Photoinduced intra-molecular electron transfer in aniline-containing Ru(II) polypyridine complexes

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Abstract

The photoinduced intra-molecular electron transfer in three aniline-containing Ru(II) polypyridine complexes, [Ru(bpy)$_2$(bpy-bmam)] (PF$_6$)$_2$ (**2**), Ru(dcbpy)(bpy-bmam)(NCS)$_2$ (**3**), and Ru(dcbpy)(bpy-mam)(NCS)$_2$ (**4**) (bpy-bmam = 4,4′-bis(*N*-methyl-anilinomethyl)-2,2′-bipyridine, bpy-mam = 4-methyl-4′-(*N*-methyl-anilinomethyl)-2,2′-bipyridine, dcbpy = 4,4′-dicarboxyl-2,2′-bipyridine, bpy = 2,2′-bipyridine), was investigated using steady-state and time-resolved absorption and emission spectra, and photoinduced inter-molecular electron transfer between [Ru(bpy)$_2$(dmbpy)](PF$_6$)$_2$ (**1**) (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) and *N,N*-dimethylaniline was also studied for comparison. While inter-molecular reductive quenching of **1**'s emission by aniline was less efficient, nearly half emission was quenched intra-molecularly in **2**. Upon photoinduced electron injection onto the conduction band of TiO$_2$ from **3** or **4** anchored on the TiO$_2$ surface, intra-molecular electron transfer from aniline moiety to Ru(III) orbital occurred rapidly with rate constants of 3.4×10^7 and $2.6 \times 10^7\,\mathrm{s^{-1}}$, respectively, restricting the interfacial recombination of injected electrons with Ru(III) and as a result improving the photoelectrochemical behavior of **3** or **4** when used in dye-sensitized nanocrystalline semiconductor solar cells.
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1. Introduction

Dye-sensitized nanocrystalline semiconductor solar cells (DSSC) based on Ru(II) polypyridine complexes and TiO$_2$ have been investigated widely and intensively over the past decades due to their simple fabrication technique, low cost, high photoelectric conversion efficiency and long term stability [1–4]. In DSSC Ru(II) polypyridine complexes absorb sunlight to reach excited state, from which they inject electrons onto the conduction band of nanocrystalline TiO$_2$ and transform to oxidized state. The oxidized Ru(II) polypyridine complexes are then reduced to the ground state by I$^-$ present in the electrolyte filled between the TiO$_2$ photoanode and Pt-loaded cathode, while the consumed I$^-$ nearby the photoanode is regenerated via the reduction of I$_3^-$ at cathode by electrons injected from excited dyes, collected at the back contact of the photoanode, and finally transported

to the cathode through the external load. One of the factors limiting the photoelectric conversion efficiency of DSSC is the interfacial recombination of injected electrons in TiO$_2$ conduction band with oxidized Ru(II) polypyridine complexes. To restrict such recombination process, Bignozzi and Argazzi [5] synthesized a novel Ru(II) polypyridine complex, in which phenothiazine (PTZ), a well known electron donor, was appended onto a bipyridine ligand. The strategy underlying the design of this sensitizer was to vectorially translate the "hole" away from the interface by intra-molecular electron transfer as shown in Scheme 1. Compared to PTZ-modified bipyridine, aniline-attaching bipyridine, in principle, can provide a wide range of redox potentials and systematic variation in the driving force for electron transfer by changing substituents on the aniline [6]. We recently synthesized two new Ru(II) polypyridine complexes, Ru (dcbpy)(LL)(NCS)$_2$, where LL is 4,4′-bis(*N*-methyl-anilinomethyl)-2,2′-bipyridine (bpy-bmam) for **3** and 4-methyl-4′-(*N*-methyl-anilinomethyl)-2,2′-bipyridine (bpy-mam) for **4**, respectively (dcbpy = 4,4′-dicarboxyl-2,2′-bipyridine, see Scheme 2) [7]. A DSSC based on **3** exhibited higher photoelectric conversion efficiency than that

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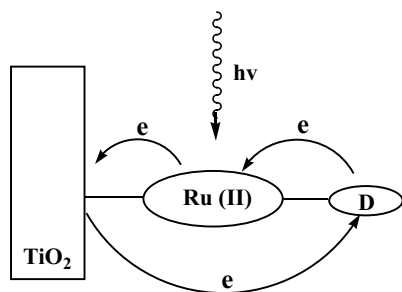
Scheme 1.

of **4**, which was ascribed to a more efficient intra-molecular electron transfer between aniline and Ru(II) polypyridine chromophore occurred in **3** due to the presence of two donor groups [7]. In this paper, time-resolved spectrum techniques were applied to study the intra-molecular electron transfer in **3** and **4** immobilized on nanocrystalline TiO$_2$. Moreover, two model complexes [Ru(bpy)$_2$(dmbpy)](PF$_6$)$_2$ (**1**) and [Ru(bpy)$_2$(bpy-bmam)](PF$_6$)$_2$ (**2**) (bpy = 2,2′-bipyridine, dmbpy = 4,4′-dimethyl-2,2′-bipyridine, see Scheme 2) were also studied to give a clear picture on the inter- and intra-molecular electron transfer between aniline and Ru(II) polypyridine chromophores.

2. Experimental

2.1. Materials

Acetonitrile of spectrophotometric grade (Aldrich) and unhydrous methanol and ethanol of analytical grade were used as received. *N,N*-dimethylaniline (Aldrich) was

redistilled prior to use. Colloidal TiO$_2$ (anatase) paste with particle diameter of 13 nm was purchased from Solaronix, SA, Switzerland. The fluorine-doped SnO$_2$ conductive glass has a sheet resistance of 20 Ω and a transmission of 80%.

The preparation and characterization of complexes **3** and **4** were reported previously [7]. Complexes **1** and **2** were synthesized following reference method [8] and identified by ^{1}H NMR.
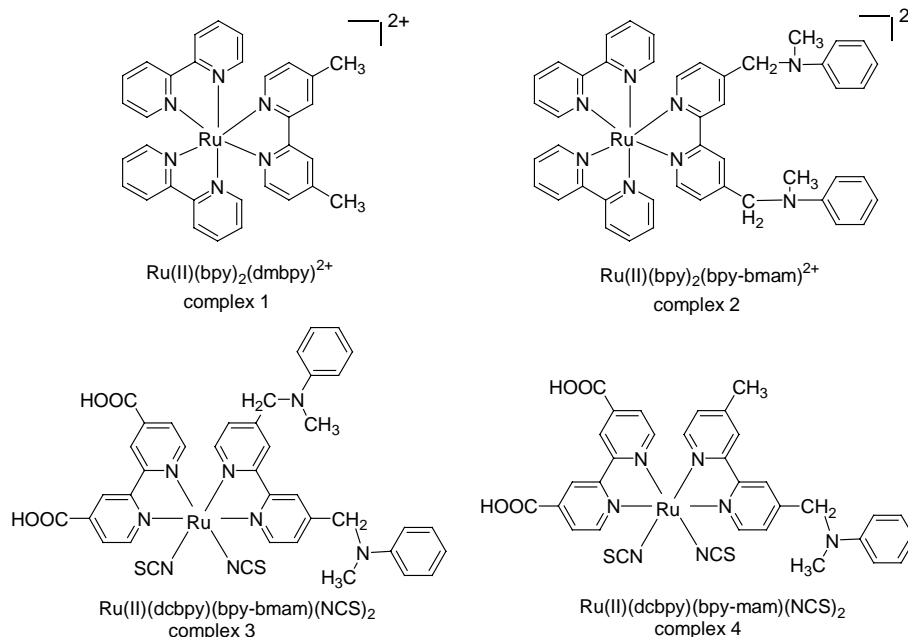
[Ru(bpy)$_2$(dmbpy)](PF$_6$)$_2$ (**1**) ^{1}H NMR (d$_6$-acetone, 300 MHz) δ: 8.81 (d, 4H), 8.68 (s, 2H), 8.18 (t, 4H), 8.04 (t, 4H), 7.83 (d, 2H), 7.58 (m, 4H), 7.39 (d, 2H), 2.56 (s, 6H).

[Ru(bpy)$_2$(bpy-bmam)](PF$_6$)$_2$ (**2**) ^{1}H NMR (d$_6$-acetone, 300 MHz) δ: 8.78 (d, 2H), 8.76 (d, 2H), 8.64 (d, 2H), 8.19 (t, 2H), 8.16 (t, 2H), 7.98 (t, 4H), 7.83 (d, 2H), 7.55 (t, 2H), 7.53 (t, 2H), 7.35 (d, 2H), 7.16 (t, 4H), 6.70 (d, 4H), 6.67 (t, 2H), 4.78 (s, 6H), 3.02(s, 4H).

A reported method [2] was used to prepare dye-sensitized TiO$_2$ electrodes. Briefly, colloidal TiO$_2$ paste was applied and then uniformly spread on conductive glass with a glass rod. After calcined at 450 °C for 30 min, it was put into an unhydrous ethanol solution of complex **3** or **4** (5 × 10^{-4} mol l^{-1}) while it was hot (80 °C) and soaked for 8 h. Then it was washed with unhydrous ethanol to remove Ru complex not adsorbed firmly on TiO$_2$ and dried at ambient temperature.

2.2. Measurements and instrumentation

^{1}H NMR spectra were taken on a Varian DPX-300 FT-NMR spectrometer. UV-Vis absorption spectra were recorded with a SHIMADZU UV-1601PC spectrophotometer. Steady-state fluorescence emission spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer.

Ru(II)(bpy)$_2$(dmbpy)$^{2+}$
complex 1

Ru(II)(bpy)$_2$(bpy-bmam)$^{2+}$
complex 2

Ru(II)(dcbpy)(bpy-bmam)(NCS)$_2$
complex 3

Ru(II)(dcbpy)(bpy-mam)(NCS)$_2$
complex 4

Scheme 2.

Luminescence lifetime was measured on a Horiba NAES-1100 spectrophotometer using single photon counting technique. Redox potentials were obtained on an EG & G Model 283 Potentiostat with cyclic voltammetry. Nanosecond flash photolysis studies were made with the second harmonic of a YAG laser ($\lambda_{ex} = 532$ nm, 8 mJ per pulse). A pulsed xenon lamp was used as the probe source traveling in small angle geometry relative to the excitation light. The transmitted light passing through the sample was fractioned through a multichromator and was detected by an OMA-III system. The time resolved emission spectra were measured as follows: a regenerative amplifier Ti:sapphire laser (Tsunami, Spectra Physics) pumped by a mode-locked argon ion laser (Beamlock, Spectra Physics) was used as a light source. The wavelength of the system was tuned from 800 to 513 nm by OPA (OPA-800C, Spectra Physics) (FWHM = 120 fs, 1 KHz, 0.5 mJ). The resulting fluorescence was collected into a multichromator (Hamamatsu C5094) and detected with a streak camera (Hamamatsu C2909). The instrumental response time was about 30 ps.

3. Results and discussion

3.1. Photoinduced inter-molecular electron transfer between complex 1 and N,N-dimethylaniline

Fig. 1 shows the UV-Vis absorption spectrum of complex **1**, in which a typical metal-to-ligand charge transfer (MLCT) transition in the visible region and bipyridine ligand-based $\pi \rightarrow \pi^*$ transition with maximum at 290 nm can be resolved distinctly. Excitation upon MLCT band can produce a strong luminescence originating from ^{3}MLCT emission (Fig. 2). In the presence of N,N-dimethylaniline the ^{3}MLCT emission was quenched and the quenching behavior followed Stern–Volmer equation (Eq. (1) and Fig. 3) [9]:
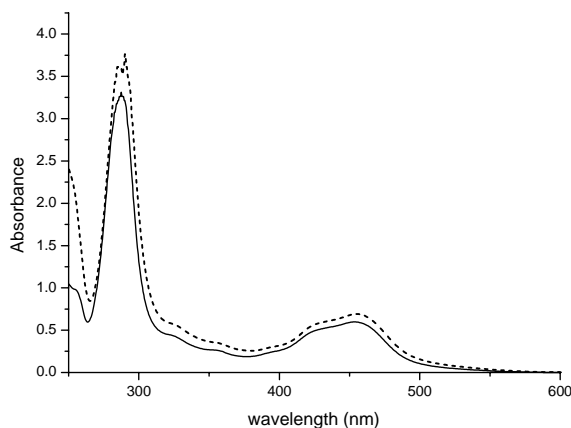
$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \tag{1}$$
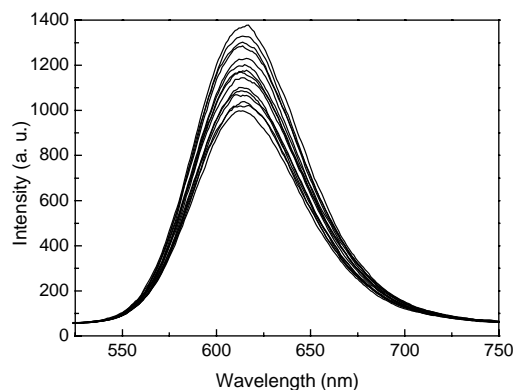

Fig. 2. Emission spectra of complex **1** ($\lambda_{ex} = 460$ nm) in the presence of varied concentration of (0–0.64 mol l^{-1}) N,N-dimethylaniline in acetonitrile.

where I_0 and I are, respectively, the emission intensity of the luminophore solution before and after the addition of quencher, $[Q]$ is the quencher's concentration, k_q the bimolecular quenching constant, and τ_0 is the luminescence lifetime of the luminophore. Thus, k_q is calculated to be 7.1×10^5 mol l^{-1} s^{-1} from the slope (0.58 mol l^{-1}) by taking $\tau_0 = 820$ ns (measured with single photon counting technique). However, the emission quenching was not very efficient and only 28% was quenched at a relatively high concentration (0.64 mol l^{-1}) of N,N-dimethylaniline.

The emission quenching can be ascribed to the reduction of excited complex **1** by N,N-dimethylaniline, which is thermodynamically favored by 0.18 eV, taking 0–0 transition energy of ^{3}MLCT to be 2.24 eV (estimated from the onset of ^{3}MLCT emission), oxidation potential of N,N-dimethylaniline and reduction potential of complex **1** to be 0.71 and -1.35 V versus SCE, respectively (measured with cyclic voltammetry). The similar reductive quenching of MLCT emission was also observed in a related Ru complex, [Ru(4,4′-(C(O)NEt$_2$)$_2$bpy)$_2$(dmb-tol)]$^{2+}$, where dmb-tol is 4-methyl-4′-(N-methyl-p-tolylaminomethyl)-2,2′-bipyridine [6].

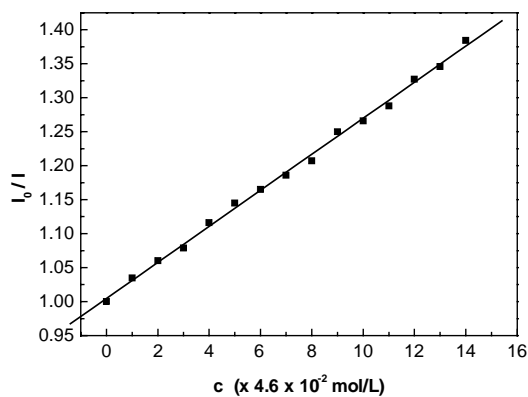Fig. 1. Absorption spectra of complex **1** (solid line) and **2** (dashed line) in methanol.

Fig. 3. Stern–Volmer plot of the luminescence quenching of complex **1** by N,N-dimethylaniline.
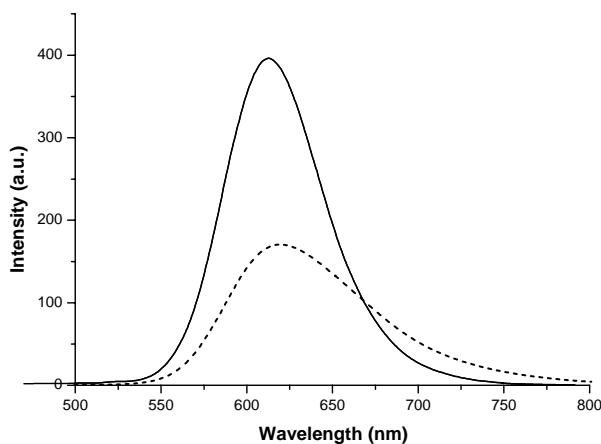
Fig. 4. Emission spectra of complexes **1** (solid line) and **2** (dashed line) in acetonitrile ($\lambda_{ex} = 460\,nm$).

3.2. Photoinduced intra-molecular electron transfer in complex 2

Complex **2** has a UV-Vis spectrum very similar to complex **1** (Fig. 1), indicating a negligible interaction between [Ru] moiety and aniline groups in the ground state. The luminescence spectrum of **2** is also very similar to but much lower in intensity than that of **1** (Fig. 4). Given the luminescence quantum yields of **1** and **2** are 0.084 and 0.047, respectively, the intra-molecular quenching efficiency is 44%, much higher than the case of inter-molecular quenching mentioned above, probably due to the vicinity of electron donor and acceptor in space.

Time-resolved emission spectra provide more evidence on the intra-molecular reductive quenching occurred in complex **2**. Intensity-normalized time-resolved emission spectra for complex **1** at varied delay time upon pulsed excitation at 460 nm are shown in Fig. 5, which are exactly superimposable, indicating there is no change in the emitting species with time. The emission intensity decayed mono-exponentially with a lifetime of 831 ns, in good agreement with the lifetime of 820 ns measured with
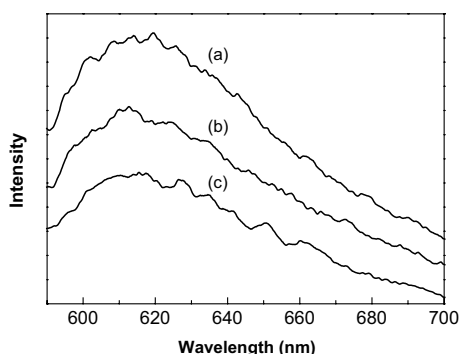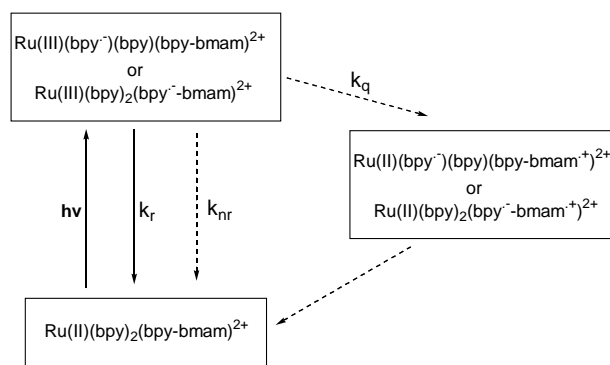

Scheme 3.

single photon counting technique. The same feature was observed in time-resolved emission spectra of complex **2**, however, the emission decayed more rapid with a lifetime of 336 ns. Thus, the non-radiative decay rate constant (k_q) via reductive quenching process as illustrated in Scheme 3 has a value of $1.8 \times 10^6\,s^{-1}$, assuming the same intrinsic radiative (k_r) and nonradiative (k_{nr}) decay rate constants in **2** as in **1** ($k_r = 1.0 \times 10^5\,s^{-1}$, $k_{nr} = 1.1 \times 10^6\,s^{-1}$).

3.3. Photoinduced intra-molecular electron transfer in complexes 3 and 4 adsorbed on TiO₂

The photophysical and photoelectrochemical properties of complexes **3** and **4** have been investigated in detail previously [7] and **3** exhibited better photoelectrochemical behavior (I_{sc} (short−circuit current) $= 10\,mA/cm^2$, V_{oc} (open−circuit voltage) $= 0.65\,V$, ff (fill factor) $= 0.64$, and η (overall photoelectric conversion efficiency) $= 7.0\%$) than **4** ($I_{sc} = 9.5\,mA/cm^2$, $V_{oc} = 0.62\,V$, ff $= 0.60$, and $\eta = 5.9\%$) in DSSC under white light irradiation (60 mW/cm²), which was attributed to the more efficient intra-molecular electron transfer occurred in **3** due to the presence of two aniline groups, though no direct spectroscopic evidence was provided at that time. Fig. 6 shows

Fig. 5. Intensity normalized time-resolved emission spectra of complex **1** ($\lambda_{exc} = 460\,nm$) in ethanol:methanol solution (4:1) at room temperature measured with the following delay/gate width settings: (a) 0.73 μs/100 ns; (b) 0.96 μs/100 ns; (c) 1.42 μs/100 ns.
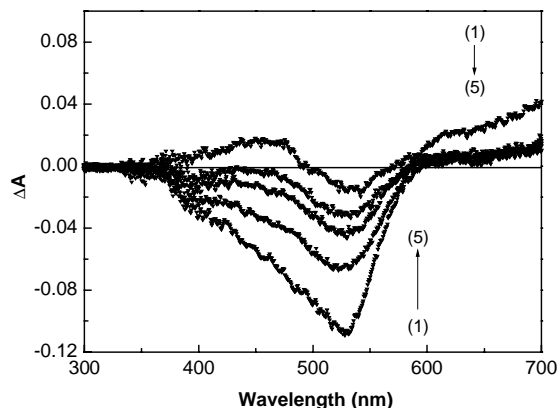

Fig. 6. Transient absorption spectra following pulsed laser excitation (532 nm) of complex **3** adsorbed on TiO₂ electrode immersed in neat acetonitrile with delay as follows: (1) 200 ns; (2) 800 ns; (3) 1800 ns; (4) 3800 ns; (5) 15 500 ns.

the transient absorption spectra of complex **3** adsorbed on TiO$_2$ electrode upon excitation at 532 nm. Lots of studies on ultra-fast processes in dye-sensitized nanocrystalline semiconductor electrodes have vindicated that electron injection from excited Ru(II) complexes to TiO$_2$ conduction band occurred in sub-ps–ps range [4,10–13], much faster than other excited state processes such as radiative decay, non-radiative decay, and intra- or inter-molecular electron transfer with electron donors or acceptors. The comparable photoelectrochemical properties of **3** and **4** with the well known Ru(dcbpy)$_2$(NCS)$_2$ suggest that an ultra-fast electron injection still occurred in **3** or **4**-adsorbed TiO$_2$. Thus, the transient absorption spectra in the early stage can be ascribed to the oxidized **3** (Ru(III)(dcbpy)(bpy-bmam)(NCS)$_2$) exclusively, which has a very strong bleaching band in 400–600 nm region due to the depletion of ground state **3**. The no observation of a positive absorption below 400 nm, a typical absorption of ^{3}MLCT state of Ru(II) polypyridine complexes originating from the bipyridine ligand-based anion [14,15], further confirmed that complex **3** had transformed to its oxidized state. On the other hand, the recombination of injected electrons with oxidized Ru complexes proceed in microsecond region due to the poor coupling between Ru(III) dπ orbital and the conduction band and the too large driving force falling in the Marcus inverted region [4]. However, the oxidized **3** decayed biexponentially (monitored at 508 nm) with a long lifetime of 1.65 μs (25%) and a very short lifetime of 29 ns (75%). Considering the presence of aniline groups in **3**, the fast decay may be ascribed to the recovery of ground state **3** by intra-molecular electron transfer with rate constant of $3.4 \times 10^7 \, \mathrm{s}^{-1}$. This assumption was confirmed by the appearance of a new positive band centered at 470 nm at delay time of 15.5 μs, which can be assigned as the absorption of aniline cation, similar to both dmb-tol$^+$ spectrum with $\lambda_{max} = 478$ nm and $\varepsilon = 4200 \, \mathrm{M}^{-1} \, \mathrm{cm}^{-1}$ at room temperature [6], and *N,N*-dimethylaniline cation spectrum generated at low temperatures [16,17]. The so delayed observation of the aniline cation is not surprising because the bleach of the MLCT state at 470 nm is far more intense ($\varepsilon = 1 \times 10^4 \, \mathrm{mol} \, \mathrm{l}^{-1} \, \mathrm{cm}^{-1}$). The slow decay may then be reasonably attributed to the recovery of ground state **3** via recombination of the injected electrons.

The transient absorption spectra of complex **4** adsorbed on TiO$_2$ is similar to that of **3** and the ground state **4** recovered biexponentially as well with time constants of 1.58 μs (25%) and 39 ns (75%). The fast recovery process may also be the result of intra-molecular electron transfer ($2.6 \times 10^7 \, \mathrm{s}^{-1}$), which proceeded less rapidly than that in **3**, consistent with the presence of one aniline group only in **4**.

As a result, the photophysical processes followed the excitation of **3** or **4** anchored onto the TiO$_2$ surface by carboxylic groups can be illustrated as follows. Upon absorption of 532 nm light, **3** or **4** was excited to the MLCT state, where an electron in Ru dπ orbital jumped into the π^* orbital of dcbpy ligand because the presence of two electron-withdrawing carboxylic groups make dcbpy-based π^* orbital the LUMO [6,18] and injected an electron from dcbpy π^* orbital onto the conduction band of TiO$_2$. Then the oxidized **3** or **4** was reduced to the ground state **3** or **4** by either aniline group intra-molecularly and rapidly or injected electron interfacially and slowly. The intra-molecular electron transfer between [Ru(III)] and aniline moieties moved the hole away from the TiO$_2$ electrode and therefore restricted interfacial recombination of injected electrons with [Ru(III)] and improved the photoelectrochemical properties.

4. Conclusion

Steady-state and time-resolved absorption and emission spectrum measurement clearly disclosed the photoinduced inter- and intra-molecular electron transfer between Ru(II) polypyridine complexes and aniline, which occurred more efficiently in intra-molecular case. When happened intra-molecularly in a Ru(II) polypyridine complex adsorbed on TiO$_2$ surface, it can effectively compete the interfacial recombination of the injected electrons in TiO$_2$ conduction band with oxidized Ru complexes. Such a process can be utilized in the design of dye molecules to improve photoelectrochemical properties in their application in DSSC.

References

[1] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO$_2$ films, Nature 353 (1991) 737–739.

[2] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, Conversion of light to electricity by *cis-X$_2$*bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) charge-transfer sensitizers ($X = $ Cl$^-$, Br$^-$, I$^-$, CN$^-$ and SCN$^-$) on nanocrystalline TiO$_2$ electrodes, J. Am. Chem. Soc. 115 (1993) 6382–6390.

[3] M.K. Nazeeruddin, P. Pechy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, Engineering of efficient panchromatic sensitizers for nanocrystalline TiO$_2$-based solar cells, J. Am. Chem. Soc. 123 (2001) 1613–1624.

[4] K. Kalyanasundaram, M. Grätzel, Applications of functionalized transition metal complexes in photonic and optoelectronic devices, Coord. Chem. Rev. 77 (1998) 347–414.

[5] C.A. Bignozzi, R. Argazzi, Long-lived photoinduced charge separation across nanocrystalline TiO$_2$ interfaces, J. Am. Chem. Soc. 117 (1995) 11815–11816.

[6] C.M. Partigianoni, S. Chodorowski-Kimmes, J.A. Treadway, D. Striplin, S.A. Trammell, T.J. Meyer, A new electron-transfer donor for photoinduced electron transfer in polypyridyl molecular assemblies, Inorg. Chem. 38 (1999) 1193–1198.

[7] L.Q. Song, P.H. Xie, X.S. Wang, Y.J. Hou, B.W. Zhang, Y. Cao, W.Y. Li, J.B. Zhang, X.R. Xiao, Y. Lin, Synthesis of new ruthenium(II) bipyridyl complexes and studies on their photophysical and photoelectrochemical properties, Chin. J. Chem. 21 (2003) 644–649.

[8] S. Anderson, E.C. Constable, K.R. Seddon, J.E. Baggott, M.J. Pilling, Preparation and characterization of 2,2′-bipyridine-4,4′-disulphonic and -5-sulphonic acids and their ruthenium(II) complexes. Excited-state properties and excited-state electron-transfer reactions of ruthenium(II) complexes containing 2,2′-bipyridine-4,4′-disulphonic acid or 2,2′-bipyridine-4,4′-dicarboxylic acid, J. Chem. Soc. Dalton Trans. (1985) 2247–2261.

[9] N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings Publishing Co. Inc., Menlo Park, CA, 1978, p. 314.

[10] J.B. Asbury, R.J. Ellingson, H.N. Ghosh, S. Ferrere, A.J. Nozik, T. Lian, Femtosecond IR study of excited-state relaxation and electronic injection dynamics of $Ru(dcbpy)_2(NCS)_2$ in solution and on nanocrystalline TiO_2 and Al_2O_3 thin films, J. Phys. Chem. B 103 (1999) 3110–3119.

[11] Y. Tachibana, S.A. Haque, I.P. Mercer, J.R. Durrant, D.R. Klug, Electron injection and recombination in dye sensitized nanocrystalline titanium dioxide films: a comparison of ruthenium bipyridyl and porphyrin sensitizer dyes, J. Phys. Chem. B 104 (2000) 1198–1205.

[12] G. Benko, J. Kallioinen, J.E.I. Korppi-Tommola, A.P. Yartsev, V. Sundstrom, Photoinduced ultrafast dye-to-semiconductor electron injection from nonthermalized and thermalized donor states, J. Am. Chem. Soc. 124 (2002) 489–493.

[13] P. Piotrowiak, E. Galoppini, Q. Wei, G.J. Meyer, P. Wiewior, Subpicosecond photoinduced charge injection from molecular tripods into mesoporous TiO_2 over the distance of 24 angstroms, J. Am. Chem. Soc. 125 (2003) 5278–5279.

[14] P.S. Braterman, A. Harriman, G.A. Heath, L. Yellowless, The electronic absorption spectrum and structure of the emitting state of the Tris(2,2′-bipyridyl)ruthenium(II) complex ion, J. Chem. Soc. Dalton Trans. (1983) 1801–1803.

[15] B. Gholamkhass, K. Koike, N. Negishi, H. Hori, T. Sano, K. Takeuchi, Adjacent-versus remote-site electron injection in TiO_2 surfaces modified with binuclear ruthenium complexes, Inorg. Chem. 42 (2003) 2919–2932.

[16] K.P.J. Williams, R.E. Hester, Free radical studies by resonance raman spectroscopy: photochemically generated para-substituted aniline cation radicals, J. Raman Spectrosc. 10 (1981) 169–172.

[17] Y.L. Chow, W.C. Danen, S.F. Nelson, D.H. Rosenblatt, Nonaromatic aminium radicals, Chem. Rev. 78 (1978) 243–274.

[18] P. Chen, K.M. Omberg, D.A. Kavaliunas, J.A. Treadway, P.A. Palmer, T.J. Meyer, Insights on the excited state electronic structures of ruthenium(II) polypyridine complexes obtained by step-scan Fourier transform infrared absorption difference time-resolved spectroscopy, Inorg. Chem. 36 (1997) 954–955.