Ruthenium(II)–Polyimine–Coumarin Light-Harvesting Molecular Arrays: Design Rationale and Application for Triplet–Triplet-Annihilation-Based Upconversion

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Abstract: Ru^{II}-bis-pyridine complexes typically absorb below 450 nm in the UV spectrum and their molar extinction coefficients are only moderate ($\varepsilon <$ 16000 m⁻¹ cm⁻¹). Thus, Ru^{II}-polyimine complexes that show intense visiblelight absorptions are of great interest. However, no effective light-harvesting ruthenium(II)/organic chromophore arrays have been reported. Herein, we report the first visible-light-harvesting Ru^{II}-coumarin arrays, which absorb at 475 nm (ϵ up to 63300 m⁻¹ cm⁻¹, 4-fold higher than typical Ru^{II}-polyimine complexes). The donor excited state in these arrays is efficiently converted into an acceptor excited state (i.e., efficient energy-transfer) without losses in the phosphorescence quantum yield of the acceptor. Based on steady-state and time-resolved spectroscopy and DFT calculations, we proposed a general rule for the design of Ru^{II}–polypyridine–chromophore light-harvesting arrays, which states that the ¹IL energy level of the ligand must be close to the respective energy level of the metal-to-

Keywords: coumarin • light-harvesting • phosphorescence • photochemistry • ruthenium ligand charge-transfer (MLCT) states. Lower energy levels of ¹IL/³IL than the corresponding ¹MLCT/³MLCT states frustrate the cascade energy-transfer process and, as a result, the harvested light energy cannot be efficiently transferred to the acceptor. We have also demonstrated that the light-harvesting effect can be used to improve the upconversion quantum yield to 15.2% (with 9,10-diphenylanthracene as a triplet-acceptor/annihilator), compared to the parent complex without the coumarin subunit, which showed an upconversion quantum yield of only 0.95%.

Introduction

Ruthenium(II)–polypyridine complexes are versatile materials for applications in artificial photosynthesis, dye-sensitized solar cells, photocatalysis, luminescent molecular probes, and photoresponsive molecular devices.^[1–9] Ru^{II}–polypyridine complexes, such as $[Ru(bpy)_3][PF_6]_2$, have particularly adventitious photophysics in that they have long phosphorescence lifetimes (from a few hundreds ns to μ s, owing to the metal-to-ligand charge transfer triplet excited state, that is, ³MLCT), large Stokes shifts (about 150 nm), and long emission wavelengths (beyond 600 nm). Unfortunately, the UV/Vis absorptions of typical Ru^{II}–polyimine com-

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plexes, such as $[Ru(bpy)_3][PF_6]_2$, are in the blue spectroscopic region (below 450 nm) and the molar absorption coefficient (ε) values are only moderate. Therefore, it is important to be able to construct Ru^{II} -polypyridine complexes that display light-harvesting ability in the visible-light range and efficiently transfer the harvested excitation energy to the coordination center (energy acceptor) to initiate cascade photophysical processes involving the triplet excited states, such as photoinduced-electron-transfer/charge-separation, photooxidation, and photovoltaics.^[7,10–12]

Previous attempts at preparing Ru^{II}-chromophore lightharvesting arrays that are effective in the visible-light spectrum have demonstrated their elusive photophysics; that is, very often, the photophysics of the ³MLCT emission or the ${}^{1}MLCT \rightarrow {}^{3}MLCT$ energy-transfer collapsed with the introduction of an organic chromophore. For example, attempts to enhance the visible-light absorption and to funnel the energy to the emissive ³MLCT state with BODIPY (borondipyrromethene) as the antenna/energy donor have been unsuccessful, as was the case with a recently reported Ir^{III}-BODIPY molecular array.^[11] BODIPY is well-known for its high fluorescence quantum yield and intense absorption in the visible spectrum (unsubstituted BODIPY shows an intense absorption at about 500 nm, $\varepsilon = 79000 \,\mathrm{m}^{-1} \mathrm{cm}^{-1}$). Whilst the naphthalimide chromophore does function as an energy donor to Ru^{II} complexes, the molar extinction coeffi-



cient (ε) at 430 nm is only enhanced by a factor of 2.0 ($\varepsilon = 2.0 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$) and the emission of the array is much weaker than that of the parent complex.^[13] To the best of our knowledge, no successful visible-light-harvesting Ru^{II}– polyimine complexes have been reported in which the total absorption is increased and in which the excited state of the energy donor is efficiently converted into the acceptor excited state (i.e., efficient energy-transfer) without losses in the quantum yield of the acceptor.

We have been interested in the photophysics of transitionmetal complexes, such as those containing Ru^{II}, for a while.^[9,14] To elucidate the photophysics of Ru^{II}–organicchromophore light-harvesting arrays, herein, we set out to design visible-light-harvesting arrays based on Ru^{II} complexes that showed intense absorption beyond 450 nm, by using coumarin as the antenna/donor and a MLCT chromophore as the acceptor. With one of these Ru^{II}–chromophore arrays, the total absorption was increased and the excited state of the energy donor was efficiently converted into the excited state of the acceptor (i.e., efficient energy-transfer) without a loss in the quantum yield of the acceptor (ε = $6.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 470 nm).

We demonstrated that the energy levels of the S_1 state of the energy donor (coumarin ligand) must be higher than those of the MLCT acceptor because the energy-transfer ${}^{1}IL \rightarrow {}^{1}MLCT \rightarrow {}^{3}MLCT$ pathway and light-harvesting becomes inefficient when the ${}^{1}IL$ energy level is lower than the ${}^{1}MLCT$ state.

As a preliminary application of the light-harvesting array, these complexes were used as triplet photosensitizers for triplet–triplet annihilation (TTA) upconversion.^[15] By using laser excitation at 473 nm (power density: 71 mW cm⁻²; note that terrestrial solar radiation is 100 mW cm⁻²), the mixed sensitizer/annihilator solution displayed a blue emission at 400 nm, as a direct result of the light-harvesting effect. Upconversion quantum yields of up to 15.2% were observed (non-coherent light with low power density was sufficient to sensitize the upconversion). Under the same experimental conditions, the parent complex, which did not show the light-harvesting effect, did not show significant upconversion.

Results and Discussions

Design of the light-harvesting array: Coumarin is wellknown for its intense absorption in the visible spectrum.^[16] Thus, we designed molecular arrays **Ru-2**, **Ru-3**, and **Ru-4** (Scheme 1) that contained coumarin subunits because the energy level of the S₁ and T₁ states of the ligands were close to the ¹MLCT and ³MLCT states of the Ru^{II} complexes, respectively (the energy levels of the T₁ excited states of the ligands were calculated by using DFT/time-dependent-DFT (TDDFT) methods, see the Supporting information).^[9,17]

Complex **Ru-1** was used as a model complex in the study. All of the ligands and complexes were obtained in satisfactory yields. Imidazole was used as a rigid linker to avoid undesired direct interactions (such as intramolecular collision) between the coumarin moiety and the MLCT chromophore (Ru^{II} coordination center). The interaction between the coumarin chromophore and the Ru^{II}-coordination center may complicate the photophysics of the arrays. The closed-ring form of the coumarin subunit in complex Ru-3 will have a slightly different ³IL state compared to that of **Ru-2**. Thus, the photophysical properties of complexes Ru-2 and Ru-3 may be different. Owing to intramolecular hydrogen-bonding interactions, we proposed that the coumarin subunits in complexes Ru-2 and Ru-3 were coplanar with the Phen ligand. To elucidate the effect of intramolecular hydrogen bonds on the photophysical properties, the coumarin subunit and the phen/imidazole ligand were separated in complex Ru-4. We observed different photophysical properties for the four complexes. DFT/TDDFT calculations were carried out to check the ³IL triplet excited state to help the design of light-harvesting arrays (see the Supporting Information).

Enhanced visible-light absorption and efficient energy-transfer from the antenna to the energy acceptor: The $S_0 \rightarrow$ ¹MLCT absorption band in parent complex **Ru-1** was observed at 450 nm (Figure 1). Complexes **Ru-2**, **Ru-3**, and **Ru-4** showed substantially more-intense absorption at 450 nm and at higher wavelengths. For example, the ε value of **Ru-2** ($6.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) was about 4.0-fold higher than that of **Ru-1** ($1.60 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The UV/Vis absorptions of the ligands were also studied and intense absorptions were found in the visible range for ligands **L2**, **L3**, and **L4** (see the Supporting Information). DFT/TDDFT calculations of the ligands clearly demonstrated that the energy level of the vertical ¹IL excited states could be precisely predicted (see the Supporting Information) and that this information will be helpful for the design of light-harvesting **Ru**^{II} arrays.

The absorption maxima of complex Ru-2 in the visible spectrum (475 nm) was close to that of **Ru-1** (Figure 1 a); thus, the energy level of the Frank-Codon ¹IL state of the coumarin ligand of complex Ru-2 was close to that of the intrinsic ¹MLCT state. However, for complex **Ru-3**, a slightly red-shifted absorption (485 nm) was observed; thus, the energy level of ¹IL state of **Ru-3** was probably lower than the ¹MLCT state. Conversely, complex **Ru-4** showed blueshifted absorption bands compared to complexes Ru-2 and Ru-3, which could be due to the lack of intramolecular hydrogen-bonding interactions or to the decreased intramolecular-charge-transfer (ICT) effect of the coumarin ligand of Ru-4. The absorption differences between the complexes in the visible range (400-550 nm) were mainly due to the coumarin ligand, based on the DFT/TDDFT calculations on the ligands (see the Supporting Information).

All of the complexes emitted at 608 nm (Figure 1b) and the fluorescence was completely quenched in all cases. Thus, we proposed that these complexes shared the same emissive ³MLCT triplet excited states. However, the complexes showed different emission intensities. Notably the emission intensity of complex **Ru-2** was 5.4 times that of **Ru-1** on excitation at 490 nm, which clearly demonstrated the effective

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Scheme 1. Synthesis of **Ru-1** and Ru^{II}–coumarin arrays **Ru-2**, **Ru-3**, and **Ru-4**: a) 1) $CH_2(COOEt)_2$, EtOH, reflux, 6 h; 2) HCl/AcH, reflux, 6 h; b) POCl₃, DMF, 0–5 °C; c) KBr, H₂SO₄/HNO₃, 100 °C, 3 h; d) CH₃COOH, reflux, 6 h; e) BrCH₂CH₂CH₂CL₁, Na₂CO₃, 100 °C, 11 h; f) HI, HCl, reflux, 60 h; g) CH₃COOH, reflux, 6 h; h) EtOH, RT, 2 h, 2,2'-bipyridine, 100 °C, 24 h; i) Br₂, acetic acid, RT; j) 4-formylphenylboronic acid, [Pd(PPh₃)₄], ethanol/tolu-ene/water (1:1:2, v/v/v).

light-harvesting of **Ru-2** in the visible spectrum because **Ru-**2 had a higher ε value at the excitation wavelength (490 nm). Thus, the emission of **Ru-2** was due to its lightharvesting effect, thereby indicting an efficient cascade energy-transfer. In other words, the total absorption was increased and the donor excited state was efficiently convert-

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Figure 1. UV/Vis absorption and phosphorescence spectra of arrays **Ru-1**, **Ru-2**, **Ru-3**, and **Ru-4**. a) UV/Vis absorption spectra $(1.0 \times 10^{-5} \text{ mol dm}^{-1} \text{ in MeCN})$; b) visible-light-harvesting effect: emission spectra of the complexes ($\lambda_{ex} = 490 \text{ nm}$, $2.0 \times 10^{-6} \text{ mol dm}^{-3}$ in MeCN). The solution was purged with Ar for 30 min before the measurements were taken. All emission spectra were measured under the same conditions (20 °C).

ed into the acceptor excited state (i.e., efficient energytransfer) without any loss in the acceptor phosphorescence quantum yield. Complex **Ru-3** showed the weakest emission and the emission of **Ru-4** was similar to **Ru-1**.

To the best of our knowledge, complex **Ru-2** is the first example of an effective Ru^{II} -chromophore light-harvesting array that shows intense absorption in the visible range (above 450 nm) and in which the harvested excitation energy is efficiently transferred to the energy acceptor (the coordination center). Ru^{II} -polypyridine-coumarin (without the NEt₂ moiety) arrays that contain carbazole moieties have been reported, but they only showed more-intense ab-

sorptions in the UV range ($\lambda < 400 \text{ nm}$).^[18] Whilst another Ru^{II} complex has shown moderate ε enhancement in the visible spectrum ($\varepsilon = 5.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 427 nm, a 5.0-fold increase over the model complex), the ³MLCT emission was greatly reduced compared to the model complex.^[13] Moreover, Ru^{II}–chromophore arrays that contained BODIPY as the antenna failed to show any phosphorescence.^[10,11] For the BODIPY-incorporated Ru^{II} arrays, we proposed that the ¹IL state energy level was lower than ¹MLCT state; thus, BODIPY was unable to funnel the absorbed excitation energy to the ¹MLCT state. Furthermore, the ³MLCT excited state was quenched by the ³IL state that was localized on the BODIPY moiety. We believe that this general rule will be useful for the design of efficient Ru^{II}-based light-harvesting arrays that work in the visible range.

The weak emission of complex **Ru-3** may be caused by non-efficient upward IC from ${}^{1}\text{IL} \rightarrow {}^{1}\text{MLCT}$ (${}^{1}\text{IL}$ energy level was lower than ${}^{1}\text{MLCT}$), or by the lower-lying ${}^{3}\text{IL}$ state. The lower energy level of the ${}^{3}\text{IL}$ state may be responsible for the weak emission.^[9,13,19] For complex **Ru-4**, we proposed that the ${}^{3}\text{IL}$ energy level of the ligand was higher than ${}^{3}\text{MLCT}$ (supported by the UV/Vis absorption spectra); thus, the intrinsic ${}^{3}\text{MLCT}$ photophysics were not perturbed and the emission of **Ru-4** was similar to that of **Ru-1**. Furthermore, the absorption of **Ru-4** at 490 nm was not significantly improved compared to that of **Ru-1** (Figure 1 a).

Furthermore, the DFT/TDDFT calculations on the ligands predicted different energy levels of the T_1 excited states: 2.70 eV (460 nm), 2.00 eV (620 nm), 1.96 eV (631 nm), and 2.16 eV (573 nm) for ligands **L-1**, **L-2**, **L-3**, and **L-4**, respectively (see the Supporting Information). We demonstrated that the DFT/TDDFT method was helpful for the rational design of light-harvesting Ru^{II}–fluorophore arrays with matched energy levels. The photophysical properties of the ligands and the complexes are summarized in Table 1.

UV/Vis absorption and excitation spectra of the complexes: Demonstration of the light-harvesting effect: To evaluate the light-harvesting effect, we compared the UV/Vis absorption spectra and the phosphorescence excitation spectra of

Table 1.	Photophysical	parameters	of the	ligands	and	the	Ru ^{II}	complexes.
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	$\lambda_{abs} [nm]^{[a]}$	$\varepsilon^{[b]}$	Emission properties					
			$\lambda_{ m em}{}^{[a]}$	Φ [%]	$I_0/I_{100}^{[e]}$	τ [ns] ^[f]	$k_{ m r} [{ m s}^{-1}]^{[{ m h}]}$	$k_{ m nr} [{ m s}^{-1}]^{[{ m h}]}$
L-1	275	3.16	421	10.2 ^[c]	1.2	4.81	2.12×10^{7}	1.87×10^{8}
L-2	442	5.08	502	37.3 ^[c]	1.3	2.56	1.46×10^{8}	2.45×10^{8}
L-3	481	3.95	512	29.7 ^[c]	1.2	2.57	1.16×10^{8}	2.74×10^{8}
L-4	418	2.33	495	5.0 ^[c]	1.3	2.85	1.75×10^{7}	3.33×10^{8}
Ru-1	457	1.62	608	14.2 ^[d]	35	1125	1.26×10^{5}	7.63×10^{5}
Ru-2	475	6.33	607	8.8 ^[d]	765	3785	2.33×10^{4}	2.41×10^{5}
Ru-3	485	6.05	608	0.5 (485 nm) ^[d] 0.8 (450 nm) ^[d]	62	2490	1.81×10^{3}	4.00×10^{5}
Ru-4	423	6.53	607	6.0 ^[d]	171	3109	1.93×10^4	3.02×10^{5}

[a] Solvent: MeCN $(1.0 \times 10^{-5} \text{ mol dm}^{-3})$. [b] Molar extinction coefficient at the absorption maxima, $\varepsilon : 10^4 \text{ m}^{-1} \text{ cm}^{-1}$. [c] Quinine sulfate used as the standard ($\Phi = 0.547$ in 0.05 M sulfuric acid). [d] Deaerated solution with [Ru(phen)(bpy)_2][PF_6]_2 ($\Phi = 0.06$ in MeCN) as the standard. [e] Ratio of the emission intensities of the complexes under N₂ (I_0) and O₂ atmospheres (I_{100}). [f] Luminescence lifetimes: $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ in MeCN. Measured in deaerated solution, [g] Radiative deactivation rate constant (k_r) and non-radiative deactivation rate constant (k_n). $k_r = \Phi_{em}/\tau_{em}$, $k_{nr} = (1-\Phi_{em})/\tau_{em}$.

the complexes (Figure 2). It is well-known that superimposable excitation/UV/Vis absorption spectra indicate an efficient light-harvesting effect.^[13,18]



Figure 2. Comparison of the normalized UV/Vis absorption and the excitation spectra of: a) **Ru-1**, b) **Ru-2**, c) **Ru-3**, and d) **Ru-4** ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$ in MeCN, 20°C). The excitation spectra of arrays **Ru-1**, **Ru-2**, and **Ru-3** were recorded at $\lambda_{em} = 608$ nm; the excitation spectrum of array **Ru-4** was recorded at $\lambda_{em} = 607$ nm.

For complex **Ru-1**, the excitation spectrum was superimposable on the UV/Vis spectrum (Figure 2a). This result was reasonable because the 450 nm band was due to the $S_0 \rightarrow^1$ MLCT transition, which effectively excited the phosphorescence. The yield of 1 MLCT \rightarrow^3 MLCT intersystem crossing (ISC) is known to be close to unity.^[20,21]

For **Ru-2**, both $S_0 \rightarrow {}^1MLCT$ and $S_0 \rightarrow {}^1IL$ transitions contributed to the absorption bands at 450 nm (Figure 1 a) and the former transition efficiently excited the phosphorescence through a $S_0 \rightarrow {}^1MLCT \rightarrow {}^3MLCT$ process. However, the fate of the $S_0 \rightarrow {}^1IL$ process was dictated by the relative energy levels of the 1IL and 1MLCT states (a direct ${}^1IL \rightarrow {}^3MLCT$ process was strongly forbidden, owing to the different spin manifold of the states involved in this transition). The ${}^1IL \rightarrow {}^1MLCT$ process was only efficient if the energy level of the ${}^1IL \rightarrow {}^1MLCT$ state of the donor (fluorophore) was higher than the 1MLCT state of the acceptor (Ru^{II}-coordination center). The excitation spectrum of complex **Ru-2** was superimposable with its UV/Vis absorption (Figure 2 b). Thus, the ${}^1IL \rightarrow {}^1MLCT \rightarrow {}^3MLCT$ process and the light-harvesting effect of **Ru-2** were efficient.

Interestingly, the excitation spectrum of complex **Ru-3** was different from its UV/Vis absorption (Figure 2 c). The excitation maximum was blue-shifted when compared to the UV/Vis absorption, which indicated that the absorption at 480 nm was inefficient to excite the phosphorescence. This conclusion was supported by the lower phosphorescence quantum yield of **Ru-3** with excitation at 485 nm than that with 450 nm excitation (Table 1). We proposed that the dis-

crepancy between the UV/Vis absorption and the excitation spectrum was due to a frustrated ${}^{1}IL \rightarrow {}^{1}MLCT$ transition, owing to the energy level of the ${}^{1}IL$ state being lower than that of the ${}^{1}MLCT$ state (Figure 1 a). Instead, we proposed that the undesired ${}^{1}MLCT \rightarrow {}^{1}IL$ energy-transfer was possible for complex **Ru-3**.

For complex **Ru-4**, the excitation/UV/Vis absorption profile was reversed. The excitation spectrum was red-shifted compared to the UV/Vis absorption spectrum and the excitation maximum was also located at 450 nm. The non-efficient ¹IL \rightarrow ¹MLCT \rightarrow ³MLCT transition at 420 nm may have been due to significant non-radiative ¹IL \rightarrow S₀ decay of the ligand (k_{nr} =3.33×10⁸ s⁻¹, Φ =5.0%; Table 1). A similar phenomenon was observed for a Ru^{II}–naphthalimide array.^[12] Furthermore, the lack of intramolecular hydrogen bonding in compound **Ru-4** may influence the photophysics.

Illustration of the photophysical process by using a Jablonski diagram: The photophysics of the arrays, that is, the emission wavelength, the phosphorescence lifetimes, and the light-harvesting effect, were summarized by a qualitative Jablonski diagram (Scheme 2). Complex Ru-1 displayed typical MLCT photophysics and the light-harvesting effect was operating for this model complex; that is, the intense absorption of the imidazole ligand in the UV range (at about 286 nm) was efficiently funneled to the ¹MLCT state because the energy level of the imidazole-localized singlet state (¹IL) was much higher than the ¹MLCT state, thereby making the ${}^{1}IL \rightarrow {}^{1}MLCT \rightarrow {}^{3}MLCT$ process efficient. Furthermore, the energy level of the ³IL state was much higher that the ³MLCT state. Therefore, there was no interaction between these two triplet states, and the intrinsic photophysics of the [Ru(bpy)₃] complex was retained.^[17]



Scheme 2. Qualitative Jablonski diagram showing the rule for effective light-harvesting of the Ru^{II}–polypyridine–chromophore arrays (**Ru-2** shown as an example). The relative energy levels of the states may vary from complex to complex. GS is the ground state (S₀), ¹MLCT* is the metal-to-ligand-charge-transfer excited state (singlet), ISC is intersystem crossing, ³MLCT is the metal-to-ligand-charge-transfer excited state (triplet), TTE is triplet–triplet equilibrium (here, it is the equilibrium between the ³MLCT and ³IL states), IC is internal conversion, ³IL is the coumarin-localized triplet excited state, ¹IL is the coumarin-localized singlet excited state, Allowed processes are marked by a tick. The spin state of the excited electronic states or the relative energy levels dictates the possibility of a process.

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Because the energy level of the ¹IL state was close to that of the ¹MLCT state for complex **Ru-2**, it displayed the lightharvesting effect, but in a more red-shifted region than Ru-1. Therefore, on absorption by the coumarin ligand at 475 nm ($\varepsilon = 63300$ cm⁻¹mol⁻¹dm³), the energy of the ¹IL state was efficiently transferred to the ¹MLCT state and finally to the emissive ³MLCT state (Figure 1b). Direct ¹IL \rightarrow ³IL transition was also possible.

A longer phosphorescence lifetime was observed for complex Ru-2 (3.8 μ s) versus Ru-1 (1.1 μ s). We proposed that the energy level of the ³IL state of complex **Ru-2** was close to the emissive ³MLCT state. Thus, a triplet-triplet equilibrium (TTE) was established.^[9,17] The ³IL state was usually a long-lived non-radiative excited state and its lifetime was much longer than that of the ³MLCT state;^[17] thus, it served as an energy reservoir to funnel energy to the emissive ³MLCT state, and the lifetime of the ³MLCT state was prolonged. A lower phosphorescence quantum yield ($\Phi = 0.09$) was observed for complex Ru-2 compared to Ru-1 ($\Phi =$ 0.14).

Nanosecond time-resolved transient difference absorption spectroscopy: The nanosecond time-resolved transient absorptions of the complexes were also studied (Figure 3). For complex **Ru-1**, typical transient absorption of the Ru^{II}–polyimine complexes was observed (Figure 3a), with the bleaching of the ground state at 450 nm (the bleaching at 600 nm was due to the emission of complex Ru-1). For complex Ru-2, both the ground-state bleach of the MLCT and the intraligand (IL) states were located at about 450 nm (Figure 3b). Furthermore, transient absorption beyond 500 nm was observed, which was tentatively assigned to the coumarin moiety. For complexes Ru-3 and Ru-4, similar transient absorption profiles were observed. The bleaching of Ru-3 at 480 nm was due to the IL state, which indicated that the ³IL component in the triplet excited state was dominant. Thus,



Above all, the unique photophysics of complex Ru-3, that is, weak emission and a blueshifted excitation spectrum compared to its UV/Vis absorption spectrum (Figure 1b and Figure 2c), were also rationalized by the Jablonski diagram (Scheme 2), for which the ligand-centered ¹IL and ³IL states had lower energy levels than the ¹MLCT and ³MLCT states of the coordination center, respectively. Two pathways were possible for the light-harvesting effect: the $^{1}IL \rightarrow ^{1}MLCT \rightarrow ^{3}MLCT$ and $^{1}IL \rightarrow ^{3}IL \rightarrow ^{3}MLCT;$ thus, reversed energy-transfer of

Figure 3. Nanosecond time-resolved transient absorption of: a) Ru-1, b) Ru-2, c) Ru-3, and d) Ru-4 (1.0× 10⁻⁵м, in MeCN, 20°C).

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was

Moreover, the low phosphores-

possible.

 $^{1}MLCT \rightarrow ^{1}IL$

we proposed that the ³IL excited state of Ru-3 was at a lower energy level than the ³MLCT state, which led to the weak emission of Ru-3.

Spin-density surfaces of the Ru^{II} complexes: The ³IL excited states of complexes Ru-2, Ru-3, and Ru-4 were confirmed by DFT calculations on the spin-density surface of the T_1 state (Figure 4). For complex Ru-1, the spin density of the



Figure 4. Spin-density distribution for the lowest triplet state of arrays Ru-1, Ru-2, Ru-3, and Ru-4. Calculated at the DFT/B3LYP/6-31G(d)/ LANL2DZ level with Gaussian 09W.[34]

triplet state was distributed over the Ru^{II} center and the bpy ligands, which was in agreement with the MLCT excited state of typical Ru^{II}-polyimine complexes. However, for complexes Ru-2, Ru-3, and Ru-4, the spin density was mainly distributed over the coumarin moiety and the Phen ligand. Thus, the ³IL state was the major component of the triplet excited states of these complexes.

cence quantum yield of complex **Ru-3** ($\Phi = 0.0045$) was rationalized by the lower energy level of the ³IL state than the ³MLCT state of the array. As a result, no efficient TTE was established between the ³MLCT and the ³IL states. The radiative rate constant ($k_r = 1.81 \times 10^3 \text{ s}^{-1}$) was much smaller than the other complexes. Furthermore, the energy gap of the ¹IL and the ³IL states may have also been important for the photophysics of the complexes. Because the ³IL state was a non-emissive excited state (the existence of this dark state was supported by the upconversion experiments, see below), the phosphorescence quantum yield of complex **Ru-3** was greatly reduced. The photophysics of complex **Ru-4** was similar to **Ru-1**.

We demonstrated that the effective absorption of the Ru^{II}-polypyridine-chromophore arrays (absorption bands) that could either lead to phosphorescence or to produce a triplet excited state), could not be extended into the redregion of the spectrum without limitations. The extent to which this restriction was imposed directly correlated with the energy level of the ¹MLCT state of the Ru^{II} complex. The apparent intense absorption in the visible range (such as with complex Ru-3) would not be funneled efficiently to the emissive ³MLCT state if the ¹IL energy level of the donor (a light-harvesting antenna-localized singlet state, for example, coumarin for Ru-3) was lower than that of the ¹MLCT state of the acceptor. In that case, the energy level of the ³IL state may have often been lower than the ³MLCT state. This role was used to rationalize many unsatisfactory attempts at the preparation of light-harvesting arrays based on Ru^{II}-polypyridine complexes and chromophores, such as BODIPY.^[11,22] Herein, we propose that, among the other reasons, BODIPY cannot serve as an efficient light-harvesting unit to induce intense phosphorescence for the Ru^{II} arrays because the energy level of the ¹IL state of BODIPY (about 500 nm, 2.48 eV) is simply lower than that of the ¹MLCT state (450 nm, 2.76 eV). Another energy-transfer pathway, ${}^{1}IL \rightarrow {}^{3}IL$, is most-probably frustrated because the heavy-atom effect on the organic chromophore in this kind of dyad is usually weak. This general rule will be useful for the design of light-harvesting Ru^{II} arrays that show intense absorption in the visible spectrum and, at the same time, intensified ³MLCT emission. However, one should be careful to apply this rule to complexes with large π -conjugated frameworks.^[9]

Application of the visible-light-harvesting arrays: Triplettriplet-annihilation-based upconversion: These new Ru^{II}based light-harvesting arrays showed intense absorption in the visible spectrum and efficient population of the triplet excited states. Thus, these complexes could be used for photochemical processes that involve triplet–triplet energytransfer. As a preliminary application of these visible-lightharvesting Ru^{II}–polypyridine–coumarin arrays, we studied the triplet–triplet annihilation (TTA) upconversion ability of these complexes as triplet photosensitizers. Light upconversion, which is the observation of an emission at a higher energy (shorter wavelength) than the excitation energy (longer wavelength), has attracted much attention owing to its applications in optoelectric materials, molecular probes, photovoltaics, and artificial photosynthesis.^[2,9,23]

Currently, several approaches are available for light upconversion. For example, two-photon absorption (TPA) dyes can absorb at longer wavelength and produce fluorescence emissions at shorter wavelength. However, TPA can usually only be achieved with coherent laser irradiation, with typical power densities of the order of $MW \text{ cm}^{-2}$ (×10⁶ W cm⁻¹).^[24] This value is well beyond the power density of a normal light source, or of terrestrial solar radiance (typically 0.10 W cm⁻²). Furthermore, the emission wavelength of a TPA dye cannot be readily tuned because it is difficult to tailor the chromophore to tune the emission wavelength, and at the same time, to maintain a large TPA cross-section.

Recently, a new method for light upconversion by using TTA has emerged (see Scheme 3).^[25-32] In this approach, an energy donor (sensitizer) is excited first. Next, the triplet state (T_1) of the sensitizer is populated through ISC, and the energy is transferred (triplet-triplet energy-transfer, TTET; [Eq. (1a)]) to the triplet state of the accepter. Then, two molecules in triplet state ³A* annihilate into a molecule in a singlet excited state (¹A*), and another molecule in the ground state (¹A) [Eq. (1b)]. Fluorescence light is then emitted from the singlet excited state $({}^{1}A^{*}; [Eq. (1c)];$ see also Scheme 3). This kind of upconversion can be achieved with non-coherent excitation at very low power density, that is, much less than 100 mW cm⁻², thereby making this method particularly suitable for a wide range of applications.^[24] Furthermore, the modular feature of the TTA upconversion makes the absorption and the emission wavelength of the TTA system amenable to wavelength tuning by judicious selection of donor (sensitizer)/acceptor (annihilator) pairs.

 ${}^{3}\text{Ru}^{*}+\text{DPA} \rightarrow \text{Ru}+{}^{3}\text{DPA}^{*} (\text{TTET})$ (1a)

 $^{3}\text{DPA}^{*}+^{3}\text{DPA}^{*} \rightarrow ^{1}\text{DPA}^{*}+\text{DPA} (\text{TTA})$ (1b)

 $^{1}\text{DPA}^{*} \rightarrow \text{DPA}+hv$ (fluorescence by emission) (1c)

However, the development of TTA-based light upconversion is still in its infancy. For example, the Ru^{II} complexes used in the TTA up-conversion are the parent complexes, which typically show poor absorption in the visible spectrum.^[15,30] Therefore, we set out to investigate the effect of light-harvesting in complexes **Ru-2**, **Ru-3** and **Ru-4** on the efficiency of upconversion.

We selected 9,10-diphenylanthracene (DPA) as the acceptor/annihilator for the TTA experiments because the triplet-state energy of DPA (1.77 eV, 700 nm) was lower than the triplet energy level of the donor/sensitizer (for example, 2.07 eV, 600 nm), which matched the requirements for the TTA upconversion system.^[15]

We observed blue fluorescence emission of DPA (at 400 nm and longer wavelength) with 473 nm laser excitation of mixtures of **Ru-2**, **Ru-3**, and **Ru-4** with DPA, respectively (Figure 5).^[15] The typical excitation power was 5 mW (power





Figure 5. Upconversion with the Ru^{II} complexes as sensitizers (in MeCN, 20 °C). a) Emission of upconverted DPA $(4.0 \times 10^{-5} \text{ M})$ and residual phosphorescence following selective excitation of the sensitizers $(1.0 \times 10^{-5} \text{ M})$ at 473 nm (71 mW cm⁻²). b) Emission of the complexes without DPA.

density: 71 mWcm⁻²), which was too low for simultaneous two-photon absorption. The anti-Stokes shift of the upconversion was 0.48 eV. However, for Ru-1, no significant upconverted fluorescence was observed under the experimental conditions (which was below the threshold for upconversion with Ru-1). Excitation of DPA or the complexes alone (473 nm laser) failed to produce any emission in the range 400-500 nm. Therefore, the fluorescence emission was the result of TTA upconversion. Besides the fluorescence bands in the range 400-500 nm, phosphorescence bands of the sensitizer were simultaneously observed (centered at 600 nm), which were due to the non-complete TTET (Figure 5a).^[31] Interestingly, although complex Ru-3 showed intense absorption that was similar to that of Ru-2, the upconversion of Ru-3 was much weaker than Ru-2. This result demonstrated that the light-harvesting effect of Ru-3 was not effective, that is, the energy of the absorbed light could not be efficiently transferred to a triplet excited state, either through $^{1}IL \rightarrow ^{1}MLCT \rightarrow ^{3}MLCT$ or $^{1}IL \rightarrow ^{3}IL$ pathways.

We measured the upconversion quantum yields (Φ_{UC}) of the complexes versus two independent standards: coumarin 6 (Φ =0.78 in EtOH) and 2,5-dibutyl-3,6-bis-phenyl-pyrrolo-[3,4-c]pyrrole-1,4-dione (DPP; Φ =0.69 in DMSO). The observed upconversion quantum yield of complex **Ru-2** was 15.2%, which was about 16 times that of parent complex **Ru-1** and of benchmark complex [Ru(dmb)₃][PF₆]₂ (dmb= 4,4'-dimethyl-2,2'-bipyridine).^[15] We observed significantly upconverted fluorescence with **Ru-2**/DPA, but little or no upconverted fluorescence with [Ru(dmb)₃][PF₆]₂ or **Ru-1**. Although the emission of **Ru-3** was weaker than that of **Ru-4** (Figure 5b), the upconverted fluorescence of **Ru-3**/DPA was significant. We believed that, with complex **Ru-3**, there must have been a triplet dark state that was populated by the 473 nm laser excitation, and that it was this state by which the TTA process was activated.^[32a,c] Dark triplet states, such as ³IL, are ideal as energy reservoirs for the triplet energy-transfer to the acceptor/annihilator.^[32a,c,f,i,j] This assumption is consistent with our photophysical studies (Figure 1). Currently, we are actively working along this line to devise transition-metal complexes with dark triplet excited states (i.e., non-luminescent, but the triplet state can be populated by photoexcitation) as sensitizers to improve the quantum yield of the TTA-based upconversion, because, in this case, the phosphorescence emission of the triplet sensitizer was actually competitive with the upconversion.

The enhancement in upconversion by light-harvesting was demonstrated by comparing the results of complexes **Ru-2** and **Ru-4**. Both complexes showed similar phosphorescence quantum yields and lifetimes (Table 1). However, the upconverted fluorescence emission intensity of complex **Ru-2** was about 3.0-fold larger than that of **Ru-4**; this ratio was in agreement with the ratio of the molar extinction coefficients of the two complexes at 473 nm. This result indicated that the light-harvesting of **Ru-2** was effective in producing the triplet excited states of the complex.

The upconversion was detectable by the naked eye (Figure 6). Under these conditions, complex **Ru-1** did not



Figure 6. Photographs of the upconversion. Upconversion spectra of the samples are shown in Figure 5. λ_{ex} =473 nm (71 mW cm⁻²), MeCN, 20 °C, c[sensitizers]=1.0×10⁻⁵ M, c[DPA]=4.0×10⁻⁵ M.

show significant upconversion. Therefore, the red phosphorescence of the complex was observed. For light-harvesting array **Ru-2**, an intense purple color was observed in the presence of DPA, owing to the efficient upconversion (fluorescence was in blue region of the spectrum). For complexes **Ru-3** and **Ru-4**, upconversion were also observed but the efficiency was lower than that of **Ru-2**.

The efficiency of the TTET process was quantitatively evaluated by quenching of the phosphorescence of the complexes with DPA as the triplet quencher, that is, the emission of the complexes was reduced in the presence of DPA (in this case, quenching of the Föster energy-transfer was impossible, owing to the non-overlapping absorption/emission spectra of the acceptor and the donor). Stern–Volmer quenching curves were constructed with the quenching data (Figure 7). Complex **Ru-2** clearly gave the most-significant



Figure 7. Stern–Volmer plots generated from quenching of the emission intensity of: $[Ru(dmb)_3]^{2+}$ (λ_{ex} =460 nm), **Ru-1** (λ_{ex} =450 nm), **Ru-2** (λ_{ex} =450 nm), **Ru-3** (λ_{ex} =480 nm), and **Ru-4** (λ_{ex} =450 nm) measured as a function of DPA (triplet quencher) concentration in CH₃CN, 20 °C.

quenching effect in the presence of DPA. The Stern–Volmer quenching constant (Table 2) was $8.80 \times 10^4 \text{ m}^{-1}$ and the bimolecular quenching constant was up to $2.32 \times 10^{10} \text{ m}^{-1} \text{ s}^{-1}$, which was close to the diffusion-controlled limit (10^9 – $10^{10} \text{ m}^{-1} \text{ s}^{-1}$). For other complexes, lower quenching constants were observed and the trend was in agreement with the life-times of the complexes.

Table 2. Parameters for the upconversion of the Ru^{II} complexes.

	$K_{\rm sv} \; (imes 10^3) \; [{ m m}^{-1}]^{[{ m b}]}$	$k_{\rm q}~(imes 10^9)~[{ m m}^{-1}{ m s}^{-1}]^{[{ m c}]}$	$arPsi_{ m UC}[\%]^{[d]}$
Ru-1	8.65	7.86	0.95
Ru-2	88.0	23.2	15.2
Ru-3	17.1	6.86	2.7
Ru-4	27.1	8.76	11.3
[Ru(dmb) ₃]	3.1	3.54	0.92

[a] In deaerated CH₃CN (1.0×10^{-5} M, 20 °C). [b] Stern–Volmer quenching constant ($K_{\rm SV}$). [c] Bimolecular quenching constants ($k_{\rm q}$). [d] Upconversion quantum yields ($\Phi_{\rm UC}$).

The upconversion efficiency was enhanced by improving the light-harvesting ability and prolonging the phosphorescence lifetimes of the energy donors/sensitizers (Figure 5):

light-harvesting would produce more ³MLCT excited states (with complex Ru-2), whereas longer phosphorescence lifetimes would enhance the TTET process (with complexes Ru-2, Ru-3, and Ru-4), and both enhancements would improve the TTA-based upconversion. The lifetime of complex Ru-1 was below the threshold of the experimental conditions (such as DPA concentration, laser power density, etc.). Therefore, no significant upconverted fluorescence was observed (for the upconversion of Ru-1 in the presence of more-concentrated DPA, see the Supporting Information). The higher upconversion efficiency of Ru-3 was due to the non-emissive ³IL state, with which the TTA process could also be initiated. The upconversion of Ru-4 was due to the long-lived triplet excited state, with which the TTET and TTA efficiency was improved. The upconversion of Ru-2 was even more efficient than that of Ru-4, owing to the enhanced light-harvesting effect of Ru-2 over Ru-4.

The principle photophysics of the TTA-based light upconversion of the arrays are summarized in Scheme 3, which shows the effects of the light-harvesting of array **Ru-2**, the extended phosphorescence lifetimes of array **Ru-2**, and the populated non-emissive ³IL state of array **Ru-3** on the TTAbased upconversion efficiency. Two pathways are possible for the light-harvesting effect: ¹IL \rightarrow ¹MLCT \rightarrow ³MLCT and ¹IL \rightarrow ³IL \rightarrow ³MLCT.



Scheme 3. Qualitative Jablonski diagram showing the sensitized TTA upconversion with $Ru^{\mbox{\tiny II}}$ complexes as the triplet photosensitizers and DPA as the triplet acceptor. The effect of the light-harvesting ability and the phosphorescence lifetime of the Ru^{II} sensitizers on the efficiency of TTA upconversion is also shown (Ru-2 shown as an example). E is energy, GS is the ground state (S₀), ¹IL* is the intraligand singlet excited state (coumarin-localized), IC is internal conversion, ¹MLCT* is the Ru^{II} based metal-to-ligand charge-transfer singlet excited state, ISC is intersystem crossing, ³MLCT* is the Ru^{II}-based metal-to-ligand-charge-transfer triplet excited state, 3IL* is the intraligand triplet excited state (coumarin-localized). We proposed that the ³IL* and ³MLCT* of array Ru-2 were in equilibrium, which prolonged the lifetime of the excited states. TTET is triplet-triplet energy transfer, ³DPA* is the triplet excited state of DPA, TTA is triplet-triplet annihilation, ¹DPA* is the singlet excited state of DPA. The emission bands observed for the sensitizers were the ³MLCT emissive excited state (herein, the ³IL* was non-emissive). The emission bands observed in the TTA experiment were the simultaneous ³MLCT* emission (phosphorescence) and ¹DPA* emission (fluorescence). The typical power density of the laser used in the upconversion was 71 mW cm⁻²

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Conclusion

We have reported the first effective visible-light-harvesting Ru^{II}-polypyridine-coumarin array, which shows enhanced absorption in the visible range and efficient energy-transfer from the light-harvesting antenna to the coordination center. The absorption of molecular array Ru-2 was in the visible range (400-500 nm) and the molar extinction coefficient ($\varepsilon = 6.33 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$ at 475 nm) was enhanced by 3.9fold compared to the parent complex (Ru-1). Previously, no effective visible-light-harvesting Ru^{II}-chromophore had been reported with efficient energy-transfer from the lightharvesting antenna to the coordination center and without loss in the acceptor phosphorescent quantum yield. We also proposed a general rule to help the design of visible-lightharvesting Ru^{II}-organic-chromophore arrays. This rule stated that the energy levels of the ¹IL and ³IL state (intraligand, the light-harvesting organic chromophore) must be close to the energy levels of the intrinsic S_1 and T_1 states of the MLCT acceptor, otherwise the ${}^{1}IL \rightarrow {}^{1}MLCT$ energytransfer is inefficient (in some circumstances, the direct ${}^{1}IL \rightarrow {}^{3}IL$ transition is frustrated owing to a weak heavyatom effect). Thus, a limitation was imposed on the attempts to shift the effective absorption of the Ru^{II}-organic-chromophore arrays to the red-end of the spectrum. As a preliminary application of the light-harvesting Ru^{II} complex, triplettriplet annihilation upconversion was performed, in which the complexes were used as triplet sensitizers, and the upconversion quantum yield was up to 15.2% (about 16.5 times that of the parent complexes, which did not show a light-harvesting effect, under the same experimental conditions). These results will be important for the design of efficient Ru^{II}-organic-chromophore light-harvesting arrays, of which the Ru-2 array reported here is the first successful example.

Experimental Section

General analytical measurements: NMR spectra were recorded on a Bruker 400 MHz spectrometer. CDCl₃ or CDCl₃/CD₃OD were used as the solvents and tetramethylsilane (TMS) was used as a reference ($\delta =$ 0.00 ppm). High-resolution mass spectra (HRMS) were determined on a LC/Q-TOF MS system (UK). Fluorescence spectra were measured on a F4500 (Hitachi) or a CRT 970 spectrofluorometer. Fluorescence lifetimes were measured with a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon). Absorption spectra were recorded on a Perkin-Elmer-Lambda-35 UV/Vis spectrophotometer. Compounds 2, 3, 5, 6, 7, 8, 9, and 10 were synthesized according to literature procedures.^[33] The spin-density surface of the Ru^{II} complexes were optimized in their triplet state geometries at the B3LYP/6-31G(d)/LANL2DZ level with Gaussian 09W.^[34] Synthesis of compound 11: After degassing a mixture of EtOH (4.0 mL)/ toluene(4 mL)/water (8.0 mL), compound 10 (150.0 mg, 0.51 mmol), 4formylphenylboronic acid (153.0 mg, 1.02 mmol), and K₂CO₃ (211.0 mg, 1.53 mmol) were added, the flask was placed under vacuum and backfilled with argon several times. Then, [Pd(PPh₃)₄] (30.0 mg, 0.026 mmol, 5.0 mol%) was added, the reaction mixture was heated at 80°C for 8 h. After being cooled to RT, the solvent was evaporated under reduced pressure and the organic phase was extracted with CH₂Cl₂ and dried over Na2SO4. The solvent was removed under reduced pressure and the crude

product was purified by column chromatography on silica gel (CH₂Cl₂) to give the light-yellow product (130.0 mg, yield: 79.4%). ¹H NMR (400 MHz, CDCl₃): $\delta = 10.03$ (s, 1H), 7.92 (m, 4H), 7.81 (s, 1H), 7.36 (d, 1H, J = 9.0 Hz), 6.63 (d, 1H, J = 8.5 Hz), 6.54 (s, 1H), 3.48–3.42 (m, 4H), 1.24 ppm (t, 6H, J = 7.0 Hz).

General method for synthesis of the imidazole-linked phenanthroline ligands: Under an Ar atmosphere, 1,10-phenanthroline-5,6-dione (100.0 mg, 0.48 mmol), the corresponding aldehyde (1.2 equiv), and ammonium acetate (685.7 mg, 9.62 mmol) were dissolved in glacial acetic acid (20 mL) and the mixture were heated to reflux for 6 h. After completion of the reaction, the mixture was cooled to RT and a majority of the solvent was removed under reduced pressure. Next, a dilute solution of NaOH was to adjust the pH value to about 7.0. A yellow precipitate formed which was collected, washed with water, and dried under vacuum overnight. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/MeOH, 10:1 v/v).

Compound L1: Compound **L1** was obtained as a pale white precipitate and purified by recrystallization (106.6 mg, 75.0%). ¹H NMR (400 MHz, [D₄]MeOH): δ = 8.74 (d, 1 H, *J* = 3.9 Hz), 8.59–8.32 (m, 1 H), 7.98 (d, 1 H, *J* = 7.8 Hz), 7.48–7.41 (m, 3 H), 4.87 ppm (m, 5 H); ¹³C NMR (100 MHz, [D₄]MeOH): δ = 151.42, 147.42, 143.14, 129.77, 129.63, 128.81, 126.47, 123.10 ppm; HRMS (ESI): *m*/*z* calcd for [C₁₉H₁₂N₄+H]⁺: 297.1140; found: 297.1135.

Compound L2: Yellow solid (130.0 mg, 62.1%); ¹H NMR (400 MHz, CDCl₃): δ =9.16 (d, 2H, J=4.2 Hz), 8.99 (s, 1H), 8.78 (d, 2H, J=5.8 Hz), 7.72–7.69 (m, 2H), 7.48 (d, 1H, J=8.0 Hz), 6.66–6.63 (m, 1H), 6.50 (d, 1H, J=2.3 Hz), 3.48–3.43 (m, 4H), 1.26 ppm (t, 6H, J=7.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ =162.1, 156.4, 151.7, 148.2, 146.8, 144.3, 141.5, 130.1, 129.4, 122.9, 110.0, 108.7, 107.7, 96.8, 45.1, 12.5 ppm; HRMS (ESI): *m/z* calcd for [C₂₆H₂₁N₅O₂+H]⁺: 436.1774; found: 436.1767.

Compound L3: Yellow solid (70.0 mg, 32.0%); ¹H NMR (400 MHz, CDCl₃): δ =9.15 (d, 2H, *J*=4.2 Hz), 8.88–8.51 (m, 3H), 7.78–7.75 (m, 2H), 7.12 (s, 1H), 3.40–3.35 (m, 4H), 2.91 (t, 2H, *J*=5.9 Hz), 2.82 (t, 2H, *J*=6.0 Hz), 2.04–2.01 ppm (m, 4H); HRMS (ESI): *m/z* calcd for [C₂₈H₂₁N₅O₂+Na]⁺: 482.1593; found: 482.1586.

Compound L4: The crude product was washed several times with CH₂Cl₂. ¹H NMR (400 MHz, CDCl₃): δ =9.25 (m, 2H), 9.04 (m, 2H), 8.32(m, 2H), 8.04–7.91(m, 4H), 7.46 (t, 2H, *J*=9.3 Hz), 6.74 (d, 1H, *J*=8.0 Hz), 6.57 (d, 1H, *J*=8.2 Hz), 3.51–3.48 (m, 4H), 1.24 ppm (t, 6H, *J*=6.8 Hz); HRMS (ESI): *m/z* calcd for [C₃₂H₂₅N₅O₂+H]⁺: 512.2087; found: 512.2090.

General method for the preparation of the Ru^{II} complexes: [RuCl₂-(cymene)] (0.5 equiv) and ligands L1–L4 (1.0 equiv) were dissolved in EtOH (5.0 mL). The mixture was stirred at RT under a N₂ atmosphere for 2 h. The reaction was monitored by TLC. Next, a solution of 2,2'-bipyridine (bpy, 2.0 equiv) in water (10 mL) was added and the mixture was heated to reflux for 22 h. After cooling, the solution was concentrated under reduced pressure and treated with a saturated aqueous solution of NH₄PF₆. A red precipitate formed which was collected by filtration. The crude product was then purified by column chromatography on silica gel (MeCN/water/saturated aqueous NaNO₃, 100/9/1 v/v) and treated again with a saturated aqueous solution of NH₄PF₆. A precipitate formed which was collected, washed with water, and dried under vacuum.

Ru-1: Red solid (36.7 mg, 75.0 %); ¹H NMR (400 MHz, [D₆]acetone): $\delta = 13.38$ (s, 1 H), 9.18 (d, 1 H, J = 8.0 Hz), 9.07 (d, 1 H, J = 8.0 Hz), 8.86–8.80 (m, 4 H), 8.37–8.32 (m, 4 H), 8.26 (t, 2 H, J = 7.7 Hz), 8.24–8.12 (m, 4 H), 7.96–7.95 (m, 4 H), 7.65–7.59 (m, 5 H), 7.40 ppm (m, 2 H). ¹³C NMR (100 MHz, [D₆]acetone): $\delta = 158.3$, 158.1, 153.8, 152.8, 152.6, 151.3, 151.1, 138.8, 138.8, 131.6, 131.4, 131.2, 131.1, 130.3, 130.1, 128.7, 128.6, 127.4, 127.2, 126.9, 125.3, 125.2 ppm; HRMS (ESI): m/z calcd for [(M-2PF₆)^{2+/} 2]: 355.0735; found: 355.0754.

Ru-2: Red solid (70.0 mg, 53.4%): ¹H NMR (400 MHz, [D₆]acetone): δ = 12.81 (s, 1 H), 9.47 (m, 1 H), 9.16 (m, 1 H), 9.03 (m, 1 H), 8.88–8.82 (m, 4H), 8.38 (d, 1 H, *J*=5.0 Hz), 8.34 (d, 1 H, *J*=5.0 Hz), 8.27 (t, 2 H, *J*= 8.0 Hz), 8.20–8.13 (m, 4 H), 7.98–7.91 (m, 4 H), 7.78–7.72 (m, 1 H), 7.65 (t, 2 H, *J*=6.5 Hz), 7.40 (t, 2 H, *J*=6.5 Hz), 6.89 (m, 1 H), 6.65 (m, 1 H), 3.63–3.61 (m, 4 H), 1.29–1.26 ppm (m, 6 H); ¹³C NMR (100 MHz,

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Ru-3: Red solid (15.1 mg, 11.9%); ¹H NMR (400 MHz, [D₆]acetone) δ = 12.74 (s, 1 H), 9.38 (d, 1 H, *J*=8.3 Hz), 9.09 (d, 1 H, *J*=8.1 Hz), 8.86–8.78 (m, 5 H), 8.34–8.29 (m, 2 H), 8.23 (t, 2 H, *J*=8.0 Hz), 8.16–8.10 (m, 4 H), 7.95–7.86 (m, 4 H), 7.61 (t, 2 H, *J*=6.1 Hz), 7.37 (t, 2 H, *J*=6.8 Hz), 7.27 (s, 1 H), 3.42–3.38 (m, 4 H), 2.82–2.78 (m, 4 H), 1.99–1.94 ppm (m, 4 H). ¹³C NMR (100 MHz, [D₆]acetone): δ =161.7, 158.3, 158.1, 152.9, 152.9, 151.2, 150.9, 150.7, 148.9, 146.8, 146.1, 143.9, 138.9, 138.8, 138.2, 131.9, 131.7, 131.6, 129.6, 128.7, 128.6, 127.6, 127.2, 126.9, 126.8, 126.8, 125.3, 125.2, 122.5, 120.9, 109.1, 106.5, 106.4, 50.8, 50.3, 21.8, 20.8, 20.7 ppm; HRMS (ESI): *m/z* calcd for [(M-2PF₆)²⁺/2]: 436.6057; found: 436.6064.

Ru-4: Red solid (48.6 mg, 42.3 %); ¹H NMR (400 MHz, [D₆]acetone): δ =9.07 (s, 2 H), 8.85–8.82 (m, 4H), 8.36 (d, 2 H, *J*=4.6 Hz), 8.31–8.24 (m, 4H), 8.20–8.14 (m, 5 H), 8.01–7.92 (m, 6 H), 7.64 (t, 2 H, *J*=6.5 Hz), 7.55 (d, 1 H, *J*=8.8 Hz), 7.42 (m, 2 H), 6.80 (d, 1 H, *J*=8.8 Hz), 6.54 (s, 1H), 3.58–3.53 (m, 4H), 1.24 ppm (t, 6H, *J*=8.0 Hz); ¹³C NMR (100 MHz, [D₆]acetone): δ =161.2, 158.3, 158.1, 157.4, 153.7, 152.9, 152.9, 152.0, 151.2, 142.1, 139.2, 138.9, 138.8, 130.6, 129.5, 129.0, 128.7, 128.6, 127.1, 125.3, 125.2, 119.4, 110.2, 109.7, 97.2, 45.3, 12.7 ppm; HRMS (ESI): *m/z* calcd for [(M-2PF₆)²⁺/2]: 462.6213; found: 462.6208

Upconversion: The upconversion were carried out with two continuouswave diode-pumped solid-state lasers (DPSSLs) with outputs at 473 and 532 nm, respectively (the power was tunable in the range of 0-200 mW). A reflecting lens was used to direct the laser beam into the sample cell so that the laser beam was not directed toward the detector window of the fluorospectrometer. A small black box was used to trap the laser beam behind the sample cell to suppress the scattered laser; thus, no notch filter was necessary. All the solutions were purged with Ar for 30 min before the measurements were taken. The typical laser power was 5 mW (the diameter of the laser spot was 3 mm; thus, the power density of the laser was about 71 mW cm⁻²). The upconversion quantum yields were determined with two dyes: coumarin 6 (Φ =0.78 in EtOH) and 2,5dibutyl-3,6-bis-phenyl-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP; $\Phi = 0.69$ in DMSO) as the quantum-yield standards, and the quantum yields were calculated by using [Eq. (2)],^[25b] where $\Phi_{\rm UC}$, $A_{\rm unk}$, $I_{\rm unk}$, and $\eta_{\rm unk}$ represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the samples, respectively. The upconversion quantum yields determined with the two standards were basically the same with relative errors permissible; the final value was the average of the two.

$$\phi_{UC} = 2\phi_{std} (\frac{A_{std}}{A_{unk}}) (\frac{I_{unk}}{I_{std}})^2 (\frac{\eta_{unk}}{\eta_{std}})^2$$
(2)

Photographs of the upconversion were taken with a Samsung NV5 CCD digital camera. The exposure time was 1 s (the default value of the digital camera under the experimental conditions).

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