

Ruthenium(II) Polyimine–Coumarin Dyad with Non-emissive ^3IL Excited State as Sensitizer for Triplet–Triplet Annihilation Based Upconversion**

Shaomin Ji, Huimin Guo, Wenting Wu, Wanhua Wu, and Jianzhang Zhao*

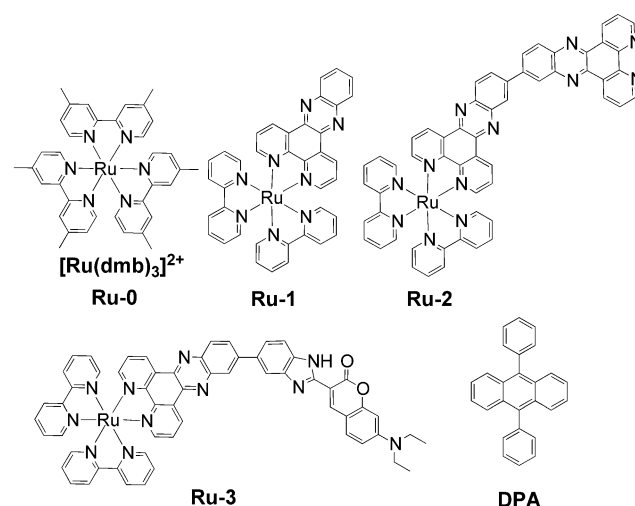
Upconversion (UC) has attracted much attention due to its potential applications for photovoltaics, photocatalysis, non-linear photonics, and so forth.^[1–12] In principle, two techniques are available for upconversion from a chemist's perspective. The first one is to use two-photon absorption (TPA) fluorescent dyes.^[4] However, this approach suffers from fundamental drawbacks, for example, coherent light with high power density (typically MW cm^{-2} , that is, 10^6 W cm^{-2}) is required for excitation, which is well beyond the energy level of normal light sources (the terrestrial solar radiation is ca. 0.10 W cm^{-2}).^[4] Furthermore, it is difficult to modify the molecular structures of TPA dyes to achieve a specific upconversion wavelength and at the same time to keep a high TPA cross section.

A new approach for upconversion is based on triplet–triplet annihilation (TTA), which is promising for practical applications, such as photovoltaics (e.g. dye-sensitized solar cells).^[4–17] In this approach, a triplet sensitizer, normally a transition-metal complex with triplet excited states that are accessible upon photoexcitation (e.g. platinum(II) or palladium(II) porphyrin complexes), is used to harvest the excitation energy and transfer it to the triplet acceptor (annihilator/emitter, such as anthracene, perylene, etc.) via triplet–triplet energy transfer (TTET; see the Jablonski diagram in the Supporting Information). The excitation and emission wavelengths of TTA upconversion can be readily changed by independent selection of the triplet sensitizers and triplet acceptors, and the excitation power can be as low as a few mW cm^{-2} (lower than solar light).^[1,2,5]

Recently we showed that long-lived ^3IL (intraligand) excited states are more efficient to sensitize TTA upconversion,^[12] than the normal short-lived $^3\text{MLCT}$ excited states

(MLCT = metal-to-ligand charge transfer).^[17,18] However, we believe that the current understanding of TTA UC is still premature. For example, currently all the triplet sensitizers used for TTA UC are phosphorescent materials.^[1,2,5,12–16] However, we propose that it is unnecessary for a triplet sensitizers to be phosphorescent to sensitize a photophysical process^[19] such as TTA UC. On the contrary, the phosphorescence is actually detrimental to the TTET process as well as to upconversion because the radiative decay of the triplet excited state of the sensitizer (i.e., phosphorescence) is a decay channel which is competitive to TTET. Therefore, we envision that non-phosphorescent transition metal complexes with triplet excited states populated upon photoexcitation can sensitize the TTA UC. This new concept will greatly increase the availability of the triplet sensitizers. Herein we reported the first example of TTA upconversion with a ruthenium(II) polyimine–coumarin dyad that shows a non-emissive ^3IL excited state and gives very weak phosphorescence but significant upconversion capability.

We designed a dyad of a coumarin-containing Ru^{II} polyimine complex as the triplet sensitizer (Ru-3, Scheme 1). Coumarin was selected for its intense absorption in the visible region. To isolate the coumarin chromophore from the Ru^{II} coordination center (otherwise the system is no longer supramolecular, and the photophysics of two subunits will collapse into one), we used biphenyl and dppz (dipy-



Scheme 1. Chemical structures of the sensitizers and the triplet acceptor 9,10-diphenylanthracene (DPA). Note that the complexes are dications and the PF_6^- anions were omitted for clarity.

[*] S. Ji, Dr. H. Guo, W. Wu, W. Wu, Prof. J. Zhao
State Key Laboratory of Fine Chemicals
School of Chemical Engineering
Dalian University of Technology
E-208 West Campus, 2 Ling-Gong Road, Dalian 116024 (China)
E-mail: zhaojzh@dlut.edu.cn
Homepage: <http://finechem.dlut.edu.cn/zhaojianzhang/guohm/index.htm>

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ido[3,2-a:2',3'-c]phenazine) as the rigid linker between the two subunits. Thus an ^3IL excited state (predicted by DFT calculations to be close in energy to the $^3\text{MLCT}$ state) is introduced into the photophysical manifold, the $^3\text{MLCT}$ state can possibly be quenched, given that the ^3IL state is lower in energy than the $^3\text{MLCT}$ state.^[18] But importantly, the ^3IL excited state can be populated upon photoexcitation. Ru-1 and Ru-2 were prepared as model complexes. The reported complex Ru-0 was used to compare the upconversion.^[17] The synthesis of the compounds is straightforward (see the Supporting Information for synthesis details).^[20]

The UV/Vis absorption of the complexes (Figure 1) indicates intense absorption (light-harvesting effect) for Ru-3 (at 464 nm). For Ru-2, however, the absorption of the ligand is at 410 nm. By comparison, the absorption of the model

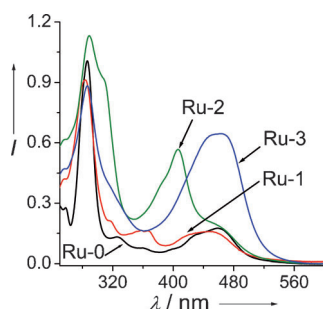


Figure 1. UV/Vis absorption spectra of Ru-0, Ru-1, Ru-2, and Ru-3 in CH_3CN ($1.0 \times 10^{-5} \text{ M}$; 20°C).

complexes Ru-0 and Ru-1 is much weaker in the visible region. The native MLCT absorption of all the complexes was observed at 450 nm.^[18,21–23] Note that the absorption of Ru-3 ($\epsilon = 64478 \text{ M}^{-1} \text{ cm}^{-1}$) is four times more intense than the model complex Ru-1 ($\epsilon = 15879 \text{ M}^{-1} \text{ cm}^{-1}$ at 447 nm). We envision that the energy levels of the ^3IL state of coumarin subunit in Ru-3 will be close to the $^3\text{MLCT}$ state. These anticipations were confirmed by DFT/TDDFT calculations (see the Supporting Information).

The emission of the complexes upon 473 nm laser excitation were studied (Figure 2a). Ru-0 gives the most intense emission ($\Phi_p = 7.3\%$, Table 1), followed by Ru-1 ($\Phi_p = 7.9\%$). Ru-2 gives weaker emission than Ru-1. For Ru-3, however, the emission is extremely weak ($\Phi_p = 0.2\%$), despite of its intense absorption at 473 nm ($\epsilon = 62354 \text{ M}^{-1} \text{ cm}^{-1}$). We propose that the $^3\text{MLCT}$ state was profoundly perturbed in Ru-3 by a non-emissive triplet excited state, most probably a ^3IL excited state localized on the coumarin subunit (as indicated by transient absorption and spin density analysis, see below).^[18,20,24,25] We found that the emission of Ru-3 was enhanced by protonation with trifluoroacetic acid (see the Supporting Information). It should be pointed out that the photophysics of Ru^{II} dppz complexes are sensitive to the environment, such as the polarity of the solvents or protonation of the dppz ligands.^[26] Thus the upconversions with the complexes as triplet sensitizers will be discussed after revealing the photophysics of the complexes.

To study the triplet excited states of the complexes, the time-resolved transient absorption was investigated

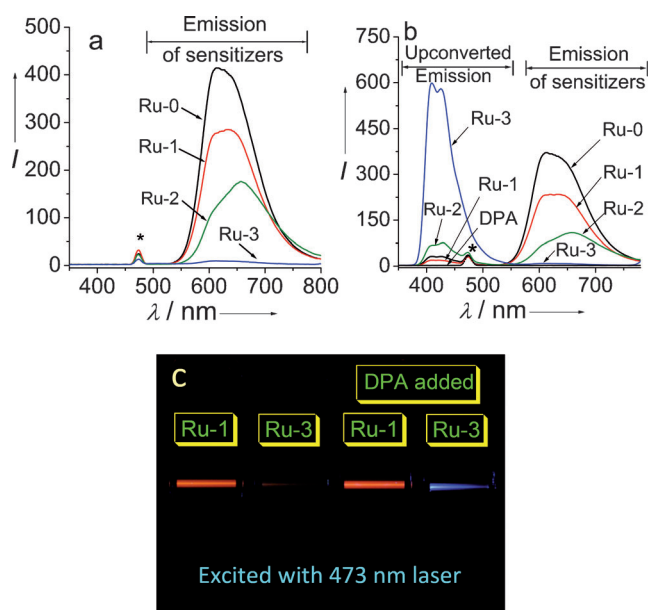


Figure 2. Emission and upconversion of the sensitizers with 473 nm laser (5 mW) excitation. a) Emission of the sensitizers alone. The spectra were not normalized in order to show the different emission intensity. b) Upconverted DPA fluorescence and residual phosphorescence of the mixture of DPA ($4.3 \times 10^{-5} \text{ M}$) and Ru-0, Ru-1, Ru-2, and Ru-3, respectively. c) Photographs of the upconversion with Ru-1 and Ru-3 as the sensitizers. In CH_3CN ($1.0 \times 10^{-5} \text{ M}$; 20°C). The asterisks in (a) and (b) indicate laser scattering.

Table 1: Photophysical parameters of the Ru^{II} diimine complexes.^[a]

	λ_{abs} [nm]	λ_{em} [nm]	ϵ [$\text{M}^{-1} \text{ cm}^{-1}$] ^[b]	Φ_p [%] ^[c]	τ [ns] ^[d]	τ [ns] ^[e]	Φ_{UC} [%] ^[f]
Ru-0	460	600	17490	7.3	806	848	0.6
Ru-1	447	622	15879	7.9	695	713	0.4
Ru-2	450	638	20312	2.4	607	506	1.3
Ru-3	464	618	64478	0.2	2242	1364	2.7

[a] In CH_3CN ($1.0 \times 10^{-5} \text{ M}$). [b] Molar extinction coefficient at the absorption maximum. [c] Phosphorescence quantum yield. [d] Triplet excited-state lifetime, measured by transient absorption. In deaerated CH_3CN . [e] Phosphorescence lifetime, measured with the phosphorescence method. [f] Upconversion quantum yields.

(Figure 3). For Ru-1, bleaching at 450 nm was found, which is due to depletion of the ground state upon photoexcitation. Transient absorption at 320 nm was found for Ru-1, which is

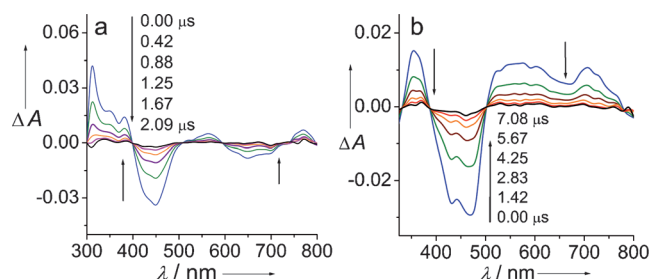


Figure 3. Nanosecond time-resolved transient difference absorption spectra of a) Ru-1 and b) Ru-3. Arrows indicate the elapsed time after a 532 nm laser flash. In deoxygenated CH_3CN ($1.0 \times 10^{-5} \text{ M}$; 20°C).

typical for Ru^{II} polyimine complexes.^[24,27] Similar transients were observed for Ru-0 (see the Supporting Information). Thus the populated triplet excited states of Ru-1 and Ru-0 upon photoexcitation are the normal ³MLCT excited states of the Ru^{II} polyimine complexes.^[22,27–29]

For Ru-3, however, drastically different transients were observed (Figure 3b). Significant bleaching was observed at 470 and 450 nm. Furthermore, transient absorption bands in the range of 500–750 nm developed. These features are different from the typical MLCT transitions of Ru^{II} complexes and are attributed to the ³IL excited state localized on the coumarin moiety, as supported by DFT/TDDFT calculations and the spin density of the complexes (Figure 4). Thus the weak emission of Ru-3 (Table 1) can be rationalized by the non-emissive ³IL excited state.^[18,30,31]

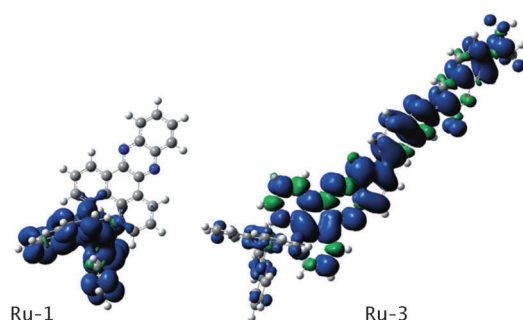


Figure 4. Spin-density surface of Ru-1 and Ru-3 at the optimized triplet-state geometry. Calculated at the B3LYP/6-31G/LANL2DZ level with Gaussian 09W.^[32]

For Ru-2, we also propose that the ³IL excited state is populated upon photoexcitation (see the Supporting Information). This is the first time that the ³IL excited state of coumarin was observed with time-resolved transient absorption spectroscopy. Previously, a Ru^{II}–coumarin dyad was reported but no transient absorption was studied.^[33] Furthermore, the previously reported Ru^{II}–coumarin dyad shows normal ³MLCT emission features (such as typical ³MLCT emission wavelength, quantum yields, and phosphorescence lifetime), because the ³IL excited state is much higher in energy than the ³MLCT excited state, thus leaving the latter unperturbed.^[33]

The lowest-lying triplet excited states of the sensitizers were also investigated by calculating the spin density surface (Figure 4). For Ru-1, the spin density is localized on the bipyridyl (bpy) units and the Ru atom, but not on dppz, which is in full agreement with the emissive ³MLCT excited state. A ³IL state localized on dppz is usually non-emissive. In our case, Ru-1 is phosphorescent in CH₃CN, thus we believe that the ³MLCT state is lower in energy than the ³IL state.^[34,35] For Ru-3, however, the spin density surface is distributed on the coumarin and dppz moieties. The Ru^{II} atom and bpy ligands contribute much less than in Ru-1, which makes Ru-3 weakly phosphorescent. This information clearly indicates an ³IL excited state for Ru-3. A similar spin density surface was found for Ru-2 (see the Supporting Information). The spin

density analysis is in full agreement with the transient absorptions (Figure 3).

Now the upconversion with the complexes as triplet sensitizer can be well understood (Figure 2b). DPA was used as triplet acceptor for the TTA upconversion (Scheme 1). Upconverted fluorescence was observed for Ru-2 and Ru-3 as the triplet sensitizers (upconversion quantum yield Φ_{UC} = 1.3% and 2.7%, respectively). Note that Ru-3 gives very poor emission (Figure 2a, Table 1). We demonstrated that the upconversion was greatly enhanced with increasing DPA concentration (see Figure S36 in the Supporting Information), but without any phosphorescence to be quenched. Thus, the significant upconversion of Ru-3 (Figure 2b) is against the performance of the reported sensitizers, that is, the upconverted fluorescence emission of the acceptor is accompanied by quenching of the phosphorescence of the sensitizer.^[5] As the transient spectra show significant ³IL components for the excited-state manifolds of Ru-3, it is reasonable to propose that the TTET occurred mainly between a dark (non-emissive) triplet excited state of Ru-3, most probably the non-emissive ³IL excited state, and the triplet acceptor DPA. For Ru-1, much weaker upconversion was observed (Φ_{UC} = 0.4%). The upconversion with weakly phosphorescent sensitizer (Ru-3) is demonstrated by photographs in Figure 2c. To our knowledge, this is the first time that a non-emissive triplet excited state of a transition-metal complex was used for TTA upconversion.^[1–12]

In conclusion, we propose that transition-metal complexes with non-emissive triplet excited states can be used as sensitizers for the triplet–triplet annihilation (TTA) based upconversion. Herein we described the first example with a Ru^{II} complex that shows very weak phosphorescence (Φ_p = 0.2%) but significant upconversion (Φ_{UC} = 2.7%) compared to a model complex that gives a much higher Φ_p value (7.9%) but much lower Φ_{UC} (0.4%). The non-emissive ³IL excited state (dppz–coumarin localized) of the complex is confirmed with time-resolved transient absorption spectra and spin density analysis of the triplet state (DFT calculations). Our result will greatly increase the availability of triplet sensitizers for triplet–triplet annihilation based upconversion and other appropriate photophysical processes.

Experimental Section

Phosphorescence quantum yields of the complexes were measured with [Ru(bpy)₂(Phen)][PF₆]₂ as the reference (Φ_p = 6.0% in deaerated CH₃CN; Phen = phenanthroline). The luminescence images were obtained using Canon A2000 digital cameras. A diode-pumped solid-state (DPSS) laser was used for the upconversions (473 nm). The samples were purged with N₂ or Ar for 30 min before measurement. The upconversion quantum yields (Φ_{UC}) were determined with [Ru(dmb)₃][PF₆]₂ as the quantum-yield standard (Φ_p = 7.3% in deaerated CH₃CN, dmb = 4,4'-dimethyl-2,2'-bipyridine) and the quantum yields were calculated with Equation (1),^[5] 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 (unk = unknown). The equation is multiplied by factor of two in order to make the maximum quantum yield to be unity.^[5] For the synthesis of the complexes and

spectroscopic experimental details, please refer to the Supporting Information.

$$\Phi_{\text{UC}} = 2\Phi_{\text{std}} \left(\frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left(\frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left(\frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad (1)$$

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