Improved performance of dye-sensitized solar cells by tuning the properties of ruthenium complexes containing conjugated bipyridine ligands

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Abstract

Three heteroleptic ruthenium complexes cis-[Ru(H₂dcbpy)(L)(NCS)₂], where H₂dcbpy is 4,4′-dicarboxy-2,2′-bipyridine and L is 4-(4-(N,N-di-(p-anisyl)amino)styryl)-4′-methyl-2,2′-bipyridine (Dye-1), 4-(4-(N,N-di-(p-hexyloxyphenyl)amino)styryl)-4′-methyl-2,2′-bipyridine (Dye-2) or 4-(5-(N,N-di-(p-hexyloxyphenyl)amino)-thiophene-2-yl-ethenyl)-4′-methyl-2,2′-bipyridine (Dye-3) have been synthesized and characterized. The influence of differently conjugated bipyridine ligands on these complexes was studied using UV-Vis spectroscopy and cyclic voltammetry. These heteroleptic complexes show appreciably broad absorption ranges and quite high extinction coefficients. These new dyes were used as photosensitizers in nanocrystalline TiO₂ dye-sensitized solar cells. It was found that the difference in light-harvesting property between Dye-1, Dye-2 and Dye-3 is associated mainly with molar extinction coefficients and alignment of the HOMO–LUMO energy levels. The power conversion efficiencies of solar cells based on Dye-1 and Dye-2 are 4.21% and 4.41%, while Dye-3 delivered a lower efficiency of 2.88% under the same device fabrication and measurement conditions.

Keywords: dye-sensitized solar cell, heteroleptic ruthenium complex, conjugated ligand, molar extinction coefficient, HOMO-LUMO energy level

Classification numbers: 2.03, 4.02, 5.04

1. Introduction

Dye-sensitized solar cells (DSSCs) are very promising types of organic photovoltaic cell due to their high efficiency and potential application as a low-cost technology for the conversion of light energy into electricity [1–5]. The properties of photosensitizers are one of the most important factors that influence the solar cell performance. Some polypyridine ruthenium (II) complexes have been used as efficient sensitzers because they have an intense metal-to-ligand charge transfer (MLCT) transition in the visible region to absorb the solar radiation. Another advantage of using ruthenium sensitzers is their relative stability in oxidized and reduced forms and the ease of tuning their spectral, photo-physical and electrochemical properties by introducing an appropriate ligand [6–12].

The best energy conversion for DSSCs has been developed by Grätzel and co-workers by employing cis-dithiocyanatobis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium (II) (known as N3 dye), giving broad absorption spectra in the visible region. They can produce solar energy to electricity conversion efficiencies (η) up to 11% under AM 1.5 G irradiation with a nanostructured TiO₂ electrode and iodine redox electrolyte [13–16].
Metal-complex sensitizers are usually designed with anchoring ligands and ancillary ligands. Anchoring ligands are responsible for grafting the dye on the semiconductor surface and providing intimate electronic coupling between their excited-state wave functions and the conduction band of the semiconductor. Ancillary ligands can be used for tuning the overall properties of the complexes.

To ensure fast and efficient electron injection, the energy levels of the dye—the lowest unoccupied molecular orbital (LUMO)—must be higher than that of the TiO$_2$ conduction band edge. To generate the neutral dye molecule, the highest occupied molecular orbital (HOMO) must align below the oxidation potential of the redox mediator. An understanding of the relative positions of the energy levels of the dye adsorbed on the semiconductor is useful for explaining the efficiency of electron transfer from the excited dye to the semiconductor and device performance.

Modification of the dye is one of the strategies to improve the performance of DSSCs. A possible way of finding new metal-complex sensitizers with good conversion efficiencies was investigated by attaching a $\pi$-conjugated group to the ancillary ligand. Replacement of one of the H$_2$dc bpy anchoring ligands with a highly conjugated ancillary ligand results in an increase of extinction coefficients and therefore the photocurrent density of the DSSCs [8, 17–19].

In this paper, we report the synthesis and photoelectrochemical properties of heteroleptic ruthenium complexes of type cis-[Ru(H$_2$dc bpy)(L)(NCS)$_2$]$_2$, where H$_2$dc bpy = 4, 4$'$-dicarboxy-2,2$'$-bipyridine and L = 4-(4-(N,N-di-(p- anisyl)amino)styryl)-4$'$-methyl-2,2$'$-bipyridine, 4-(4-(N,N-di-(p-hexyloxoyphenyl)amino)-styryl)-4$'$-methyl-2,2$'$-bipyridine, or 4-(5-(N,N-di-(p-hexyloxoyphenyl)amino)thiophen-2-yl-ethenyl)-4$'$-methyl-2,2$'$-bipyridine. Ligand L with extended $\pi$ conjugation in the new ruthenium complex acts as an ancillary ligand to tune the overall properties of the complex. These ligands contain both conjugated fragments and alkyl chains on the outer parts of the ancillary ligands. The photovoltaic performance of DSSCs based on these new complex dyes as photosensitizers is reported.

2. Experimental

2.1. Materials and instruments

All materials were reagent grade and were used as received. All synthetic reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified according to the published methods. N,N-di-p-anisylamine and N,N-di-p-hexyloxoyphenylamine were synthesized according to a procedure in the literature [22, 23]. TiO$_2$ nanoparticles were purchased from Solaronix S. A. (Solaronix-T, Lausanne, Switzerland). Fluorine-doped tin oxide (FTO) electrodes with a sheet resistance of 8 $\Omega$ per square were supplied from Samsung Corning Co., Korea.

$^1$H-NMR spectra were recorded on a Varian INOVA 400 MHz NMR spectrometer in CDCl$_3$ or (DMSO)-d$_6$. ESI-MS was performed on a HP 1100 LC/MS with acetonitrile as solvent and FAB-MS on a JMS-700 HRMS. Absorption spectra were recorded on a OPTIZEN 2120 UV-vis spectrophotometer. Electrochemical measurements were performed under a nitrogen atmosphere and the electrolyte used was 0.1 M tetrabutylammonium tetafluoroborate (Bu$_4$NB$_4$F$_4$) in acetonitrile. Cyclic voltammetry (CV) was recorded using a three-electrode system consisting of Ag/Ag$^+$ (0.01 M AgNO$_3$, 0.1 M Bu$_4$NB$_4$F$_4$, CH$_3$CN) as the reference electrode, a platinum wire as counter electrode and a FTO/TiO$_2$/Dye photoelectrode as the working electrode. All potentials are calibrated by the ferrocene/ferrocenium (Fe/Fe$^+$) couple potential ($E = +212$ mV versus Ag/AgNO$_3$).

2.2. The synthesis of ligands and ruthenium complexes

Dye-1, Dye-2 and Dye-3 were prepared by a one-pot synthetic route using ligand-1, ligand-2 and ligand-3. The procedure for preparing these dyes is shown in scheme 1 [24].

2.3. Fabrication of the DSSC devices

Photoanodes of the DSSCs were prepared from a colloidal suspension of nanosized TiO$_2$ particles (Nanoxide-T, Solaronix, average size 13 nm) by a doctor blade technique. The electrodes were sintered at 500$^\circ$C for 30 min in air to obtain TiO$_2$ films with a thickness of 8 $\mu$m measured by a Dektak 6M Stylus Profiler. These electrodes were immersed in solution containing 0.5 mM of Ruthenium dyes for one day while still hot (80$^\circ$C). Chenodeoxycholic acid (1 mM) was added into the dye solution as a coadsorbent to prevent dye aggregation [25]. The solvents for the dye solutions were DMF/t-BuOH (3:7, vv) for Dye-1 and CH$_3$CN/t-BuOH (1:1, vv) for N3, Dye-2 and Dye-3. Platinum-coated counter electrodes were obtained by spreading a drop of 5 $\times$ 10$^{-3}$ M H$_2$PtCl$_6$ (Fluka) solution in isopropanol on the surface of FTO glass and were treated in an oven at 400$^\circ$C for 15 min. The electrolyte was composed of 0.1 M lithium iodide, 0.1 M iodine, 0.5 M 4-tert-butylpyridine and 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide in acetonitrile. Photovoltaic characterization was carried out by illuminating the cell with a 1000 W Xenon lamp (Spectra-Physics) as a solar simulator. The light source was calibrated to 100 mW cm$^{-2}$ by a standard NREL Si solar cell equipped with a KG-5 filter to approximate AM 1.5G one sun light intensity. An active area of about 1 cm$^2$ was irradiated. Current–voltage curves were obtained by measuring the photocurrent of the cell using a Keithley mode 2400 digital source meter (Keithley, USA) under an applied external potential scan. IPCE values were measured as a function of wavelength from 300 nm to 800 nm using a specially designed IPCE system for DSSCs (PV Measurement, Inc.). A 75 W Xenon lamp was used as the light source for the generation of a monochromatic beam. Calibrations were performed with a silicon photodiode using a NIST-calibrated photodiode G425 as the standard and IPCE values were collected at a low chopping speed of 10 Hz.

The molecular structures of Dye-1, Dye-2 and Dye-3 and the preparation of ligands and complexes are given in scheme 1.
3. Results and discussion

3.1. $^1H$-NMR spectral data

The syntheses of conjugated ligands (ligand-1, ligand-2 and ligand-3) are based on a multi-step synthetic pathway, starting from N,N-di-p-anisylamine and N,N-di-p-(hexyloxy) phenylamine. The next reaction step involves the N-arylation of these amines with 4-bromobenzaldehyde (ligand-1 and ligand-2) and 5-bromo-2-thiophene carboxaldehyde (ligand-3). These ligands were synthesized by two steps: nucleophilic addition of the anion of dimethylbipyridine with aldehyde intermediates, followed by dehydration of the corresponding alcohol in refluxing acetic acid. Ruthenium complexes were synthesized in a one-pot synthesis starting from a dichloro(p-cymene)ruthenium (II) dimer in DMF for 13 h. The crude products were purified on a Sephadex LH-20 column using methanol as eluent. The $^1H$-NMR profiles of ruthenium complexes (figure 1) are complicated because of the presence of NCS ligands makes pyridine rings magnetically non-equivalent. Hence, the $^1H$-NMR spectra exhibit a total number of resonances equal to the total number of aromatic and heterocyclic protons in the complex. There are two 2,2'-bipyridine ligands in different electronic environments. As a result, they show resonance peaks in the aromatic region corresponding to four pyridine rings. The resonance peaks in the aliphatic region are due to methoxy and hexyloxy protons.

3.2. Absorption spectra

The absorption spectral data for Dye-1, Dye-2 and Dye-3 are shown in table 1 and figure 2(a). All the dyes show broad and intense visible bands between 393 and 526 nm which are due to metal-to-ligand charge transfer transitions (MLCT) [3, 15]. The absorption bands at about 300 nm are assigned to the intra ligand ($\pi-\pi^*$) transitions of bipyridine ligands. These
Figure 1. 1H-NMR spectra of Dye-1, Dye-2 and Dye-3 in (DMSO)-d6. For clarity, the peaks in the aliphatic region are not shown.

Table 1. Photophysical and electrochemical properties of Ruthenium Dyes 1–3 and N3.

|          | \(\lambda_{\text{max}}^{\text{MLCT}}/\text{nm} \times 10^3\) | \(\lambda_{\text{em}}^{\text{max}}/\text{nm}\) | HOMO \(a\) | LUMO \(b\) | \(E_{\text{gap}}\) \((\text{eV})\) |
|----------|---------------------------------------------------------------|------------------|-------------|-------------|----------------|
| Dye-1    | 526 (19.75)                                                   | 618              | -5.39       | -3.39       | 2.05           |
| Dye-2    | 526 (20.56)                                                   | 621              | -5.40       | -3.32       | 2.08           |
| Dye-3    | -                                                            | 625              | -5.26       | -3.25       | 2.01           |
| N3       | 530 (14.5)                                                    |                  | -5.52       | -3.84       | 1.68           |

\(a\)HOMO was calculated versus the vacuum level from the onset oxidation potential.

\(b\)Band gap was estimated from the intersection of absorption and emission spectra in DMF (excitation wavelength 325 nm).

results are in agreement with the homoleptic N3 dye. The absorption of Dye-1 exhibits three bands centered at 306, 429 and 526 nm. The band at 306 nm is assigned to the \(\pi-\pi^*\) transition of the ligand-centered transition due to dcbpy units. The second maximum at 429 nm is attributed to the \(\pi-\pi^*\) transition of the ligand-1 and one of the MLCT transitions for Dye-1. The absorption band at 526 nm corresponds to the MLCT caused by NCS ligands. Similar absorption bands can be obtained for Dye-2 with three bands at 304, 433 and 526 nm. In the case of Dye-3, only two distinct absorption bands could be observed: the band at 302 nm and a broad band from 480 to 540 nm.

The \(\pi\) delocalization in conjugated ligands (ligand-1, ligand-2 and ligand-3) creates an increase in the molar extinction coefficient for these dyes. Therefore, very high molar extinction coefficients of MLCT bands of 20 560 M\(^{-1}\)cm\(^{-1}\) \((526 \text{ nm})\) for Dye-2 in the visible region were obtained.

Figure 2(b) shows the absorption peak wavelengths of adsorbed dyes on TiO\(_2\) films. The enhanced absorptivity of these dyes compared to N3 was observed.

Figure 2. Absorption spectra of (a) N3, Dye-1, Dye-2 and Dye-3 in DMF (concentration: 1.23 \times 10^{-5} \text{M}) and (b) adsorbed on TiO\(_2\) films.

3.3. Energy levels

In order to design and synthesize suitable sensitizers for DSSCs, matching between the band structure of the metal complex and the energy level of the semiconductor electrode, the redox electrolyte or the hole conductor is very important. Indeed, the HOMO (highest occupied molecular orbital) level of the excited state of the dye should be well matched with the lower bound of the conduction band of TiO\(_2\) to ensure fast and efficient electron injection. Its redox potential should be sufficiently positive that it can be regenerated through electron donation from a redox couple, such as \(I^-/I^3^-\) [21].

Energy levels of the HOMO and LUMO (lowest unoccupied molecular orbital) derived from the oxidation potentials of metal complexes are displayed in table 1. The corresponding HOMO of Dye-3 (\(-5.26\text{ eV}\)) is higher in comparison with those of Dye-1 (\(-5.39\text{ eV}\)) and Dye-2 (\(-5.40\text{ eV}\)) with respect to zero vacuum energy level. It can be explained that Dye-3 carries an easily oxidizable ligand.

The HOMO levels of these dyes are much more negative than the conduction band level of TiO\(_2\). Therefore, their LUMO levels are sufficiently negative to inject electrons into the conduction band of TiO\(_2\). Table 1 also gives the band gap energy values obtained from CV results.
Dye-sensitized solar cells were prepared employing Dye-1, Dye-2 and Dye-3 and their performance was compared with the standard N3 dye. The current–voltage characteristics of these solar cells measured under AM 1.5G conditions are shown in figure 3(a). The detailed device parameters are summarized in table 2. Solar cells based on N3, Dye-1, Dye-2, and Dye-3 exhibit efficiencies of 3.86, 4.21, 4.41 and 2.88%, respectively. Both Dye-1 and Dye-2 show higher \( V_{OC} \) than that of N3. These enhanced IPCE values are mainly contributed by the high absorption coefficients of these complexes. The performance of the device using Dye-3 is unfortunately lower than that of N3. The thiophene moiety incorporated in ligand-3 results in lower power conversion efficiency although it shows better absorptivity than that of N3. The higher device efficiency of dye with a phenyl spacer than that with a thiethyl spacer is attributed to the more efficient charge transfer in the former. The use of appropriate co-adsorbents or solvent in the dye assembly process may be able to fix these defects and enhance performance of Dye-2. This work is in progress and the results will be reported elsewhere.

The high \( \eta \) values caused by higher values of \( J_{SC} \) are mainly contributed by the high absorption coefficients of these complexes. The performance of the device using Dye-3 is unfortunately lower than that of N3. The thiophene moiety incorporated in ligand-3 results in lower power conversion efficiency although it shows better absorptivity than that of N3. The higher device efficiency of dye with a phenyl spacer than that with a thiethyl spacer is attributed to the more efficient charge transfer in the former. The use of appropriate co-adsorbents or solvent in the dye assembly process may be able to fix these defects and enhance performance of Dye-2. This work is in progress and the results will be reported elsewhere.

Table 2. Photovoltaic performances of DSSCs based on N3, Dye-1, Dye-2 and Dye-3 under standard AM 1.5G spectral conditions and at 100 mW cm\(^{-2}\) light intensity. \( V_{OC} \): open circuit voltage; \( J_{SC} \): short circuit voltage; \( FF \): fill factor; \( \eta \): power conversion efficiency.

| Cell area (cm\(^2\)) | \( J_{SC} \) (mA cm\(^{-2}\)) | \( V_{OC} \) (V) | \( FF \) (%) | \( \eta \) (%) |
|---------------------|-----------------|--------------|-----------|-----------|
| N3                  | 1.052           | 10.17        | 0.618     | 0.613     | 3.86     |
| Dye-1               | 1.051           | 11.18        | 0.661     | 0.569     | 4.21     |
| Dye-2               | 1.030           | 12.35        | 0.644     | 0.555     | 4.41     |
| Dye-3               | 1.047           | 9.07         | 0.559     | 0.568     | 2.88     |

increase the lifetime of the electron on TiO\(_2\) (reducing the possibility of recombination of the electrons on TiO\(_2\) with the holes on the complex dye in excited state). Hydrophobicity is also important in designing new sensitizers for optimization of DSSCs. The Dye-2 dye contains only two carboxylic acids to facilitate least intermolecular hydrogen bondings. We found that the Dye-2-sensitized cell has a relatively lower fill factor compared to other dyes. This may due to the defects of the dye monolayer on the TiO\(_2\) electrode. The use of appropriate co-adsorbents or solvent in the dye assembly process may be able to fix these defects and enhance performance of Dye-2.

Figure 3. (a) Current density–voltage characteristics of DSSC devices with N3, HMP-1, HMP-2 and HMP-3 as photosensitizers under AM 1.5G (100 mW cm\(^{-2}\)) illumination (thickness of TiO\(_2\): 8 \( \mu \)m; cell active area: 1 cm\(^2\)), and (b) spectra of incident photon-to-current conversion efficiencies (IPCE) for DSSCs. Reference cell: Si solar cell calibrated from NREL.

### 3.4. Photovoltaic performance

The incident photon-to-current conversion efficiency (IPCE) spectra of Dye-1, Dye-2, Dye-3 and N3-sensitized solar cells are illustrated in figure 3(b). Broad bands cover almost the entire visible spectrum from 400 nm to 700 nm with maxima of 66.93% at 540 nm, 66.56% at 530 nm, 51.3% at 560 nm and 67.25% at 540 nm for Dye-1, Dye-2, Dye-3 and N3-sensitized solar cells, respectively. The IPCE values of N3, Dye-1 and Dye-2 are similar in the short wavelength range up to 550 nm. In long wavelengths Dye-2 shows higher IPCE values than those of these dyes. These enhanced IPCE values imply that good electronic coupling between the dye and...
TiO$_2$ electrode and the new sensitizer acts as a more efficient electron donor to the conduction band of TiO$_2$ films upon excitation. The IPCE values of the cells are slightly lower than the short circuit photocurrent density ($J_{SC}$) appearing in the $I-V$ characteristic curve because the light intensities used to measure these data are not the same (the incident light employed in IPCE measurement is not continuous and the intensity is lower).

4. Conclusions

Three heteroleptic ruthenium (II) complexes with conjugated bipyridine ligands were designed, synthesized and characterized by spectroscopic methods. The best synthesized dye named as Dye-2 shows power conversion efficiency 14% higher than that of N3 dye under the same cell fabrication and measurement procedures. It can be concluded that the relatively higher $J_{SC}$ value is due to the enhanced molar extinction coefficient facilitating a charge generation cascade that generally increases electron-hole separation by retarding the charge recombination. These dyes depend on both molar extinction coefficients and the localization of HOMO-LUMO energy levels. Further investigations on the design and synthesis of other structures of ruthenium complexes with rigid, electron-rich units attached on an ancillary ligand are in progress.

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