# Synthesis of New Ruthenium(II) Bipyridyl Complexes and Studies on Their Photophysical and Photoelectrochemical Properties

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Two new mixed-ligand ruthenium(II) complexes, Ru(dcbpy)-(LL)(NCS)$_2$[where dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine, LL = 4,4'-bis(N-methyl-anilinomethyl)-2,2'-bipyridine (1) or 4-methyl-4'-N-methyl-anilinomethyl-2,2'-bipyridine (2)], were synthesized, and the photophysical properties of these complexes were studied. The metal-to-ligand charge transfer (MLCT) transitions of these complexes exhibited solvatochromic effect due to the existence of NCS ligands. The MLCT energies also strongly depend on the pH values of the solutions because of protonation and deprotonation of the carboxyl groups. The p$K_a$ values of the ground state, 4.0 for 1 and 3.8 for 2, were obtained from the titration curves. The photoelectrochemical properties of 1 and 2 as sensitizers in sandwich-type solar cells have been studied. Complex 1 exhibited better photoelectrochemical behavior than complex 2 as expected. It was proved that the design of mixed-ligand complex by introducing electron donating group in one of the ligands should be a promising approach.

**Keywords**    ruthenium complex, photophysical property, solvatochromic effect

## Introduction

Dye-sensitized solar cells (DSSC) have become the focus of many investigations since Michael Grätzel and co-workers made the dye molecules adsorbed on a porous network of the interconnected nanometer-sized crystallines of a wide bandgap semiconductor.[1-3] An impressive solar-to-electrical energy conversion efficiency of 10% has been reported and it makes practical application feasible.[4] This system consists of a dye-coated semiconductor electrode and a counter electrode arranged in a sandwich configuration and the inter-electrode space is filled with an electrolyte containing a redox mediator (A/A$^-$). The Ru(II) polypyridyl complexes containing carboxyl groups are often used as the dyes, TiO$_2$ as the semiconductor, and (I$^-$/I$_3^-$) as the redox mediator.

In such a system, efficient solar energy conversion is connected with sufficient light absorption by the adsorbed dye molecules, efficient electron injection from the excited dye into the TiO$_2$ conduction band and efficient reduction of the oxidized dye by the redox mediator. Therefore it is crucial to choose a suitable dye. The Ru(II) polypyridyl complexes containing 4,4'-dicarboxyl-2,2'-bipyridine (dcbpy) and NCS ligands have become the optimized sensitizers due to their good stability, suitable ground- and excited-state properties, suitable redox properties and the intense light harvest abilities in the visible region.

The photophysical properties of the ruthenium complexes reflect how the complexes behave as sensitizers in a DSSC device. They are connected with the conversion efficiency of the solar cells directly. So detailed studies on the photophysical properties of such complexes are of fundamental interest in order to elucidate how various environmental factors can be used to modulate photoelectrochemical process. Almost all the photophysical properties of the ruthenium complexes are related to their metal-to-ligand charge transfer (MLCT) transitions. The MLCT bands resulting from Ru(II) $t_{2g} \rightarrow \pi^*$ (ligand) transitions dominate almost all the visible region in the absorption spectra and they can be tuned by changing the microenvironment around the molecule. Specific interactions between the complex and the medium can influence both the MLCT transition energies and redox potentials in a significant way. A number of papers dealing with medium effects such as changing solvent polarity[5-7] or pH of the solution[8-10] on the photophysical properties of the polypyridyl ruthenium complexes have been reported.

In the present paper, the synthesis and characterization of two new sensitizers Ru(dcbpy)(LL)(NCS)$_2$[where dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine, LL = 4,4'-bis-(N-methyl-anilino-methyl)-2,2'-bipyridine (1) or 4-methyl-4'-N-methyl-anilinomethyl-2,2'-bipyridine (2)] are reported (Scheme 1). In these senstizers, an electron donating group, N-methyl-aniline, was introduced. In principle, the redox potentials of this type of complex can be modulated in a certain range by varying substituent on

the aniline. At the same time, it was expected that the existing of the electron donating group can decrease the rate of recombination from the conduction band to the oxidized sensitizers or to the electrolyte.[11] The carboxyl group, in addition to acting as an anchoring group to the surface of $TiO_2$, also provides an orbital basis for direct electronic coupling with the surface of $TiO_2$.[12] The NCS ligand can make the MLCT bands red-shifted and enhance the visible absorption of the complex. The influences of pH value of solution and solvent polarity on the photophysical properties of these two complexes have been discussed. The photoelectrochemical performance of 1 and 2 as charge-transfer photosensitizers in nanocrystalline $TiO_2$-based solar cells were investigated and complex 1 exhibited better photoelectrochemical behavior than complex 2 as expected. It was proved that the design of mixed-ligand complex by introducing electron donating groups in one of the ligands should be a promising approach.

**Scheme 1**



1: $R^1 = R^2 =$   2: $R^1 = H, R^2 =$
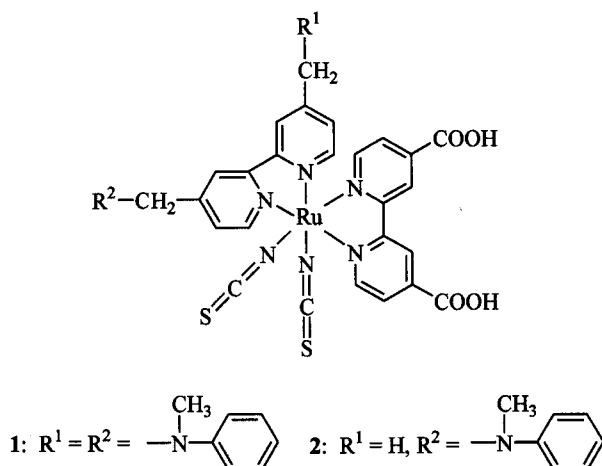
## Experimental

### Analytical measurements

$^1H$ NMR spectra were recorded on a Bruker DPX-400 (400 MHz) FT-NMR spectrometer using TMS as internal reference. Elemental analyses were conducted with an Italian Carloerba 1160 elemental analyzer. UV/visible spectra were recorded on a SHIMADZU UV-1601PC spectrophotometer at 298 K.

The pH values were determined using a pH glass electrode as working electrode and a saturated calomel electrode as reference on an ordinary pHS-3C pH meter after calibrating with standard pH solutions. The titration curve was made by UV-vis measurements over the pH range of 2.7—11. The stock solutions ($5 \times 10^{-5}$ mol/L, 100 mL) of 1 and 2 were prepared respectively in water by adding 10 mL of DMSO to avoid precipitation of the complex. 0.01 mol KCl was added to the solutions to keep constant ionic strength. The initial pH of the solutions was adjusted to 11 by adding 0.1 mol/L NaOH solutions. The

acidity of the solutions was adjusted by the addition of $H_2SO_4$ solutions. The acid was added in such a way that throughout the entire measurement the changes of the volume can be negligible. After each addition of acid, the solutions equilibrated for 5 min before measuring. Estimated errors are as follows: absorption maxima, $\pm 1$ nm; $pK_a$, $\pm 0.1$.

Photoelectrochemical experiments were carried out on a sandwich-type solar cell. A 450 W xenon lamp was used as light source and the incident light intensity was 60 mW/$cm^2$. Open circuit photovoltages and short circuit photocurrents were recorded with 179 Digital Multimeter. The dye-sensitized nanocrystalline $TiO_2$ electrodes were used as the working electrode and a platinized $SnO_2$ conducting glass as the counter electrode. The electrolyte consisting of LiI (0.1 mol/L), $I_2$(0.1 mol/L), 1-methyl-3-ethylimidazole (0.6 mol/L), 4-tert-butylpyridine (0.5 mol/L) in methoxypropionitrile solvent was introduced into the interelectrode space. The $TiO_2$ working electrodes were prepared using a reported technique.[12] The adsorption of the dyes was completed by dipping the freshly prepared nanocrystalline $TiO_2$ electrodes which was still warm (ca. 80 ℃) into a $5 \times 10^{-4}$ mol/L dye solution of absolute ethanol for at least 15 h.

### Materials

All chemicals were of reagent grade and without further purification before use. Hydrated ruthenium trichloride and 4,4'-dimethyl-2,2'-bipyridine were obtained from Aldrich. 4,4'-Dicarboxylic-2,2'-bipyridine,[13] 4,4'-dibromomethyl-2,2'-bipyridine and 4-methyl-4'-bromo-methyl-2,2'-bipyridine[14] and Ru(DMSO)$_4$Cl$_2$[15] were prepared by reported methods.

### Synthesis of 4,4'-bis (N-methyl-anilinomethyl)-2,2'-bipyridine (LL$_1$)

4, 4'-Dibromomethyl-2, 2'-bipyridine (0.342 g, $1 \times 10^{-3}$ mol) and N-methyl-aniline (0.26 mL, $2.4 \times 10^{-3}$ mol) were combined in 10 mL of dimethyl formamide (DMF). The mixture was refluxed for 20 h under $N_2$. After the solution was cooled, the solvent was evaporated under reduced pressure. The final product was purified by using column chromatography with basic alumina (200—300 mesh) as the solid support and hexane/EtOAc (9:1, $V:V$) as eluent. The second fraction was collected and evaporated to give LL$_1$(0.32 g, 81%). $^1H$ NMR (CDCl$_3$, 400 MHz) $\delta$: 8.61 (d, 2H), 8.38 (s, 2H), 7.26 (d, 2H), 7.21—7.25 (m, 4H), 6.77—6.72 (m, 6H), 4.63 (s, 4H), 3.10 (s, 6H).

### Synthesis of 4-methyl-4'-N-methyl-anilinomethyl-2,2'-bipyridine (LL$_2$)

LL$_2$ was synthesized by the same procedure for LL$_1$ except that 4-methyl-4'-bromomethyl-2, 2'-bipyridine was

used. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 8.59 (d, 1H), 8.55 (d, 1H), 8.33 (s, 1H), 8.24 (s, 1H), 7.24—7.16 (m, 4H), 6.77—6.72 (m, 3H), 4.62 (s, 2H), 3.11 (s, 3H), 2.46 (s, 3H).

## Synthesis of Ru(dcbpy)(DMSO)$_2$Cl$_2$

Ru(DMSO)$_4$Cl$_2$ (0.242 g, $5 \times 10^{-4}$ mol) and dcbpy (0.122 g, $5 \times 10^{-4}$ mol) were combined in 20 mL of DMF. The reaction mixture was refluxed under N$_2$ for 4 h, and then cooled to room temperature. The solvent was removed under vacuum, and the residue was redissolved in acetone to remove the unreacted materials. Massive diethyl ether was added to the solution to precipitate the target complex. The precipitate was filtered and dried (0.22 g, 77%). Anal. calcd for C$_{16}$H$_{20}$N$_2$O$_6$S$_2 \cdot$ RuCl$_2 \cdot$ 2H$_2$O: C 31.58, H 3.95, N 4.60; found C 31.61, H 3.90, N 4.63.

## Synthesis of Ru(dcbpy)(LL$_1$)(NCS)$_2$(1)

The complex Ru(dcbpy)(DMSO)$_2$Cl$_2$(0.190 g, 2.5 $\times 10^{-4}$ mol) and LL$_1$(0.098 g, $2.5 \times 10^{-4}$ mol) were dissolved in 20 mL of DMF. The reaction flask was wrapped with aluminum foil and refluxed under N$_2$ for 6 h. KNCS (0.458 g, $5 \times 10^{-3}$ mol) was dissolved in 2 mL of distilled water and then transferred to the reaction mixture. The reaction was continued for another 6 h. After cooled to room temperature, the mixed solvents were removed under vacuum. The residue was redissolved in 10 mL of 0.2 mol/L NaOH to give a dark purple solution with some suspension. The solution was filtered, the pH of the filtrate was lowered to about 2 by adding dilute CF$_3$SO$_3$H solution to give a dense precipitate. The solid was collected, washed with water (3 $\times$ 10 mL) and dried under vacuum (yield 0.162 g, 76%). $^1$H NMR ($d_6$-DMSO, 400 MHz) $\delta$: 9.41 (d, 1H), 9.10 (d, 1H), 9.07 (s, 1H), 8.92 (s, 1H), 8.52 (s, 1H), 8.38 (s, 1H), 8.26 (d, 1H), 7.83 (d, 1H), 7.75 (d, 1H), 7.62 (d, 1H), 7.36 (d, 1H), 7.23—7.21 (m, 2H), 7.07—7.09 (m, 2H), 6.84—6.92 (m, 3H), 6.61—6.71 (m, 4H), 4.90 (s, 2H), 4.67 (s, 2H), 3.17 (s, 3H), 2.96 (s, 3H). Anal. calcd for C$_{40}$H$_{34}$N$_8$O$_4$S$_2 \cdot$ Ru $\cdot$ 3H$_2$O: C 52.81, H 4.40, N 12.32; found C 52.75, H 4.36, N 12.25.

## Synthesis of Ru(dcbpy)(LL$_2$)(NCS)$_2$(2)

Complex 2 was synthesized by the same procedure as 1 except that LL$_2$ was used. $^1$H NMR ($d_6$-acetone, 400 MHz) $\delta$: 9.66 (d, 1H), 9.35 (d, 1H), 9.11 (s, 1H), 8.95 (s, 1H), 8.76 (s, 1H), 8.50 (s, 1H), 8.32 (d, 1H), 7.95 (d, 1H), 7.83 (d, 1H), 7.76—7.72 (m, 2H), 7.68—7.61 (m, 5H), 7.08 (d, 1H), 5.30 (s, 2H), 3.66 (s, 3H), 2.69 (s, 3H). Anal. calcd for C$_{33}$H$_{27}$N$_7$O$_4$S$_2 \cdot$ Ru $\cdot$ 2H$_2$O: C 50.38, H 3.94, N 12.47; found C 50.32, H 3.89, N 12.51.

## Results and discussion

### Synthesis

Compared with the synthetic route using [Ru(CO)$_2$Cl$_2$]$_n$[16] as a precursor to synthesize the mixed-ligand Ru(II) bipyridine complex, these two complexes were synthesized in fewer steps and higher yields utilizing Ru(DMSO)$_4$Cl$_2$ as a precursor by stepwise assembly. It provides a general process for synthesizing mixed-ligand ruthenium bipyridine complexes. This type of mixed-ligand complexes kept the carboxyl group as an anchoring group to the surface of TiO$_2$. On the other hand, their properties can be modulated by the other ligand that is different from the dcbpy ligand. For obtaining a higher yield, the sequence of coordination is crucial. The successive coordination of the electron acceptor dcbpy, the donor LL, and then the NCS ligand should be better than other coordinating orders because the coordination ability of the donor LL is stronger than that of the acceptor ligand such as dcbpy ligand. Single crystals of these two complexes were not obtained in our experiment although a variety of methods have been attempted.

### Absorption properties

Fig. 1 shows the absorption spectra of 1 in different solvents. There are two broad and intense bands in the region of 350—650 nm due to the well-known MLCT transitions involved in the dcbpy ligand. The MLCT transitions based on the Ru(II) $t_{2g} \rightarrow \pi^*$ (LL$_1$) are not so evident and only appear as a shoulder at 480 nm in THF. At the same time, the MLCT bands based on the Ru(II) $t_{2g} \rightarrow \pi^*$ (dcbpy) become broad compared with those of other complexes containing only one type of ligand and the region between the two MLCT bands trends to a platform. This phenomenon can be originated from the overlap of the MLCT bands based on dcbpy and LL$_1$ ligand respectively, and it will benefit the light harvest. The MLCT transitions are solvent sensitive and the lowest energy MLCT band shifts
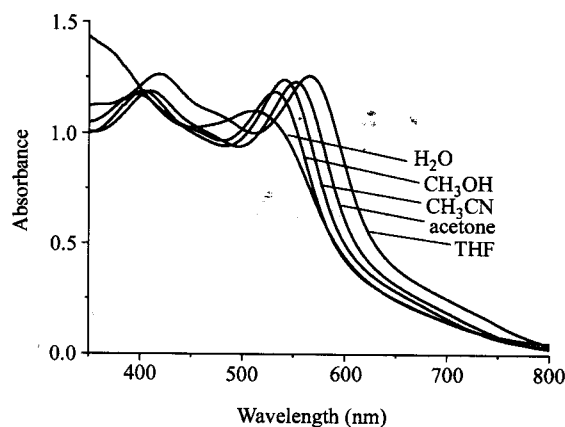


**Fig. 1**    Absorption spectra of 1 in different solvents (2.47 $\times$ 10$^{-4}$ mol/L).

about 50 nm on going from water to THF for these two complexes (Table 1). This solvatochromic effect can be caused by two factors. One is the donor-acceptor interaction between the solvent molecules and the lone pair electrons of the thiocyanate sulfur.[17] Many complexes of Ru(II) containing CN or SCN ligand have this property.[18] The other is that the solvents with different dielectric constants have different stabilizations on the ground and excited states of such complexes.[19]

**Table 1**  Absorption spectral properties of **1** and **2** in different solvents at room temperatue

| Solvent | Absorption max (nm) | | Dielectric constant |
|---|---|---|---|
| | **1** | **2** | |
| $H_2O$ | 510 | 512 | 100 |
| $CH_3OH$ | 531 | 527 | 33.1 |
| $CH_3CN$ | 541 | 536 | 37.5 |
| DMSO | 542 | 537 | 46.7 |
| $CH_3COCH_3$ | 552 | 545 | 20.7 |
| THF | 565 | 563 | 7.6 |

*Acid/base dependence of the absorption spectra and determination of the ground-state $pK_a$ values*

When dissolved in aqueous solutions, the ground-state absorption spectra of these two complexes are strongly dependent upon the acidity of the medium. Fig. 2(a) shows the absorption spectra of **1** in aqueous solutions as a function of pH. The observed spectral changes are completely reversible. When the pH of the solution is lowered, the lowest energy MLCT band shifts from 508 nm to 534 nm. This phenomenon can be assigned to the existence of the carboxyl group in **1**, because the protonation and deprotonation of the carboxyl group will affect the LUMO of this ligand.[20] At low pH, the protonation of the carboxyl group renders the dcbpy ligand a better π acceptor, so the MLCT transition energy is lowered. On the contrary, at high pH, the anionic form of the dcbpy ligand would raise the $\pi^*$ orbital energy, so the MLCT transition would be blue-shifted. Upon lowering pH of the solution, both the intraligand transition $(\pi \to \pi^*)$ at 300 nm which is assigned to the $LL_1$ ligand and the shoulder at about 310 nm which is dcbpy based lose intensity and slightly shift to low energy. These changes verify that new forms of this complex with different extinct coefficients appear within the pH region.

In Fig. 2(a), among pH 11—3.7, there are two distinct isobestic points at 530 nm for MLCT transition and at 312 nm for intraligand transition respectively. The isobestic points verify the existence of two species in this pH region, which are assigned to the monoprotonated and deprotonated forms of the complex. Below pH 3.7, the spectra traced off the above isobestic points. Another set of isobestic points which belong to the diprotonated and monoprotonated forms of **1** should appear, but upon de-

creasing pH of the solution, the precipitation of the diprotonated forms of **1** becomes apparent, so the second set of isobestic points can not be observed.[21]
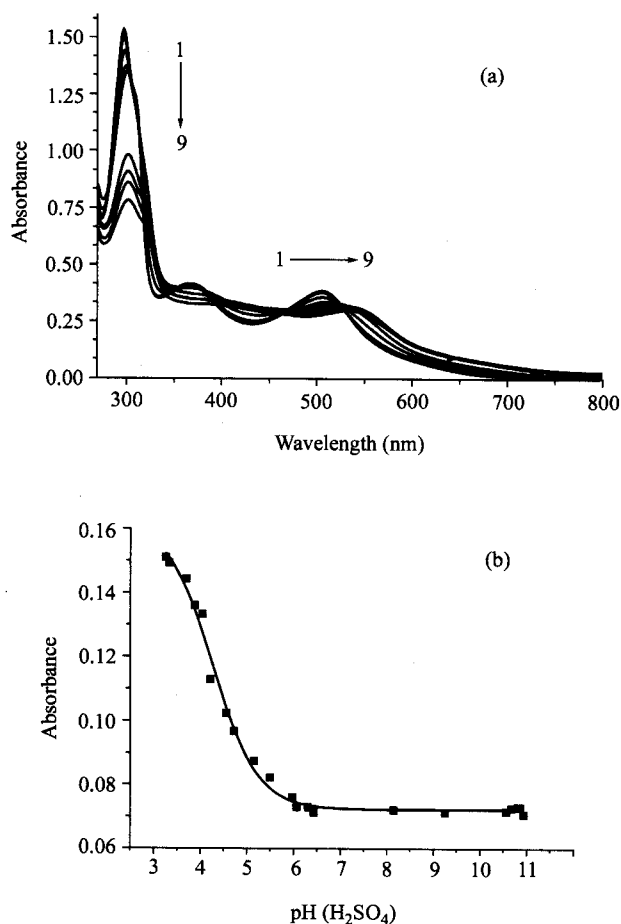


**Fig. 2**  (a) Absorption spectra of **1** in aqueous solutions with various pH values. From 1 to 9: 11; 6.4; 5.5; 4.7; 4.2; 3.7; 3.6; 3.3; 3.1. (b) Absorbance changes of **1** at 606 nm as a function of pH value from 11 to 3.1.

The $pK_a$ values can be obtained from titration curve,[22] which reflect the relationship between the absorbance at a given wavelength and pH of the aqueous solution. Fig. 2(b) shows the expected sigmoidal curve by plotting the absorbance changes of **1** at 606 nm versus pH. Over the pH range of 11—6.0, the absorption spectra are pH independent. But below pH 6.0, lowering of pH leads to significant spectral changes. There is a clear inflection point at pH 4.0, which is assigned to the $pK_{a2}$ of the dcbpy ligand (Scheme 2). The $pK_{a1}$ of the dcbpy ligand can not be obtained because of the precipitation of the diprotonated forms of **1**. In the experiment, the $pK_a$ belonging to the acid-base equilibrium of aniline in $LL_1$ ligand can not be observed by this spectrophotometric method. The methylene group in $LL_1$ ligand weakens the electronic communication between the bipyridyl and aniline moiety, so the protonation and deprotonation of aniline has only little effect on the UV-visible absorption spectrum.

**Scheme 2**

$$Ru(COO^-)_2 + H^+ \xrightarrow{pK_{a2}} Ru(COOH)(COO^-)$$

$$Ru(COOH)(COO^-) + H^+ \xrightarrow{pK_{a1}} Ru(COOH)_2$$
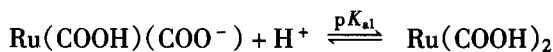
The obtained $pK_{a2}$ 4.0 of **1** is attributed to the carboxyl group of the pyridine moiety that is *trans* to the NCS ligand because this pyridine moiety is more basic due to the $\pi$-back-donation of Ru(II), which is caused by the stronger electron-donating property of NCS ligand. The $pK_a$ of the carboxyl moiety in dcbpy ligand is more acidic than that of the free ligand $(pK_{a2} = 4.2)$.[23] This suggests that the coordination of the ligand reduces the electron density of the carboxyl moiety, resulting from the electrostatic interaction effect by the coordination of the ligand to the ruthenium center.

Protonation and deprotonation of **2** also affect its absorption spectra strongly (Fig. 3(a)). Upon lowering pH of the solution from 10.5 to 2.7, the lowest energy MLCT band shifts from 499 nm to 525 nm. In the UV region, the $\pi \rightarrow \pi^*$ transitions also lose intensity and slightly shift to low energy. Two isobestic points at 524 nm and 313 nm among pH 8.8—3.6 were also observed and they were attributed to the absorption of the deprotonated and monoprotonated forms of **2**. The absorption changes at 570 nm as
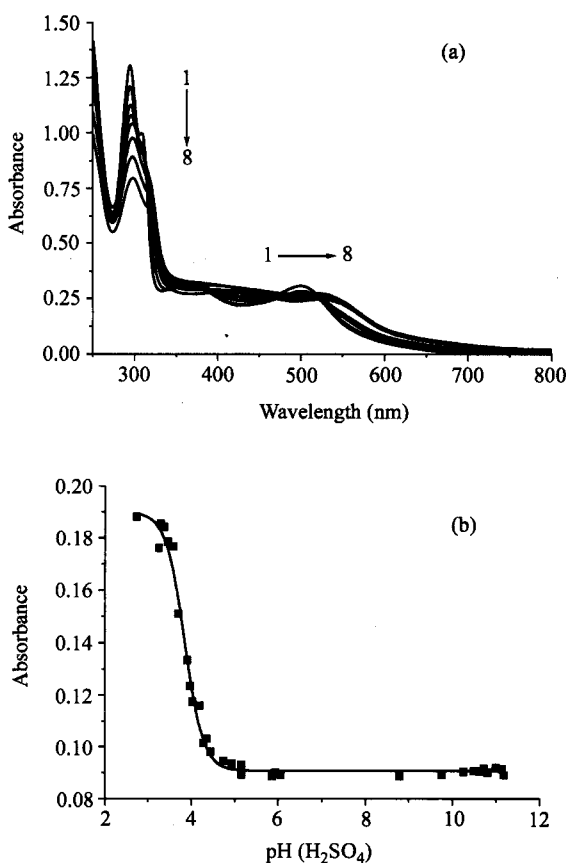


**Fig. 3**  (a) Absorption spectra of **2** in aqueous solutions with various pH values. From 1 to 8: 8.8; 4.4; 4.0; 3.9; 3.6; 3.3; 3.2; 2.7. (b) Absorbance changes of **2** at 570 nm as a function of pH value from 10.5 to 2.7.

a function of pH value from 2.7 to 10.5 yielded the ground state $pK_{a2}$ value as 3.8 (Fig. 3 (b)). As what happened on **1** at lower pH, the precipitation of the diprotonated forms of **2** made it impossible to obtain its $pK_{a1}$ value. The $pK_{a2}$ values obtained above for **1** and **2** were 4.0 and 3.8 respectively. The stronger basicity of **1** can be attributed to the fact that the electron-donating ability of the two aniline groups in **1** is much stronger than that of **2**, and there is only one aniline group in this complex. The stronger electron-donating ability increased the electron density on the carboxyl group of **1** and thus made it more basic.

*Photoelectrochemical properties*

The photoelectrochemical properties of **1** and **2** as sensitizers in sandwich-type solar cells have been studied. The current-voltage characteristics obtained under irradiation of 60 $mW/cm^2$ white light from a 450 W xenon lamp are shown in Fig. 4 and Table 2.
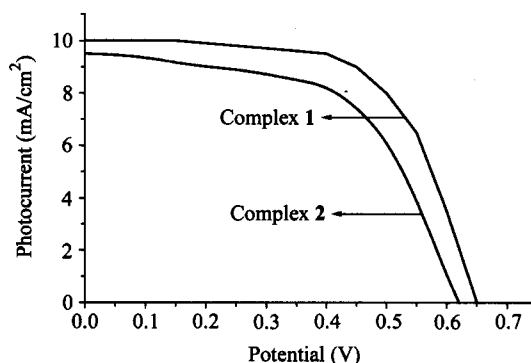


**Fig. 4**  Photocurrent-voltage curves of complex **1** and **2** as sensitizers for a sandwich-type solar cell. Conditions are as follows: electrolyte, 0.1 mol/L LiI, 0.1 mol/L $I_2$, 0.6 mol/L 1-methyl-3-ethylimidazole, 0.5 mol/L 4-*tert*-butyl-pyridine in methoxylpropionitrile; light intensity, 60 $mW/cm^2$; size of $TiO_2$ electrode, 0.2 $cm^2$.

**Table 2**  Results of photovoltaic measurements of complexes **1** and **2**

| Sensitizer | $I_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $ff$ | $\eta$ (%) |
|---|---|---|---|---|
| 1 | 10 | 0.65 | 0.64 | 7.0 |
| 2 | 9.5 | 0.62 | 0.60 | 5.9 |

It was found that for complex **1**, a short-circuit photocurrent $(I_{sc})$ of 10 mA/cm$^2$ and an open-circuit voltage $(V_{oc})$ of 0.65 V were obtained. The fill factor $(ff)$ and overall conversion efficiency $(\eta)$ was 0.64 and 7.0% respectively. Under the same condition, for complex **2**, $I_{sc} = 9.5$ mA/cm$^2$, $V_{oc} = 0.62$ V, $ff = 0.60$, $\eta = 5.9\%$. The photoelectrochemical behavior of complex **1** as sensitzer was slightly better than that of complex **2**. In complex Ru(dcbH)$_2$(bpy-PTZ)$^{2+}$, where PTZ is phenothiazine, the observation of the absorption of PTZ$^+$ following electron injection into $TiO_2$ confirms the intramolecular

electron transfer from PTZ to Ru(III).[11] So the possible reason for the result obtained should be that two electron donating groups in complex 1 is more efficient in decreasing the rate of recombination than that of 2. It also proved that the design of mixed-ligand complex by introducing an electron donating group in one of the ligands should be a promising approach. Varying substituent on the aniline group can modulate the redox properties of this kind of complex and it give a possible access to improve the photo-electrochemical behavior of these complexes. The further studies on the complexes with different substituents on the aniline group are in progress.

## Conclusions

Two new ruthenium bipyridyl complexes with good yields were designed and synthesized in fewer steps. Their photophysical properties in different solvents and at different pH values were studied. The ground state $pK_a$ values for 1 and 2 were 4.0 and 3.8 respectively. The photoelectrochemical properties of 1 and 2 as senstizers in a DSSC device were also investigated and an overall conversion efficiency of 7.0% and 5.9% for 1 and 2 respectively was obtained. As it was expected, the complex 1 with two electron donating groups exhibited more efficient photoelectrochemical behavior than complex 2 which has only one electron donating group.

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