Photochemistry

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Ruthenium(II) Polyimine Complexes with a Long-Lived ^{3}IL Excited State or a ^{3}MLCT/^{3}IL Equilibrium: Efficient Triplet Sensitizers for Low-Power Upconversion**

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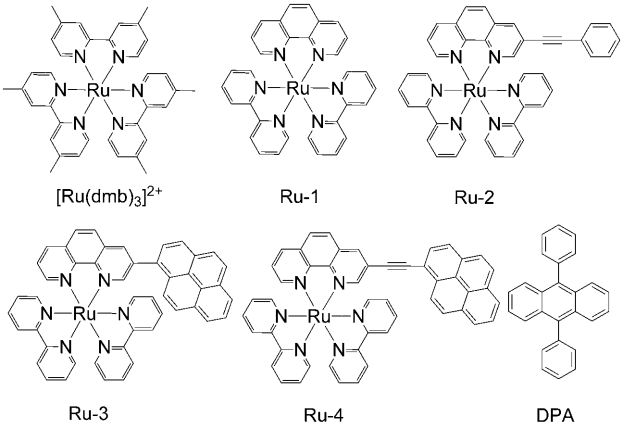
Upconversion (UC), which is the observation of emission (or population of excited states) at higher energy after excitation at lower energy, has attracted much attention because of potential applications such as solar cells, photocatalysis, photonics, and molecular probes.[1–4] In principle, two techniques are available for upconversion. The first technique is the use of two-photon-absorption (TPA) fluorescent dyes. However, this approach suffers from fundamental drawbacks, for example, a coherent laser with a high power density (typically 10^6 W cm^{-2}) is necessary for the excitation, which is considerably higher than the energy of normal light sources (terrestrial solar radiation is ca. 0.10 W cm^{-2}, AM1.5G).[2] Furthermore, it is difficult to tailor the molecular structures of TPA dyes to achieve a specific upconversion wavelength and simultaneously maintain a high TPA cross-section.[4]

As an alternative to TPA-based upconversion, triplet–triplet-annihilation (TTA)-based upconversion [Eq. (1)] has

$$
\begin{aligned}
&{}^3\mathrm{Ru}^* + \mathrm{Annihilator} \rightarrow \mathrm{Ru} + {}^3\mathrm{Annihilator}^* \ (\mathrm{TTET})\\
&{}^3\mathrm{Annihilator}^* + {}^3\mathrm{Annihilator}^* \rightarrow {}^1\mathrm{Annihilator}^* + \mathrm{Annihilator} \ (\mathrm{TTA})\\
&{}^1\mathrm{Annihilator}^* \rightarrow \mathrm{Annihilator} + h\nu \ (\text{fluorescence emission})
\end{aligned}
\qquad (1)
$$

recently emerged and is believed to be promising for practical applications such as dye-sensitized solar cells.[5,6] In this approach, a sensitizer is used, which is normally a transition-metal complex with accessible triplet excited states, such as Ru^{II} polypyridine complexes for which the metal-to-ligand charge-transfer (^{3}MLCT) excited state can be populated by photoexcitation (e.g., $[Ru(dmb)_3]^{2+}$, Scheme 1; dmb = 4,4'-dimethyl-2,2'-bipyridine). The sensitizer harvests the exciting light and transfers the energy to the acceptor (the annihilator, usually polycyclic aromatic hydrocarbons, such as anthracene) by triplet–triplet energy transfer (TTET). Two acceptor molecules in the triplet excited state will annihilate by collision and generate one molecule in the singlet excited state and another molecule in the ground state. Radiative relaxation of the singlet excited annihilator molecules produces the upconverted fluorescence [Eq. (1)].



Scheme 1. Chemical structures of the sensitizer Ru^{II} complexes and the triplet acceptor/annihilator DPA. Note the complexes are dications and the PF_6^- ions are omitted for clarity.

This modular upconversion approach is of particular interest because the excitation and the emission energy can be independently tuned by judicious selection of the sensitizer and the annihilator (that have matching energy levels, see the Supporting Information for a Jablonski diagram).

However, the development of TTA-based upconversion is still in its infancy. For example, the Ru^{II} complexes used are limited to the parent structures such as $[Ru(dmb)_3]^{2+}$.[5a] However, the lifetime (τ) of the typical ^{3}MLCT state of the parent Ru^{II} polyimine complexes is less than 1.0 μs (τ = 0.84 μs in CH_3CN and 0.33 μs in H_2O for $[Ru(dmb)_3]^{2+}$).[5a,7] Little is known about the effect of the excited-state lifetimes on the upconversion efficiency. Recently, we and others found that the lifetimes of Ru^{II} complexes can be substantially prolonged by switching the emissive state from the usual ^{3}MLCT state to the intraligand excited state (^{3}IL), or by establishing an equilibrium between the ^{3}MLCT and the ^{3}IL excited states.[8,9]

To the best of our knowledge, no Ru^{II} complexes with long-lived excited states have been used for TTA-based upconversion. Herein we report how TTA-based upconversion can be achieved by using a Ru^{II} complex with a long-lived ^{3}IL excited state. Our results demonstrate that the ^{3}IL excited

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state is much more efficient in sensitizing the TTA-based upconversion than the ^{3}MLCT excited states.

Five Ru^{II} polypyridine complexes with different excited-state lifetimes were studied (Scheme 1). We previously demonstrated that Ru-4 shows a much longer excited-state lifetime (because of the ^{3}IL state, $\tau = 58.4$ μs) than Ru-1 (which has a ^{3}MLCT state, $\tau = 0.45$ μs). Furthermore, we found that the luminescent sensing of O_2 with Ru-4 is 77 times more sensitive than with the parent complex Ru-1.[8] The luminescent sensing of O_2 is based on triplet–triplet energy transfer from the Ru^{II} complex to O_2, and is similar to the TTET step for the TTA-based upconversion [Eq. (1)]. Thus we envision that TTA-based upconversion can be greatly improved by using Ru-4, which has a long-lived ^{3}IL excited state, rather than Ru-1 or $[Ru(dmb)_3]^{2+}$, which have typical relatively short-lived ^{3}MLCT excited states.

Ru-1 and Ru-4 show absorption bands centered at approximately 450 nm (Figure 1; see the Supporting Information for data for other complexes). The absorption of Ru-1

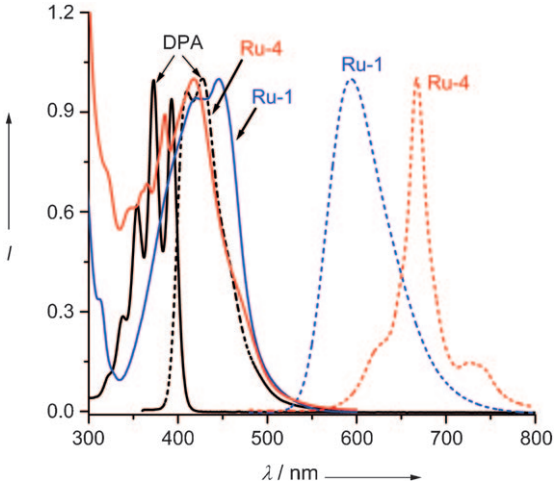

Figure 1. Normalized absorbance (solid lines) and emission spectra (dotted lines) of DPA ($\lambda_{ex} = 380$ nm), Ru-1 ($\lambda_{ex} = 446$ nm), and Ru-4 ($\lambda_{ex} = 418$ nm) in CH_3CN (1.0×10^{-5} M; 25 °C).

in the visible region arises from the $S_0 \rightarrow {}^1$MLCT transition. However, both $S_0 \rightarrow {}^1$IL (pyrene-localized) and $S_0 \rightarrow {}^1$MLCT transitions contribute to the absorption bands for Ru-4 in the region 400–500 nm.[8]

Ru-1 shows typical ^{3}MLCT emission with a lifetime of 0.45 μs, and the lifetime of Ru-2 is 2.44 μs. An equilibrium between the ^{3}MLCT and the ^{3}IL (pyrene-localized) excited states of Ru-3 results in a lifetime of 9.22 μs.[8] The emissive state of Ru-4 is the ^{3}IL state. The emission of Ru-1, Ru-2, and Ru-3 are centered at approximately 600 nm, which is typical for the ^{3}MLCT emission of Ru^{II} polypyridine complexes. A pyrene-centered phosphorescence band was observed at $\lambda_{max} = 667$ nm for Ru-4 (Figure 1).[8]

Similar emission profiles were observed for all the complexes (except Ru-4) upon excitation with a 473 nm laser (Figure 2a). The upconversion of the complexes was studied by using 9,10-diphenylanthracene (DPA; Figure 2b) as the acceptor/annihilator because of its appropriate T_1

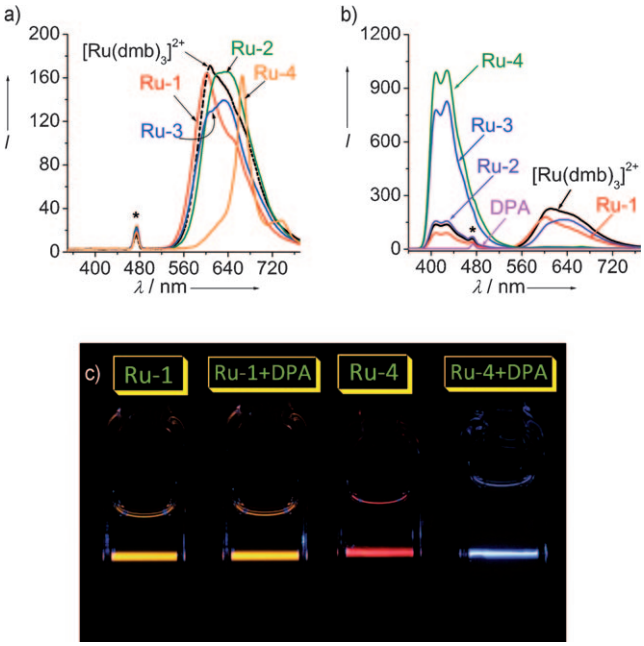

Figure 2. Emission and upconversion of the complexes with 473 nm laser excitation. a) Emission of the Ru^{II} complexes ($\lambda_{ex} = 473$ nm, 5 mW). The spectra are not normalized in order to show the different emission intensities of the complexes. b) Upconverted DPA fluorescence and residual phosphorescence of the mixtures of DPA (4.3×10^{-5} M) and $[Ru(dmb)_3]^{2+}$, Ru-1, Ru-2, Ru-3, or Ru-4. c) Photographs of the upconversion (samples from (a) and (b) in deaerated CH_3CN solution; 1.0×10^{-5} M; 25 °C). The asterisks in (a) and (b) indicate laser scattering.

energy level (1.77 eV) and high fluorescence quantum yield ($\Phi_F = 0.95$).[5] The blue fluorescence of DPA was observed upon excitation of the mixture of DPA and the complexes with a 473 nm laser (Figure 2b). The anti-Stokes shift is 0.48 eV (473 nm→400 nm). Interestingly, the strongest upconverted fluorescence was observed for Ru-4, although this complex shows the weakest phosphorescence (Table 1). The upconverted fluorescence of Ru-1 is the weakest, and Ru-3 also gives significant upconversion. We attribute the high upconversion efficiencies of Ru-3 and Ru-4 to the long lifetimes of the ^{3}IL excited states.[8,9] For the other complexes, however, much weaker upconverted fluorescence of DPA was observed. The low upconversion capability of the complexes Ru-1, Ru-2, and $[Ru(dmb)_3]^{2+}$ is due to the short lifetime of the ^{3}MLCT excited state.

Table 1: Photophysical properties of Ru^{II} complexes with ^{3}MLCT excited states and ^{3}IL excited states.[a]

	τ_P [μs][b]	Φ_P[c]	K_{sv} [10^3 M^{-1}]	k_q [10^9 M^{-1} s^{-1}]	Φ_{UC}[d]
$[Ru(dmb)_3]^{2+}$	0.84	0.073	4.45	5.30	0.010
Ru-1	0.45	0.060	4.59	10.2	0.009
Ru-2	2.44	0.063	14.7	6.04	0.045
Ru-3	9.22	0.008	170.0	18.5	0.098
Ru-4	58.4	0.003	993.0	17.0	0.096

[a] Recorded in deaerated CH_3CN solution at 25 °C. [b] Phosphorescence lifetime. [c] Phosphorescence quantum yield. [d] Upconversion quantum yields.

Furthermore, it should be noted that the phosphorescence of Ru-3 and Ru-4 were completely quenched by DPA (4.3×10^{-5} M), thus indicating that an efficient TTET process occurs between these two complexes and DPA. However, the residual phosphorescence is significant for $[Ru(dmb)_3]^{2+}$, Ru-1, and Ru-2 (Figure 2b).

The upconversion quantum yields (Φ_{UC}) are given in (Table 1).[5e] A Φ_{UC} value of 1.0% was calculated for the parent complex $[Ru(dmb)_3]^{2+}$ under our experimental conditions. A similar Φ_{UC} value of 0.9% was calculated for Ru-1, however, Φ_{UC} values of 9.8% and 9.6% were calculated for Ru-3 and Ru-4, respectively.

We propose that the UC efficiency of Ru-4 may be reduced by the smaller energy gap between its ^{3}IL state and the $^3\pi$–π^* state of DPA ($\Delta E_{T\text{-}T}=707\ cm^{-1}$), whereas ΔE is much bigger for other complexes such as Ru-3 ($\Delta E_{T\text{-}T}=2054\ cm^{-1}$). Thus the driving force for the TTET of Ru-4 is much smaller than the other complexes in this study. We propose that complexes with similar lifetimes but larger ΔE values than Ru-4 will give even larger Φ_{UC} values.

Notably, the upconversion is achieved with a DPA concentration that is 1000 times lower than that required for the upconversion with $[Ru(dmb)_3]^{2+}$.[5c] Our experiments thus clearly demonstrate that the ^{3}IL excited state is much more efficient for sensitizing TTA-based UC than the normal ^{3}MLCT excited state of the Ru^{II} polyimine complexes.

Upconversion with Ru-4 can be detected with the naked eye (Figure 2c). The phosphorescence of Ru-1 is orange ($\lambda_{em}=600$ nm), and the emission of Ru-4 (^{3}IL emission) is deep red ($\lambda_{em}=667$ nm). In the presence of DPA, upconverted bright blue emission was observed for Ru-4. The emission of a solution of Ru-1 and DPA is orange because of the very weak upconversion.

We also demonstrated that upconversion can be achieved by excitation with a 532 nm laser. The anti-Stokes shift is up to 0.77 eV (532 nm→400 nm). The upconverted fluorescence emission of Ru-4 is the most intense, followed by that of Ru-3 (Figure S5 in the Supporting Information).

TTET is one of the critical steps of TTA-based upconversion. In order to quantitatively study the TTET, we investigated DPA quenching on the phosphorescence of the complexes [Eq. (2) and Figure 3]. The emission signals of

$$I_0/I = 1 + K_{SV}[DPA], \qquad K_{SV} = k_q\,\tau_0 \tag{2}$$

Ru-4 and Ru-3 are substantially more sensitive to DPA quenching than Ru-1, Ru-2, and $[Ru(dmb)_3]^{2+}$. For example, the Stern–Volmer quenching constant of Ru-4 ($K_{SV}=9.93\times10^5\ M^{-1}$) is 223 times that of $[Ru(dmb)_3]^{2+}$ ($K_{SV}=4.45\times10^3\ M^{-1}$). The bimolecular quenching constant of Ru-4 ($k_q=1.70\times10^{10}\ M^{-1}s^{-1}$) is 3.2 times that of $[Ru(dmb)_3]^{2+}$ ($k_q=5.30\times10^9\ M^{-1}s^{-1}$; Table 1). The K_{SV} and k_q values of Ru-4 are approximately 5 to 10 times higher than the reported values, for example, with Pt^{II} tetraphenyltetrabenzoporphyrin as the sensitizers.[1,6] The much higher K_{SV} value for Ru-4 than for $[Ru(dmb)_3]^{2+}$ arises from the longer lifetime of the ^{3}IL excited state of Ru-4 compared to the shorter lifetime of the ^{3}MLCT excited state of $[Ru(dmb)_3]^{2+}$ (the same explanation is applicable for Ru-1 and Ru-2). Such an efficient TTET process will result in efficient TTA-based upconversion.

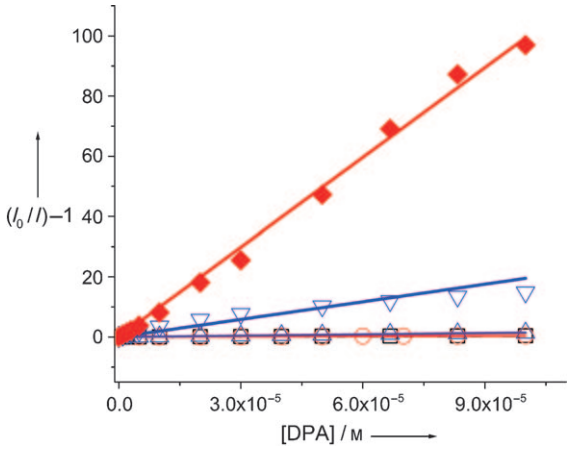

Figure 3. Stern–Volmer plots for phosphorescence quenching of $[Ru(dmb)_3]^{2+}$ (□, $\lambda_{ex}=460$ nm), Ru-1 (○, $\lambda_{ex}=446$ nm), Ru-2 (△, $\lambda_{ex}=450$ nm), Ru-3 (▽, $\lambda_{ex}=450$ nm), and Ru-4 (◆, $\lambda_{ex}=418$ nm). Phosphorescence was measured as a function of DPA concentration in CH_3CN (1.0×10^{-5} M; 25 °C).

Interestingly, we observed slow kinetics of upconversion for Ru-4, that is, the upconverted fluorescence does not promptly reach the maximum upon excitation, instead, we observed a slow increase of the upconverted fluorescence (see video files in the Supporting Information). We tentatively attribute this slow response to trace O_2 in the solution. This effect is also discernable in Figure 2c. The emission pathway for Ru-4 alone is regular, but the emission pathway of the upconversion of Ru-4 is irregular. Furthermore, we noticed that the upconversion ceased after diffusion of trace O_2 into the vial, although the phosphorescence is still persistent. We suggest that the quenching of the TTA-based UC by traces of O_2 may be developed as a novel highly sensitive method for O_2 detection.

In conclusion, the long-lived ^{3}IL excited state ($\tau=58.4$ μs) and the equilibrated ^{3}MLCT/^{3}IL excited state ($\tau=9.22$ μs) of pyrene-containing Ru^{II} complexes were used to sensitize TTA-based upconversion (with DPA as the acceptor/annihilator). Excitation with either 473 nm or 532 nm lasers generates the upconverted fluorescence at 400 nm, with an anti-Stokes shift of up to 0.77 eV. The typical power density of the excitation is 0.07 $W\,cm^{-2}$, which is lower than terrestrial solar radiation. The quenching constant of the ^{3}IL state with DPA is 223 times higher than that of the ^{3}MLCT state with DPA. The upconversion quantum yield of the long-lived ^{3}IL excited state ($\Phi_{UC}=9.6\%$) is approximately 10 times higher than that of $[Ru(dmb)_3]^{2+}$ ($\Phi_{UC}=1.0\%$), for which the ^{3}MLCT state ($\tau=0.84$ μs) is the usual excited state. Our results will be useful for the preparation of efficient triplet sensitizers for TTA-based upconversion and for the application of these energy transformation schemes, such as in dye-sensitized solar cells.

Experimental Section

Luminescence quantum yields of the complexes were measured with $[Ru(bpy)_2(phen)](PF_6)_2$ as the reference ($\Phi = 6.0\%$ in deaerated CH_3CN; phen = 1,10-phenanthroline). Luminescence images were obtained using Samsung NV5 and Canon A2000 digital cameras. The exposure times are the default values of the camera. The syntheses of complexes Ru-1, Ru-2, Ru-3, and Ru-4 have been reported previously.[8]

A diode-pumped solid-state (DPSS) laser was used for the upconversion experiments. The samples were purged with N_2 or Ar for 30 min before measurement. The upconversion quantum yields were determined with 4-dicyanomethylene-6-(*p*-dimethylaminostyryl)-2-methyl-4*H*-pyran (DCM) as the quantum yield standard ($\Phi_F = 0.10$ in CH_2Cl_2) and the quantum yields were calculated by using Equation (3),[5e] where Φ_{UC}, A_{unk}, I_{unk}, and η_{unk} represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the samples and the solvents, respectively. The equation is multiplied by a factor of 2 so that the maximum quantum yield is unity.[5e]

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \quad (3)$$

The videos of the phosphorescence and upconversion were filmed with a Canon A2000 digital camera. The complex, as well as the mixture of Ru-4/DPA were dissolved in deaerated CH_3CN. The concentrations of the complexes were 1.0×10^{-5} M and the concentration of DPA was 4.3×10^{-5} M. For detail experimental setups, see the Supporting Information.

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