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# Molecular design of ruthenium(II) polypyridyl photosensitizers for efficient nanocrystalline TiO$_2$ solar cells

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## Abstract

Transition metal complexes using polypyridine ligands are finding increasing use in the dye sensitized solar cells. To improve further the efficiency of this cell, an enhanced spectral response of the sensitizer in the lower energies is required. In this paper we review our effort in the molecular design of the ruthenium polypyridyl complexes for nanocrystalline TiO$_2$-based solar cells. The poor cell efficiency in Ru(4,4′-dicarboxy-2,2′-biquinoline)$_2$(NCS)$_2$/TiO$_2$ system may be ascribed to the low excited-state oxidation potential, which plays a crucial role in the electron-transfer process. Ru(2-(2-(4-carboxypyridyl))-4-carboxyquinoline)$_2$(NCS)$_2$, when anchored to nanocrystalline TiO$_2$ films, achieves efficient sensitization over the whole visible range extending up to 900 nm, yielding incident photon-to-current conversion efficiency (IPCE) of 55%. The low cell efficiency of Ru(4-4′-dicarboxy-2,2′-bypyridine)$_2$(ethyl-2-cyano-3,3-dimercaptoacrylate) may be due to slow regeneration of the dye by electron donation from iodide following charge injection into the TiO$_2$. Tuning of HOMO and LUMO energy level show that an efficient sensitizer should possess ground-state and excited-state redox potentials of 0.5 and $-0.8$ V vs. SCE, respectively. Transient absorption studies of Ru phenanthroline complexes show that the efficiency of electron injection is strongly affected by the number of carboxyl groups of the sensitizing dye. The β-diketonate complex [Ru(4-4′-dicarboxy-2,2′-bypyridine)$_2$(acetylacetonato)]Cl, when anchored to nanocrystalline TiO$_2$ films, achieves very efficient sensitization across the entire visible region, yielding 60% IPCE. A new series of panchromatic sensitizers of Ru(tricarboxyterpyridine)(β-diketonato)(NCS) type have been developed. Ru(4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine)(1,1,1-trifluoropentane-2,4-dionato)(NCS) achieved an efficient sensitization of nanocrystalline TiO$_2$ solar cells over the whole visible range extending into near IR region and displaying a maximum around 600 nm, where IPCE approaches a high value of 70%.
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*Keywords:* Ruthenium(II) complexes; Polypyridine ligands; Photosensitizers; Solar cells

## 1. Introduction

An attractive and cheaper approach for the conversion of solar light into electrical energy has been to utilize large-bandgap oxide semiconductors such as TiO$_2$ to absorb solar light [1]. Dye sensitization of large-bandgap oxide semiconductors has been investigated for many years [2–4]. In the 1990s a major photoelectrochemical solar cell development was obtained with the introduction of fractal thin film dye sensitized solar cells devised by O'Regan and Grätzel [5]. In this solar cell, a monolayer of dyes is attached to the surface of nanocrystalline TiO$_2$ film. Photoexcitation of the dye results in the injection of an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from a redox system, such as iodide/triiodide couple. Several organic dyes [3,4,6,7] and transition metal complexes [5,8–17] have been employed in the solar cells to sensitize nanocrystalline TiO$_2$ semiconductors.

The most efficient transition metal complexes employed so far in these solar cells are Ru(II) polypyridyl complexes [5,8,11,18] because of their intense charge-transfer (CT) absorption in the whole visible range, moderately intense emission with fairly long lifetime in fluid solutions at ambient temperatures, high quantum yield for the formation of the lowest CT excited state, and redox reactivity and ease of tunability of redox properties [19–21]. The photoexcitation of the metal-to-ligand charge-transfer (MLCT) excited states of the adsorbed dye leads to an efficient injection of electrons into the conduction band of TiO$_2$. Incident photon-to-current conversion efficiencies (IPCE) exceeding 70% have been

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reported in several cases [5,8,9,22,23]. Recently, Lewis and coworkers [13] reported that CT polypyridyl complexes of Os(II) extended the light absorption and spectral response of nanocrystalline TiO$_2$ photoelectrodes to longer wavelengths while also providing high external quantum yields for photocurrent flow similar to their analogous Ru(II) complexes. In our previous studies, we have demonstrated that CT complexes of square planar platinum(II) diimine dithiolate can also efficiently sensitize nanocrystalline TiO$_2$ [14,24]. Alternative MLCT sensitizers based on Fe(II) [15], Re(I) [16], and Cu(I) [17] have also been employed in solar cells to sensitize nanocrystalline TiO$_2$ semiconductors, but the solar light to electricity conversion efficiency is significantly lower than that observed with the Ru(II)- and Os(II)-based sensitizers.

Molecular design of ruthenium polypyridyl photosensitizers for nanocrystalline TiO$_2$ solar cells that can absorb visible light of all colors presents a challenging task. The dye should have suitable ground- and excited-state redox properties so that the two key electron-transfer steps (charge injection and regeneration of the dye) occur efficiently. It is very difficult to fulfill both requirements simultaneously during designing a CT sensitizer. Systematic tuning of the LUMO and HOMO energy levels of the ruthenium polypyridyl complexes are necessary to estimate the optimal threshold wavelength for maximum power conversion of a single-junction converter. Here we have discussed our effort in the molecular engineering of the composition of ruthenium complex to develop efficient photosensitizers for TiO$_2$-based solar cells.

## 2. Tuning of LUMO energy level: quinoline-based Ru(II) polypyridyl sensitizers

*cis*-Dithiocyanato-bis(4-4′-dicarboxy-2,2′-bypyridine)ruthenium(II) (Ru(dcbpy)$_2$(NCS)$_2$) is one of the efficient ruthenium polypyridyl sensitizer reported by Grätzel and coworkers [8]. However, the main drawback of this sensitizer is the lack of absorption in the red region of the visible spectrum (Fig. 1). Ru(dcbpy)$_2$(NCS)$_2$, when an-
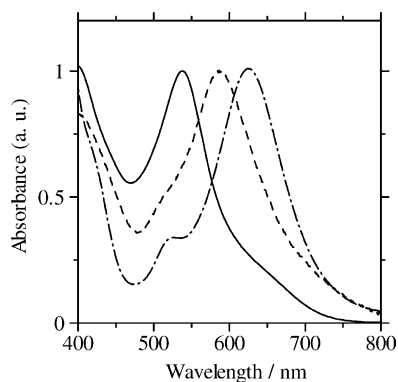


Fig. 1. Absorption spectra of Ru(dcbpy)$_2$(NCS)$_2$ (—), Ru(dcpq)$_2$(NCS)$_2$ (———), and Ru(dcbiq)$_2$(NCS)$_2$ (–·–) in ethanol–methanol (4:1) solution at 298 K.
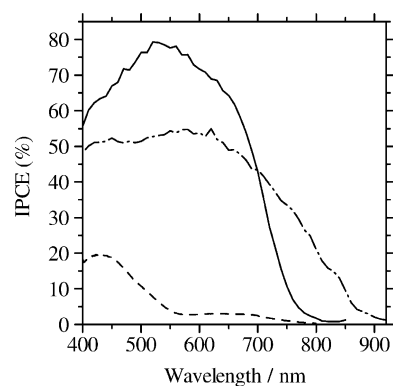


Fig. 2. Photocurrent action spectra of nanocrystalline TiO$_2$ films sensitized by complexes Ru(dcbpy)$_2$(NCS)$_2$ (—), Ru(dcpq)$_2$(NCS)$_2$ (———), and Ru(dcbiq)$_2$(NCS)$_2$ (–·–). The IPCE is plotted as a function of wavelength. A sandwich type cell configuration was used to measure these spectra.

chored to nanocrystalline TiO$_2$ films, achieves very efficient sensitization over the whole visible range, yielding IPCE about 80% (Fig. 2). To further improve the efficiency of this system, an enhanced spectral response of the sensitizer in the lower energies is required while maintaining sufficient thermodynamic driving forces for the both electron-transfer and dye regeneration processes. In the ruthenium polypyridyl complexes, absorption properties can be tuned to lower energy region by introducing a ligand with a low-lying $\pi^*$ molecular orbital [21,25–30] or by destabilization of the metal t$_{2g}$ orbital with a strong donor ligand [23,24,31,32]. We have tuned the lowest MLCT absorption band up to 700 nm (Fig. 1) by systematic tuning of the LUMO energy level of ruthenium polypyridyl complexes of *cis*-RuL$_2$(NCS)$_2$ type where L is one of the two diimine ligands with low-lying $\pi^*$ molecular orbital: 2-(2-(4-carboxypyridyl))-4-carboxyquinoline (dcpq) and 4,4′-dicarboxy-2,2′-biquinoline (dcbiq) (Scheme 1) [28–30]. The photophysical and photoelectrochemical data of these complexes are summarized in Table 1. Fig. 2 shows the photocurrent action spectra for Ru(dcbiq)$_2$(NCS)$_2$, Ru(dcpq)$_2$(NCS)$_2$ and Ru(dcbpy)$_2$(NCS)$_2$ adsorbed on TiO$_2$.

Ru(dcbiq)$_2$(NCS)$_2$ shows a broad MLCT absorption band in the whole visible region with a peak at 627 nm (Fig. 1). Ru(dcbiq)$_2$(NCS)$_2$ presents a low light harvesting efficiency (LHE) due to inefficient driving force for electron injection into the conduction band of TiO$_2$ from its lowest excited MLCT state. Fig. 3 shows the photocurrent action spectra for Ru(dcbiq)$_2$(NCS)$_2$ adsorbed on TiO$_2$ and SnO$_2$ films where the IPCE and absorbed photon-to-current conversion efficiencies (APCE) values are plotted as a function of wavelength and along with the absorption spectra of the adsorbed dye. On TiO$_2$ film (Fig. 3a), the lower energy MLCT band (700 nm) has higher absorbance value than the higher energy MLCT band (530 nm) but their relative contributions to the action spectra are opposite to their absorbance values. The injection quantum yield (APCE) for the higher energy

Table 1
Photophysical and photoelectrochemical properties of ruthenium polypyridyl sensitizers[a]

| Sensitizer | $\lambda_{abs, max}$[b] (nm) | $\lambda_{em, max}$[b] (nm) (77 K) | $E(Ru^{3+/2+})$[c] (vs. SCE) | $E^*(Ru^{3+/2+})$[d] (vs. SCE) | IPCE (%) | $J_{sc}$ (mA) | Reference |
|---|---|---|---|---|---|---|---|
| Ru(dcbpy)$_2$(NCS)$_2$ | 532 | 718 | +0.85 | −1.0 | 80 | 15.1 | [8] |
| Ru(dcpq)$_2$(NCS)$_2$ | 586 | 780 | +0.86 | −0.9 | 55 | 13.1 | [30] |
| Ru(dcbiq)$_2$(NCS)$_2$ | 627 | 873 | +0.92 | −0.6 | 5 | 0.8 | [28] |
| Ru(dcbpy)$_2$(qdt) | 517 | 735 | +0.84 | −0.9 | 45 | 11.1 | [32] |
| Ru(dcbpy)$_2$(ecda) | 582 | 770 | +0.46 | −1.14 | 30 | 5.4 | [32] |
| Ru(dcbpy)$_2$(bdt) | 662 | – | +0.30 | −1.16 | 7 | 2.1 | [32] |
| Ru(dcbpy)$_2$(tdt) | 670 | – | +0.28 | −1.18 | – | 1.1 | [32] |
| Ru(dcphen)$_2$(NCS)$_2$ | 522 | 800 | +0.84 | −1.0 | 75 | 12.5 | [35] |
| Ru(dcphen)(phen)(NCS)$_2$ | 485 | 750 | +0.89 | −1.1 | 30 | 8.8 | [35] |
| Ru(mcphen)$_2$(NCS)$_2$ | 500 | 770 | +0.76 | −1.2 | 42 | 6.1 | [35] |
| Ru(mcphen)(phen)(NCS)$_2$ | 493 | 770 | +0.70 | −1.3 | 7 | 4.5 | [35] |
| Ru(dcbpy)$_2$(acac) | 525 | 733 | +0.65 | −1.12 | 52 | 13.2 | [23] |
| Ru(dcbpy)$_2$(Meac) | 532 | 757 | +0.63 | −1.14 | – | 8.6 | [23] |
| Ru(dcbpy)$_2$(dbmo) | 517 | 722 | +0.74 | −1.03 | – | 8.7 | [23] |
| Ru(tctpy)(NCS)$_3$ | 610 | 950 | +0.66 | −0.95 | 75 | 17.9 | [22] |
| Ru(tctpy) (tfac)(NCS) | 606 | 940 | +0.70 | −0.95 | 70 | 18.0 | [39] |
| Ru(tctpy) (tfed)(NCS) | 610 | 950 | +0.70 | −0.95 | – | 17.0 | – |

[a] dcbpy: 4-4′-dicarboxy-2,2′-bypyridine; dcpq: 2-(2-(4-carboxypyridyl))-4-carboxyquinoline; dcbiq: 4,4′-dicarboxy-2,2′-biquinoline; qdt: quinoxaline-2,3-dithiolate; ecda: ethyl-2-cyano-3,3-dimercaptoacrylate; bdt: 1,2-benzenedithiolate; tdt: 3,4-toluenedithiolate; phen: 1,10-phenanthroline; dcphen: 4,7-dicarboxy-1,10-phenanthroline; mcphen: 4-monocarboxy-1,10-phenanthroline; acac: acetylacetonate; Meac: 3-methyl-2,4-pentanedionate; dbmo: 1,3-diphenyl-1,3-propanedionate; tctpy: 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine; tfac: 1,1,1-trifluoropentane-2,4-dionato; tfed: 1,1,1-trifluoroeicosane-2,4-dionato.

[b] In ethanol–methanol (4:1) solution at room temperature.

[c] Half-wave potentials assigned to the $Ru^{3+/2+}$ couple for the sensitizers.

[d] Calculated from $E^*(Ru^{3+/2+}) = E(Ru^{3+/2+}) - E^{0-0}$; $E^{0-0}$ values were estimated from the crossing point of the emission and absorption spectra, when the most intense MLCT absorption band and the emission peak were adjusted the same height.

(480 nm) transition is nearly 25%, whereas it is only about 4% from the lower energy (700 nm) transition. The IPCE spectrum for Ru(dcbiq)$_2$(NCS)$_2$ on SnO$_2$ film, which has a conduction band edge ~0.5 V [33] more positive than TiO$_2$,

qualitatively trace the dye's absorbance feature. Between 450 and 800 nm, APCE spectrum is nearly flat, indicating an efficient injection occurred in this area at all energies. The lowest excited MLCT state of Ru(dcbiq)$_2$(NCS)$_2$ is energetically allowed to transfer an electron into the conduction band of SnO$_2$ but not into TiO$_2$. Although the lowest excited MLCT state is not thermodynamically favorable for electron injection in the Ru(dcbiq)$_2$(NCS)$_2$/TiO$_2$ film, the small
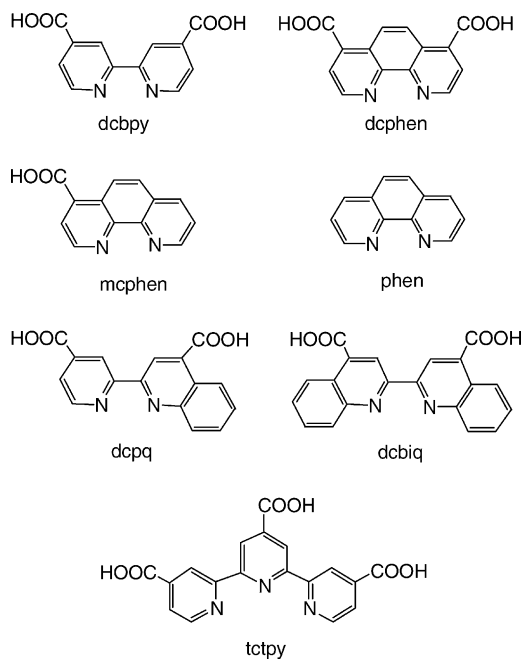


Scheme 1. Structures of polypyridine ligands that are being used in solar cell studies.
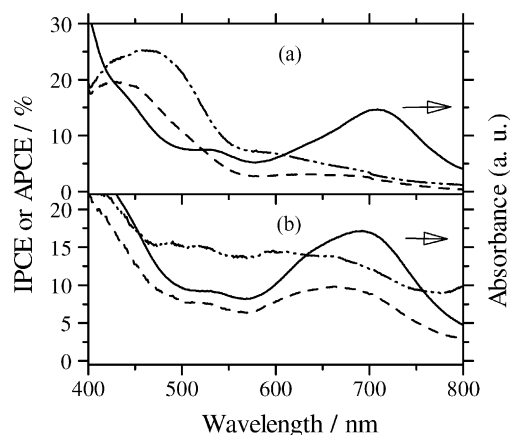


Fig. 3. Incident photon-to-current efficiency (———), absorbed photon-to-current efficiency (–··–) and absorption spectra (—) of Ru(dcbiq)$_2$(NCS)$_2$ anchored to transparent films of TiO$_2$ (a) and SnO$_2$ (b). Absorption spectra are corrected for absorbance of corresponding undyed films. The IPCE and APCE are plotted as a function of wavelength.

APCE value ($\approx 3\%$) observed between 550 and 800 nm is due to the hot electron injection. Here both electron injection and vibrational relaxation processes are competing with each other.

Ru(dcpq)$_2$(NCS)$_2$ complex has MLCT absorption band at 586 nm which is blue shifted to 41 nm compared to the same of Ru(dcbiq)$_2$(NCS)$_2$. This is because of higher energy $\pi^*$ level of dcpq than dcbiq. The excited-state oxidation potential of Ru(dcpq)$_2$(NCS)$_2$ is estimated to be $-0.8$ V vs. SCE which is little higher than the conduction band of TiO$_2$. Ru(dcpq)$_2$(NCS)$_2$, when anchored to nanocrystalline TiO$_2$ films, achieves efficient sensitization over the whole visible and near IR range extending up to 900 nm, yielding IPCE 55% (Fig. 2). A short-circuit photocurrent density obtained was 13.1 mA/cm$^2$. The low IPCE value compare to Ru(dcbpy)$_2$(NCS)$_2$ sensitizer at MLCT absorption peak may be due to unfavorable driving force for electron injection step in the solar cell mechanism. Work on the optimization of the cell efficiency and injection quantum yield is in progress.

## 3. Tuning of HOMO energy level: dithiolate-based Ru(II) polypyridyl sensitizers

In Section 2 we have discussed about the tuning of LUMO energy level to find out the minimum driving force between the conduction band of the TiO$_2$ and the excited-state oxidation potential of the sensitizer while keeping efficient charge injection into the TiO$_2$. Near-infrared response can also be gained by upward shifting of the ruthenium t$_{2g}$ (HOMO) energy levels [23,24,31,32]. Furthermore, the HOMO position cannot be varied freely as the redox potential of the dye must be maintained sufficiently positive to ascertain rapid regeneration of the dye by electron donation from iodide following charge injection into the TiO$_2$. We have reported a series of ruthenium polypyridine complexes of the type Ru(dcbpy)$_2$L where L is one of the four dithiolate ligands shown in Scheme 2: quinoxaline-2,3-dithiolate (qdt), ethyl-2-cyano-3,3-dimercaptoacrylate (ecda), 1,2-benzenedithiolate (bdt) and 3,4-toluenedithiolate (tdt) [32]. Here, we have tuned the metal t$_{2g}$ orbital (HOMO) energy about 600 mV using the above four dithiolate ligands while the acceptor orbital (LUMO) energy remains nearly constant (Table 1). The decrease in MLCT transition energy arises mainly from the increase in the energy of the metal t$_{2g}$ orbital (HOMO).

The most efficient sensitizer in this series is Ru(dcbpy)$_2$-(qdt), showing the IPCE value of 45% at 500 nm and a short-circuit photocurrent of 11.1 mA cm$^{-2}$ (Fig. 4). However, its light harvesting at longer wavelengths ($>$650 nm) is very poor. Though Ru(dcbpy)$_2$(ecda) complex has superior panchromatic light harvesting properties to the Ru(dcbpy)$_2$(qdt) sensitizer but it shows poor overall photovoltaic performance (IPCE$_{max}$ = 30%, $J_{sc}$ = 5.4 mA cm$^{-2}$). Ru(dcbpy)$_2$(bdt) and Ru(dcbpy)$_2$(tdt) com-
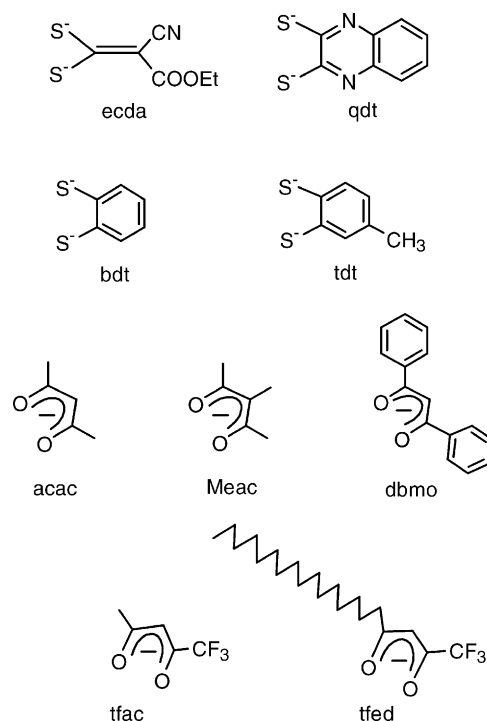
Scheme 2. Structures of non-chromophoric chelating ligands that are being used in solar cell studies.

plexes show a drastically reduced IPCE value of $<$7% at the lowest energy absorption band maxima (Table 1).

IPCE is directly related to the LHE, the quantum yield of the charge injection ($\phi_{inj}$), and the efficiency of collecting the injected charge at back contact ($\eta_c$), and is expressed by

$$IPCE = LHE(\lambda)\phi_{inj}\eta_c \qquad (1)$$

The excited-state oxidation potential of the Ru(dcbpy)(dithiolate) sensitizers are sufficiently negative ($<-0.93$ vs. SCE) that it is expected to inject electrons efficiently into the TiO$_2$. The excited-state lifetime of all dyes is in the nanosecond time scale, which is about three orders of magnitude longer than the reported electron injection rate [34]. Therefore, $\phi_{inj}$
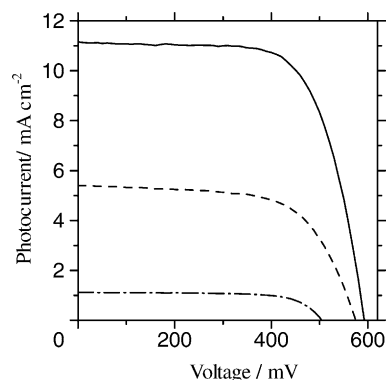
Fig. 4. Photocurrent–voltage characteristics of representative TiO$_2$ electrodes sensitized with dye: Ru(dcbpy)$_2$(qdt) (——), Ru(dcbpy)$_2$(ecda) (———) and Ru(dcbpy)$_2$(tdt) (–·–).

will be high and similar for all the sensitized-TiO$_2$ electrodes studied.

The recombination rates of injected electrons with the oxidized dye is an important factor affecting electron collection efficiency ($\eta_c$). The recombination rates will increase with changing the oxidation values to more negative potential. After electron injection, a competition is set up between charge recombination and iodide oxidation by oxidized dye. Considering the relative driving forces of these complexes, the charge recombination rates will increase in the order Ru(dcbpy)$_2$(qdt) < Ru(dcbpy)$_2$(ecda) < Ru(dcbpy)$_2$(bdt) < Ru(dcbpy)$_2$(tdt). The low injection efficiency (IPCE$_{max}$ = 30%) of the Ru(dcbpy)$_2$(ecda) complex compared to the Ru(dcbpy)$_2$(qdt) complex can be explained by the fact that this complex has Ru$^{3+/2+}$ ground-state oxidation potential about 0.4 V more negative compared to those of the Ru(dcbpy)$_2$(qdt) complex and the back reaction of injected electrons with Ru(III) comes to compete with the regeneration of Ru(II) through reaction with iodide. This effect will become more predominant in the bdt and tdt complexes, where the Ru$^{3+/2+}$ potentials are very close to the I$_3^-$/I$^-$ redox couple. The ground-state potential of Ru(dcbpy)$_2$(ecda) (+0.46 V vs. SCE) offers a lower limit for the ground-state redox potential of the dye in the current configuration of the electrochemical cell and redox couple.

## 4. Ru(II) phenanthroline sensitizers with different number of anchoring groups

We have reported an efficient phenanthroline-based sensitizer, *cis*-bis(4,7-dicarboxy-1,10-phenanthroline)dithiocyanato ruthenium(II) (Ru(dcphen)$_2$(NCS)$_2$), when anchored to nanocrystalline TiO$_2$ films, achieves very efficient sensitization over the whole visible range, yielding 78% IPCE. A solar energy to electricity conversion efficiency of 6.6% was obtained under the standard AM 1.5 irradiation with a short-circuit photocurrent density of 12.5 mA cm$^{-2}$, an open-circuit photovoltage of 0.74 V, and a fill factor of 0.71 (Fig. 5) [35]. Ru(dcphen)$_2$(NCS)$_2$ contain four carboxyl groups attached to the phenanthroline ligand to ensure efficient adsorption of the dye on the surface of the amphoteric oxide TiO$_2$ and promote electronic coupling between the donor levels of the excited dye and the acceptor levels of the semiconductor for efficient electron injection. For further design of efficient Ru(II) polypyridyl sensitizers, especially to suppress dye aggregation, we have investigated the minimum number of carboxyl groups in phenanthroline-based Ru complexes that are necessary for efficient electron injection [35–37]. Four Ru phenanthroline complexes Ru(dcphen)$_2$(NCS)$_2$, Ru(dcphen)(phen)(NCS)$_2$, Ru(mcphen)$_2$(NCS)$_2$ and Ru(mcphen)(phen)(NCS)$_2$ where mcphen is 4-monocarboxy-1,10-phenanthroline and phen is 1,10-phenanthroline having carboxyl groups between 4 and 1 have been anchored to TiO$_2$ for cell performance studies (Scheme 3). Photochemical properties show that all
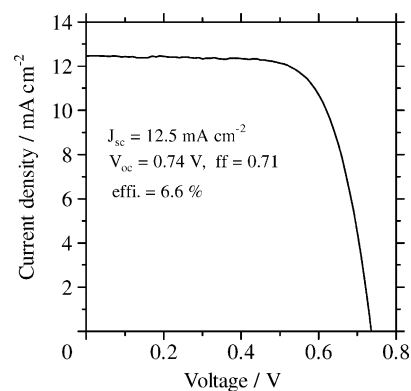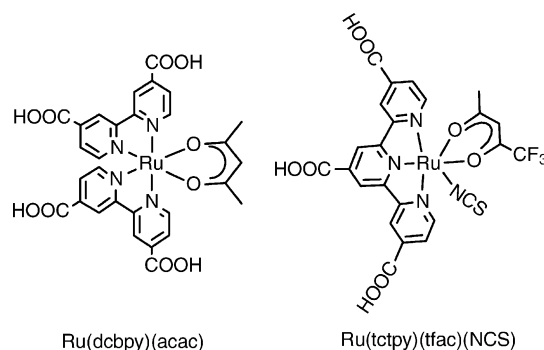


Fig. 5. Photocurrent–voltage characteristics of representative TiO$_2$ electrodes sensitized with dye: Ru(dcphen)$_2$(NCS)$_2$. Solar energy to electricity conversion efficiency is 6.6% with $J_{sc}$ of 12.5 mA cm$^{-2}$, $V_{oc}$ of 0.74 V, and $f_f$ of 0.71.



Scheme 3. Schematic molecular structures of Ru(dcbpy)$_2$(acac) and Ru(tctpy)(tfac)(NCS).

four complexes have favorable ground- and excited-state redox properties for electron injection and regeneration processes (Table 1). We found that Ru(dcphen)$_2$(NCS)$_2$, Ru(dcphen)(phen)(NCS)$_2$ and Ru(mcphen)$_2$(NCS)$_2$ with two or more anchoring groups show better cell performance than Ru(mcphen)(phen)(NCS)$_2$ with only one anchoring group. Transient absorption study show that the low cell efficiency of Ru(mcphen)(phen)(NCS)$_2$/TiO$_2$ solar cell is due to the presence of inactive dyes on the TiO$_2$ surface, which are not effective for electron injection.

## 5. Ru(II) dicarboxybipyridine sensitizers with chelating oxygen donor ligands

*cis*-Ru(dcbpy)$_2$(NCS)$_2$, which has two monodentate thiocyanate donor ligands exhibits high solar light-to-electrical energy conversion efficiency [8]. The presence of monodentate donor ligands (NCS$^-$) can undergo ligand photosubstitution or photodegradation reaction via population (populating) of an upper lying ligand field excited state and these processes can be reduced by multidentate ligands [38]. Bignozzi et al. and our group have utilized different
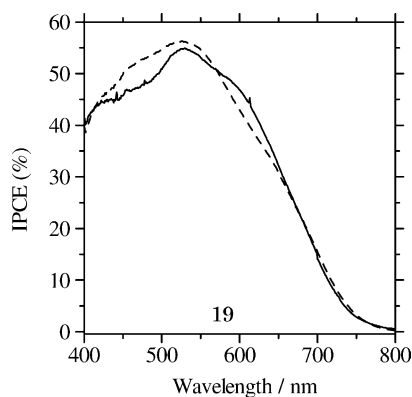
Fig. 6. Photocurrent action spectra of nanocrystalline TiO$_2$ films sensitized by complexes Ru(dcbpy)$_2$(NCS)$_2$ (—) and Ru(dcbpy)$_2$(acac) (———). The IPCE is plotted as a function of wavelength.

dithiocarbamates and dithiolates donor ligands as non-chromophoric chelating ligands to tune sensitizer absorption properties and efficiently sensitize TiO$_2$ beyond 700 nm [9,32]. We have reported a new series of novel bipyridine-ruthenium sensitizers of the type [Ru(dcbpy)$_2$(L)]Cl where L is one of the three β-diketonate ligands: acetylacetonate (acac), 3-methyl-2,4-pentanedionate (Meac), 1,3-diphenyl-1,3-propanedionate (dbmo) in place of two thio-cyanates as an ancillary ligand (Schemes 2 and 3) [23]. The strong β-donating nature of negatively charged oxygen donor destabilizes the ground-state energy level of the dye, leading to lower energy shift of MLCT transitions. This energy level can be further tuned by changing electron donor ability of three substituents on the ligand, therefore a desired electronic environment on the metal center is available. Moreover, chelating structure of this ligand makes the complex resistant towards ligand loss processes. The MLCT absorption maxima of β-diketonate complexes are red-shifted from that of thiocyanate complex cis-Ru(dcbpy)$_2$(NCS)$_2$ indicating high electron donating abilities of diketonate ligands (Table 1). The acetylace-tonate complex [Ru(dcbpy)(acac)]Cl, when anchored to nanocrystalline TiO$_2$ films, achieves very efficient sensiti-zation across the entire visible region, yielding 60% IPCE. The quantum yields exhibited by this sensitizer are well comparable to that obtained from the most efficient dithio-cyanate sensitizer cis-Ru(dcbpy)$_2$(NCS)$_2$, at every part of the spectra (Fig. 6). The diketonate complexes show quite high performance in photoelectrochemical cell. The overall solar light-to-electrical energy conversion efficiencies are in the range of 6.0–3.9%.

## 6. Recent development of Ru(II) tricarboxyterpyridyl sensitizers with chelating oxygen donor ligands

Molecular design of ruthenium(II) polypyridyl photosen-sitizers that can absorb visible light of all colors presents a challenging task. Grätzel and coworkers reported the most

successful CT sensitizer Ru(tctpy)(NCS)$_3$ (tctpy = 4, 4′,4″-tricarboxy-2,2′:6′,2″-terpyridine) which achieves 10% solar light to electricity conversion efficiency. The role of the monodentate thiocyanato ligands is to tune the spectral and redox properties of the sensitizers by destabilization of the metal t$_{2g}$ orbital. We have reported an efficient ruthe-nium(II) 4,4′-dicarboxy-2,2′-bipyridine sensitizer contain-ing one bidentate β-diketonato ligand [23]. Recently we have reported the synthesis and characterization of a new class of β-diketonato ruthenium(II) polypyridyl sensitizer of Ru(tctpy)(L)(NCS) type where L is 1,1,1-trifluoropentane-2,4-dionato (tfac) or 1,1,1-trifluoroeicosane-2,4-dionato (tfed) (Schemes 2 and 3) [39]. To suppress dye aggregation on TiO$_2$ films we have used long hydrocarbon substituted β-diketonate ligand 1,1,1-trifluoroeicosane-2,4-dione.

Both Ru(tctpy)(tfac)(NCS) and Ru(tctpy)(tfed)(NCS) exhibit an intense MLCT band at 610 nm with a distinct shoulder at 720 nm (Fig. 7). The enhanced red absorp-tion of these complexes renders them attractive candidates as a panchromatic CT sensitizer for TiO$_2$ solar cells. Ru(tctpy)(tfac)(NCS) achieved efficient sensitization of nanocrystalline TiO$_2$ solar cells over the whole visible range extending into the near IR region and displaying a maxi-mum around 600 nm, where IPCE approaches a high value of 70% in the presence of deoxycholic acid as coadsorbant (Fig. 8). The overlap integral of this curve with the stan-dard global AM 1.5 solar emission spectrum yields a pho-tocurrent density of 18 mA cm$^{-2}$ (Table 1). Under similar conditions, Ru(tctpy)(tfac)(NCS) shows higher IPCE values between 720 and 900 nm region than the Ru(tctpy)(NCS)$_3$ sensitizer. This result is consistent with the absorption spectra of these complexes. In the absence of additive both complexes produce about 3 mA cm$^{-2}$ lower photocurrents due to the formation of hydrogen-bonded aggregates on the TiO$_2$ surface. In contrast to Ru(tctpy)(tfac)(NCS) and Ru(tctpy)(NCS)$_3$, complex Ru(tctpy)(tfed)(NCS) shows higher value of photocurrent in the absence of deoxy-cholic acid. Presence of long hydrocarbon substituents in β-diketonato ligand helps to prevent surface aggregation
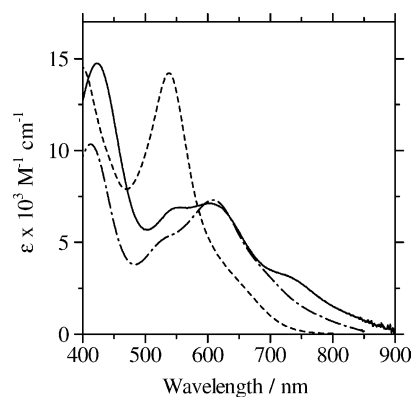


Fig. 7. Absorption spectra of Ru(dcbpy)$_2$(NCS)$_2$ (———), Ru(tctpy)(NCS)$_3$ (–·–) and Ru(tctpy)(tfac)(NCS) (—) in ethanol–methanol (4:1) solution at 298 K.
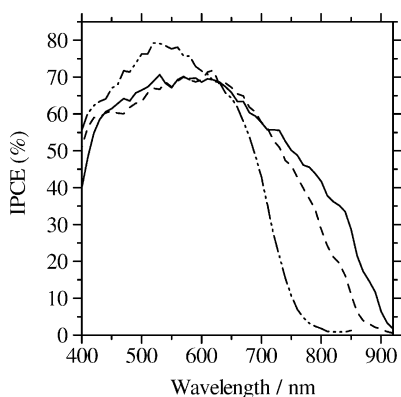
Fig. 8. Photocurrent action spectra of Ru(dcbpy)$_2$(NCS)$_2$ (———), Ru(tctpy)(NCS)$_3$ (–··–) and Ru(tctpy)(tfac)(NCS) (—) dyed films of TiO$_2$. The IPCE is plotted as a function of wavelength.

of the sensitizer. Since the modifications of electronic and steric environments in the sensitizing molecules are possible by changing the substituents on the diketonate ligand, further improvement in the solar cell efficiency will be accomplished in the near future.

## 7. Conclusions

The band selective electron injection yield (APCE) observed in dye cis-Ru(dcbiq)$_2$(NCS)$_2$/TiO$_2$ system suggests a very fast rate of electron injection to TiO$_2$, before the internal conversion event between the two lowest excited states. An efficient dye should possess suitable ground-state (0.5 V vs. SCE) and excited-state (−0.8 V vs. SCE) redox potentials to ensure fast charge injection and regeneration of the oxidized dye, respectively. Transient absorption study show that the low cell efficiency of Ru(mcphen)(phen)(NCS)$_2$/TiO$_2$ (one carboxyl group) is due to the presence of inactive dyes on the TiO$_2$ surface, which are not effective for electron injection. The β-diketonate complexes of [Ru(dcbpy)(β-diketonato)]Cl and Ru(tricarboxyterpyridine)(β-diketonato)(NCS) type, when anchored to nanocrystalline TiO$_2$ films, achieves very efficient sensitization of nanocrystalline TiO$_2$ solar cells over the whole visible range extending into the near IR region. Presence of long hydrocarbon substituents in β-diketonato ligand of Ru(tctpy)(tfed)(NCS) helps to prevent surface aggregation of the sensitizer. We have to modify the electronic and steric environments of the sensitizing dye carefully in order to develop high-performance solar cells.

## Acknowledgements

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