LETTERS

Excited-State Relaxation Dynamics of Ru(dcbpy)$_2$(NCS)$_2$, Studied by Fluorescence Upconversion Spectroscopy

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Excited-state relaxation dynamics of a ruthenium-based dye (Ru(dcbpy)$_2$(NCS)$_2$) has been investigated by femtosecond fluorescence upconversion spectroscopy. Understanding the dynamics of excited-state relaxation in this sensitizer molecule is of key importance in designing efficient photochemical storage devices. This letter presents the first direct observation of the singlet emissive state in this dye in solution, upon excitation at 410 nm. The Franck−Condon excited state is observed to decay fast (43 ± 10 fs) in ethanol and is attributed to a highly competitive intersystem crossing (ISC) and relaxation to the lowest singlet state (internal conversion, IC). From the kinetics recorded at different wavelengths, it proposed that the excited molecule undergoes a cascade relaxation along the multitude of electronic singlet levels, with a high chance for the ISC. The lifetime of some of the singlet states has been evaluated as 43 ± 10, 87 ± 13, and 162 ± 40 fs at 600, 650, and 700 nm, respectively. The results have been discussed in comparison with the report on [Ru(bpy)$_3$]$^{2+}$ and gives first-hand information about the intriguing excited-state relaxation process in the RuN3 complex.

Introduction

Inorganic compounds have long been exploited in the study of photoinduced charge-transfer processes, as well as in the quest for achieving efficient solar energy conversions.[1] Focus has been on the development of panchromatic sensitizers based on ruthenium metal complexes and their deployment in the dye-sensitized solar cell assembly.[2] Molecular engineering of such complexes that can act as panchromatic charge-transfer sensitizers for nanocrystalline semiconductor-based solar cells present a challenging task because several requirements, which are often very difficult to be met, must be fulfilled by the sensitizer.[2] The electrochemical, photophysical, ground-state, and excited-state properties of the sensitizer dye have an important role in the charge-transfer dynamics at the semiconductor interface. Generally, the metal complexes possess various types of excited states, which differ in their orbital parentage, localization within the molecule, energy, dynamics, and reactivity.[1f] Unlike organic molecules, the optical transitions in metal complexes are mainly of the metal-to-ligand charge transfer (MLCT), ligand-centered (LC), and ligand-to-metal charge transfer (LMCT) transition types, all of which have decisive roles in the formulation of the course of the excited-state chemistry. Because the electron injection process competes with the intramolecular vibrational relaxation, internal conversion (IC), intersystem crossing (ISC), interligand electron transfer (ILET) processes, etc. in the sensitizer itself, a thorough knowledge of these relaxation processes is essential in designing efficient photochemical storage devices.[1−6]

Recently, many groups have been focusing their attention on such fundamental aspects of the sensitization process involving metal complexes and subsequent dynamics both in the semiconductor and the sensitizer dye.[7−16] Among various sensitizer

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dyes, ruthenium bipyridyl/terpyridyl complexes, especially Ru-(dcbpy)$_2$(NCS)$_2$ (where dcbpy is 4,4′-dicarboxy 2,2′-bipyridine, popularly known as "RuN3" dye), has been established as one of the most efficient sensitizers for use in solar cells.[2,3] Several ultrafast studies have reported nonexponential electron injection from RuN3 to semiconductor nanoparticles with time constants ranging from ~20 fs to ~50 ps.[7−15] Recently, it has been proposed, in a thin film of RuN3-sensitized TiO$_2$, that some of the electron injection proceeds extremely rapidly from the initially populated, vibronically nonthermalized, singlet excited state, prior to electronic and nuclear relaxation of the sensitizer molecule.[9] However, despite the active role of RuN3 in the energy storage technology, very few studies have been devoted to the understanding of its early time dynamics, with hardly any reports on its singlet excited states.[9,17] Studies performed on a prototype ruthenium complex, [Ru(bpy)$_3$]$^{2+}$, have had a pivotal role in the development of inorganic photochemistry. Recent ultrafast time-resolved experiments conducted on [Ru(bpy)$_3$]$^{2+}$ have been successful in unveiling the early time excited-state dynamics of such metal complexes, to a certain extent.[18,19] In this work, we have attempted to contribute to the understanding of the relaxation dynamics of RuN3 using time-resolved fluorescence detection.

RuN3
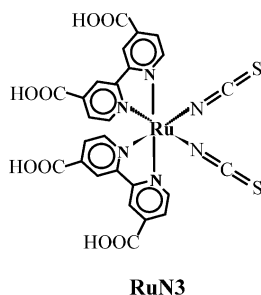
Detection of time-resolved fluorescence is considered to be one of the most sensitive and direct approaches to explore the excited-state relaxation processes.[18] Although most of the ruthenium bipyridyl complexes exhibit phosphorescence emission that is recordable even at room temperatures, the detection of fluorescence emission is a difficult task. However, our earlier work on [Ru(bpy)$_3$]$^{2+}$ and the report of the stimulated emission (SE) signal in RuN3-sensitized TiO$_2$ nanoparticles prompted us to explore the singlet state characteristics of RuN3 in solution under extreme experimental conditions.[9,18] In this letter, we present the first report on the direct observation of the singlet states of RuN3 in solution, using femtosecond fluorescence upconversion spectroscopy. The data, which demonstrates highly competitive IC/ISC processes along the multitude of singlet levels, provides first-hand information on the ultrafast singlet state relaxation dynamics of RuN3 in solution.

Experimental Section

RuN3 was purchased from Solaronix SA and was used as received. All solvents were purchased from Wako Chemicals, Japan (purity of >99.5%) and were used as received. Fluorescence decays were measured by a femtosecond fluorescence upconversion setup that has been described elsewhere.[18] Briefly, the setup was based on a Ti:sapphire system (Tsunami, 70 fs, Spectra Physics), giving ~600 mW at ~820 nm with a repetition rate of 82 MHz. The second harmonic (SH) output was used to excite the sample held in a cell with a path length of 1 mm. Polarization of the excitation beam was varied, by introducing a half wave plate in the pump beam line. For kinetic measurements, the excitation polarization was kept at the magic angle
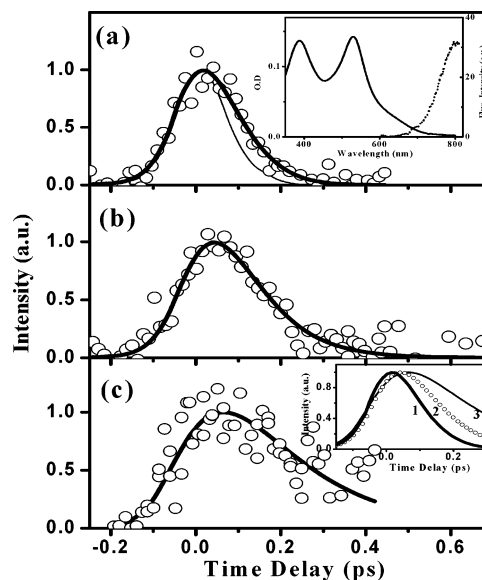
Figure 1. Fluorescence decay traces (○) of RuN3 in ethanol on excitation at 410 nm. Signals monitored at (a) 600, (b) 650, and (c) 700 nm. The thick solid lines represent the best convoluted fit, according to eqs 1 and 2. The thin line in panel a represents the cross-correlation trace. The inset in panel a shows the steady-state absorption spectrum (solid line) and emission spectrum (dotted line) in ethanol at room temperature. The inset in panel c shows the comparison of the fitted curves at 600 nm (curve 1, bold solid line), 650 nm (curve 2, circles), and 700 nm (curve 3, thin solid line).

(54.7°). The sum frequency signals from the fluorescence and gate pulse were generated and detected by an arrangement comprised of lenses, prism, spatial filters, monochromator, and a photomultiplier tube, in combination with a Stanford Research photon counter unit (SR400). Typical optical density of the sample at the excitation wavelength was ~0.5. During the measurements, the sample solutions were flowed to avoid any sample heating or decomposition. The excitation power at the sample was kept at ~10−12 mW. No excitation power dependence was observed on the transient kinetics. It may be mentioned here that the signal levels are very low, typically ~10−20 counts per second, and has been accumulated over a period of time under stable experimental conditions. The instrument response function was obtained from the cross correlation of the residual pump wavelength and the gate pulse, which gave a best fit to a Gaussian profile with a full width at half maximum (fwhm) of ~130 fs. This has been verified separately by upconverting the Raman scattered signal from water.

Results and Discussion

Steady-state UV−visible absorption and triplet state emission spectra of RuN3 in ethanol are shown in the inset of Figure 1a. The corrected emission spectrum shows a maximum at ~800 nm, which is slightly red-shifted, compared to that reported by Tachibana et al. (~775 nm) and Nazeeruddin et al. (755 nm).[5,8] The steady-state absorption/emission characteristics of RuN3 are observed to be very sensitive to the nature of the solvent, and it has been verified that these discrepancies do not arise from a possible content of water in the ethanol. More experiments are being performed this direction, which will be addressed separately.

Figure 1 shows the time-resolved fluorescence signals obtained on excitation of RuN3 at 410 nm in ethanol. Extreme care has been taken to avoid any experimental artifact in the detected signal.[18] As presented in Figure 1a, the signal at 600

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nm is close to the cross-correlation trace, indicating that a major portion of the fluorescence vanishes with a time constant much shorter than the instrument response time (fwhm ≈ 130 fs; see Figure 1a). The decay trace, $F(t)$, is fitted by convolution of the instrument response function with suitable exponential functions.[18] Interestingly, the data at 600 nm are found to best fit a function consisting of the instrument response function, $g(t)$, and a growth and decay kinetics factor, $f(t)'$, as[18]

$$F(t) = \int_{-\infty}^{t} g(t') f(t - t') \, dt' \qquad (1)$$

where

$$f(t)' = A_1 \left[\exp\left(-\frac{t}{\tau_d}\right) - \exp\left(-\frac{t}{\tau_r}\right) \right] \qquad (2)$$

where A_1 represents the amplitude, and τ_r and τ_d represent the growth and decay times, respectively. The best-fit value is adjusted by comparing the traces generated with upper and lower limit values, as described earlier.[18]

The thick solid line in Figure 1a represents the convolution fit with 35 ± 12 fs and 43 ± 10 fs as the growth and decay time constants, respectively. Furthermore, the signals monitored at longer wavelengths displayed slower growth and decay profiles. Assuming a cascade population decay process, the trace at 650 nm (Figure 1b) is best-fitted with a growth time of 43 fs (corresponding to the decay at 600 nm), which provided a decay time constant of 87 ± 13 fs. Similarly, at 700 nm (Figure 1c), the best fit with a growth time of 87 fs rendered a decay time constant of 162 ± 40 fs. Although the changes observed in the growth portion are only marginal, the differences in the decay kinetics are clear, from the comparison given in the inset of Figure 1c.

The presence of a varying growth and decay kinetics with wavelength is intriguing, when compared with the conventional model of excited-state relaxation. Generally, the excited-state dynamics of ruthenium complexes displays excitation wavelength dependence, which has been attributed mainly to the presence of a large number of spin−orbit-coupled states.[17,20] Waterland and Kelly have reported the relaxation and ILET dynamics of RuN3 upon excitation at 520 and 650 nm, where only the slower dynamics, in the range of a few picoseconds to nanoseconds, has been discussed.[17] Recently, Benko et al. have recorded the formation of the triplet state of RuN3 in solution on excitation at 530 nm and evaluated the ISC time constant as ~70 fs, which is corroborated by the kinetics of SE observed in RuN3-sensitized TiO_2 nanocrystalline film.[9] To the best of our knowledge, this observation on the formation of triplet is the only report available on the ISC dynamics of RuN3 in solution; however, no direct kinetic measurements on the excited singlet state of the RuN3 dye in solution have been reported yet.

The probability of a relaxation pathway that is similar to that of $[Ru(bpy)_3]^{2+}$ has been considered.[18] However, the fast decay time constants and other experimental observations led us to believe that the decay characteristics detected here do not originate from a triplet state, but, rather, represent emissive electronic levels in the singlet manifold itself. On the other hand, using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations, Monat et al. and Fantacci et al. have reported the existence of a multitude of closely spaced MLCT and ligand-based charge transfer (LBCT) singlet electronic states in RuN3, many of which have reasonable oscillator strengths.[21,22] Some of these states, which

are available within the excitation energy of ~3 eV, may form efficient excited states and contribute to the overall relaxation process in a significant way. Another aspect of RuN3 dye involves the nature of the MLCT excited state, specifically, whether the excited electron is localized on a single bipyridine ligand or delocalized over both.[17,19] Although such ILET rates have been reported to be slower, in comparison to the dynamics observed here, any contribution from a faster ILET dynamics cannot be ruled out completely, as demonstrated in the case of $[Ru(bpy)_3]^{2+}$ by McCusker et al.[19]

Considering these reports, it is proposed that, on excitation at 410 nm, the excited molecule undergoes a cascade relaxation along the multitude of closely spaced electronic singlet levels, with competing ISC processes. Although the 35 ± 12 fs growth observed at 600 nm may be the limit of time resolution achievable here, such fast kinetics is justified, considering the excitation at 410 nm, i.e., to a strongly coupled higher excited states. Thus, the decays (43 ± 10 fs, 87 ± 13 fs, and 162 ± 40 fs) evaluated here would represent lifetimes of some of the singlet electronic states available under 410 nm excitation and is the first report on the direct observation of emissive singlet states of RuN3 in solution. In a broad view, these lifetimes would represent the cumulative value of all the relaxation pathways from a particular state. However, with the limited data available here at a single excitation wavelength, it becomes difficult to have a clearer picture of this continuous evolution of the triplet; instead, it needs data on wavelength-dependent excitation studies.

Comparison with the photophysics of $[Ru(bpy)_3]^{2+}$ shows that remarkable differences have been observed in the relaxation mechanisms.[18] One of the reasons could be the decisive role of the coordinating ligands in ordering the excited-state energetics. In the case of RuN3, the presence of carboxylic groups and covalently linked thiocyanate groups may modify the overall excited-state processes in this molecule. It is demonstrated, in RuN3, the absorption bands originate from hybrid orbitals composed of comparable metal and thiocyanate contributions, rather than pure MLCT band in $[Ru(bpy)_3]^{2+}$.[22] Such tunability in the overall excited-state dynamics of the metal complex, by manipulating the coordinating ligands, is promising and provides a handy tool to the molecular engineering to develop more-efficient sensitizers.

In conclusion, the first report on the direct observation of the relaxation dynamics of excited singlet state of RuN3 in solution has been presented. The data suggest a cascade relaxation along the multitude of electronic singlet levels, with competing ISC processes. The lifetime of some of the singlet states has been evaluated as 43 ± 10, 87 ± 13, and 162 ± 40 fs at 600, 650, and 700 nm, respectively. In reference to the discussion in the Introduction, it would be interesting to explore the contributions of these active singlet electronic levels on the sensitization processes. It will be rewarding if measurements on the excitation wavelength dependence on the dynamics of singlet state and triplet levels are followed in a deeper sense, so that a comprehensive mechanism can be put forward to the electron injection dynamics at the interface. We are sure that the present results, demonstrating the presence of a multitude of active levels in the electronic singlet states of RuN3 and its relaxation dynamics will provide guidelines for the synthetic chemist to design sensitizer molecules for a desired goal.

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