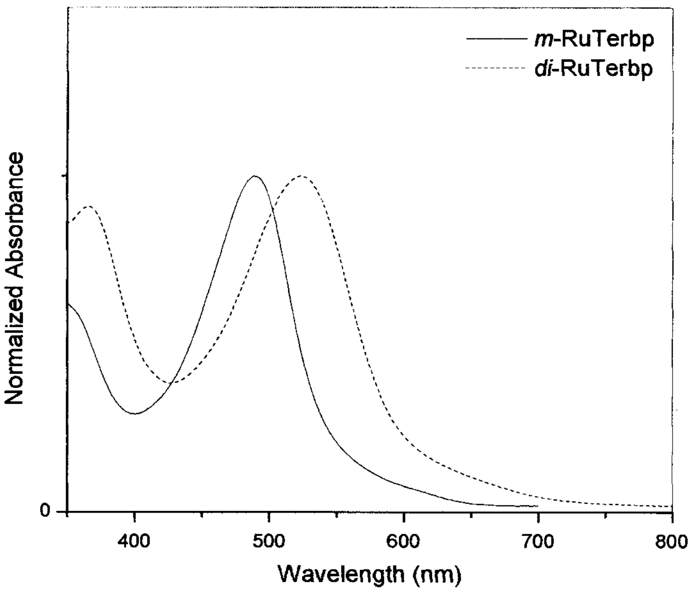


Figure 2. The UV-VIS absorption spectra of *m*-RuTerbp and *di*-RuTerbp measured in dilute NaOH solution.

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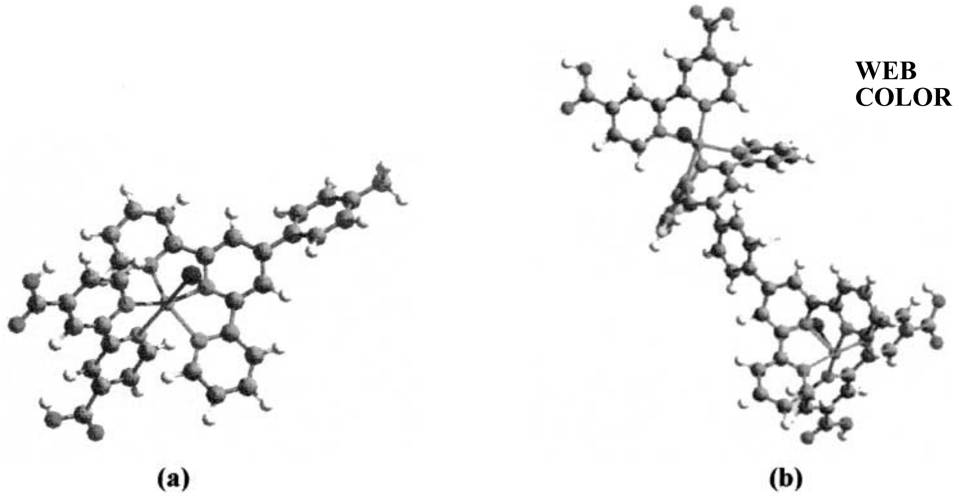

Figure 3. Optimized geometries of (a) mono (*m*-RuTerbp) and (b) dinuclear (*di*-RuTerbp) Ruthenium complexes.

We have compared the results with the energies of a standard complex, N3. As mentioned earlier, N3 is a well known and efficient dye for DSPV because the HOMO and LUMO energies of N3 are well matched with the conduction band of TiO_2 and the redox potential of the electrolyte, respectively. Though the HOMO–LUMO values obtained from the calculations cannot be directly correlated with experimental photovoltaic efficiencies, the qualitative comparison of theoretical results between the complexes gives an insight into the structural effects on their photovoltaic efficiency. Considering the N3 dye as a standard, we presume that the LUMO energy of any dye should be close to that of N3 to show good efficiency in TiO_2 based DSPV cells.

The calculated LUMO energy for the dinuclear complex, *di*-RuTerbp (-2.73 eV) is closer to N3 (-1.93 eV) than those for the mononuclear complex, *m*-RuTerbp (-4.61 eV). However, both complexes have LUMO energy levels below N3. The bathochromic MLCT absorption shift observed in the dinuclear complex compared to the mono complex is due to the extended conjugation despite the twist between phenylene spacer and terpyridyl moeity. The promising photovoltaic efficiency that is observed in these complexes could be due to the ultra fast charge transfer that is taking place from higher level excited states to the conduction band of TiO_2 rather than from lowest excited state energy levels. Earlier, Islam et al.[11] reported the ultra fast charge transfer from higher excited states in some ruthenium complexes.

CONCLUSION

We have presented the synthesis and characterization of a Ruthenium mono and dinuclear complexes with terpyridine and dcbpy type ligands for the sensitization in nanocrystalline TiO_2 based photovoltaic cells. The absorption maximum is red shifted in the dinuclear complex compared to the mononuclear complex. The dinuclear complex shows higher efficiency compared to the mono complex despite the twist between the terpyridyl ligand and the phenylene spacer. From these results, it could be argued that multinuclear complexes with extended conjugation can contribute additively to the overall photovoltaic efficiency in dye-sensitized solar cells. Further work on the synthesis of multinuclear complexes with other planar conjugated bridging ligands is underway in our laboratory.

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