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# Visible-Light Harvesting with Cyclometalated Iridium(III) Complexes Having Long-Lived $^3$IL Excited States and Their Application in Triplet–Triplet-Annihilation Based Upconversion

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Cyclometalated iridium(III) complexes with intense absorption in the visible region ($\varepsilon$ = 70920 $\mathrm{M^{-1}\,cm^{-1}}$ at 466 nm) were prepared by incorporating light-harvesting coumarin into the diimine ligand (for comparison: $\varepsilon$ = 7030 $\mathrm{M^{-1}\,cm^{-1}}$ at 371 nm for the model diimine complex without light-harvesting ability). The complexes feature long-lived intraligand triplet excited states ($^3$IL, supported by spin density analysis of the triplet state). At room temperature, lifetimes, $\tau_T$, are up to 75.5 µs, as determined by nanosecond time-resolved transient absorption spectroscopy. Despite the weak phosphorescence ($\Phi_P$ = 0.6–0.7 %) observed for the complexes, the triplet excited state ($T_1$) was demonstrated to be efficiently populated upon photoexcitation, by using the complexes as triplet sensitizers in triplet–triplet-annihilation (TTA) upconversion (upconversion quantum yields, $\Phi_{UC}$, are up to 23.4 %). We propose that weakly phosphorescent or even nonphosphorescent transition metal complexes can be used as triplet sensitizers for TTA upconversion, instead of the currently used phosphorescent complexes. Our design of the light-harvesting Ir$^{III}$ complexes will be helpful for the preparation of transition metal complexes with intense absorption of visible light and long-lived triplet excited states, which are suitable for applications in areas such as photocatalysis, photovoltaics, and upconversion.

## Introduction

Cyclometalated iridium(III) complexes have attracted much attention due to their applications in electroluminescence, photocatalysis, phosphorescent molecular probes, and so on.[1–15] Phosphorescent cyclometalated Ir$^{III}$ complexes usually feature high quantum yields and emissive metal-to-ligand charge transfer ($^3$MLCT) excited states. Recently, cyclometalated Ir$^{III}$ complexes have been used as molecular probes, for example, for detection of $Zn^{2+}$ and cysteine, for luminescent labeling of biomolecules, and so on.[9,14,15]

However, the development of Ir$^{III}$ complexes for applications in visible-light harvesting or as molecular probes is still in its early age for a number of reasons: (1) The excitation wavelengths of typical cyclometalated Ir$^{III}$ complexes are in the UV or blue region, and their absorption is weak in the visible region ($\varepsilon < 5000\ \mathrm{M^{-1}\,cm^{-1}}$).[9,14,15] This poor light-harvesting ability is a great disadvantage for many of their potential applications in photovoltaics, photocatalysis, or molecular probes.[9] (2) Attempts to prepare light-harvesting Ir$^{III}$ complexes very often reveal elusive photophysics, for example, the phosphorescence is completely quenched in an Ir$^{III}$-BODIPY dyad.[16] (3) The supramolecular photochemistry of Ir$^{III}$ complexes to optimize their photophysical properties is underdeveloped; for example, the triplet excited states of Ir$^{III}$ complexes have never been rationally tuned to access the long-lived excited states (the typical lifetime of cyclometalated Ir$^{III}$ complexes is usually less than 5.0 µs).[1] On the contrary, rich supramolecular photochemistry has been developed for Ru$^{II}$ polyimine complexes, for example, to establish the long-lived intraligand ($^3$IL) emissive state or the $^3\mathrm{MLCT}\leftrightarrow{}^3\mathrm{IL}$ equilibrium by incorporation of an organic chromophore.[1,17–19] Long-lived triplet excited states are significant for applications in photovoltaics, photocatalysis, molecular sensing, and so on.[17–19] Light-harvesting Ru$^{II}$–coumarin dyads have been designed; however, the coumarin antennas enabled absorption in the UV region.[20] To the best of our knowledge, no light-harvesting Ir$^{III}$–chromophore dyads have been reported.

In order to tackle the aforementioned challenges, we devised visible-light-harvesting cyclometalated Ir$^{III}$–coumarin molecular arrays (Ir-3 and Ir-4, Scheme 1), which show intense absorption of visible light ($\varepsilon$ = 70920 $\mathrm{M^{-1}\,cm^{-1}}$ at 466 nm). By comparison, model complex Ir-1 has an $\varepsilon$ of only 474 $\mathrm{M^{-1}\,cm^{-1}}$ at 466 nm. Room-temperature long-lived $^3$IL excited states were observed for the dyads ($\tau_T$ is 75.5 µs at room temp. for Ir-3, while it is only 0.77 µs for Ir-1). Although UV-absorbing ruthenium-based chromophores exist, we now report a light-harvesting cyclometalated Ir$^{III}$ molecular array with intense absorption in the visible range

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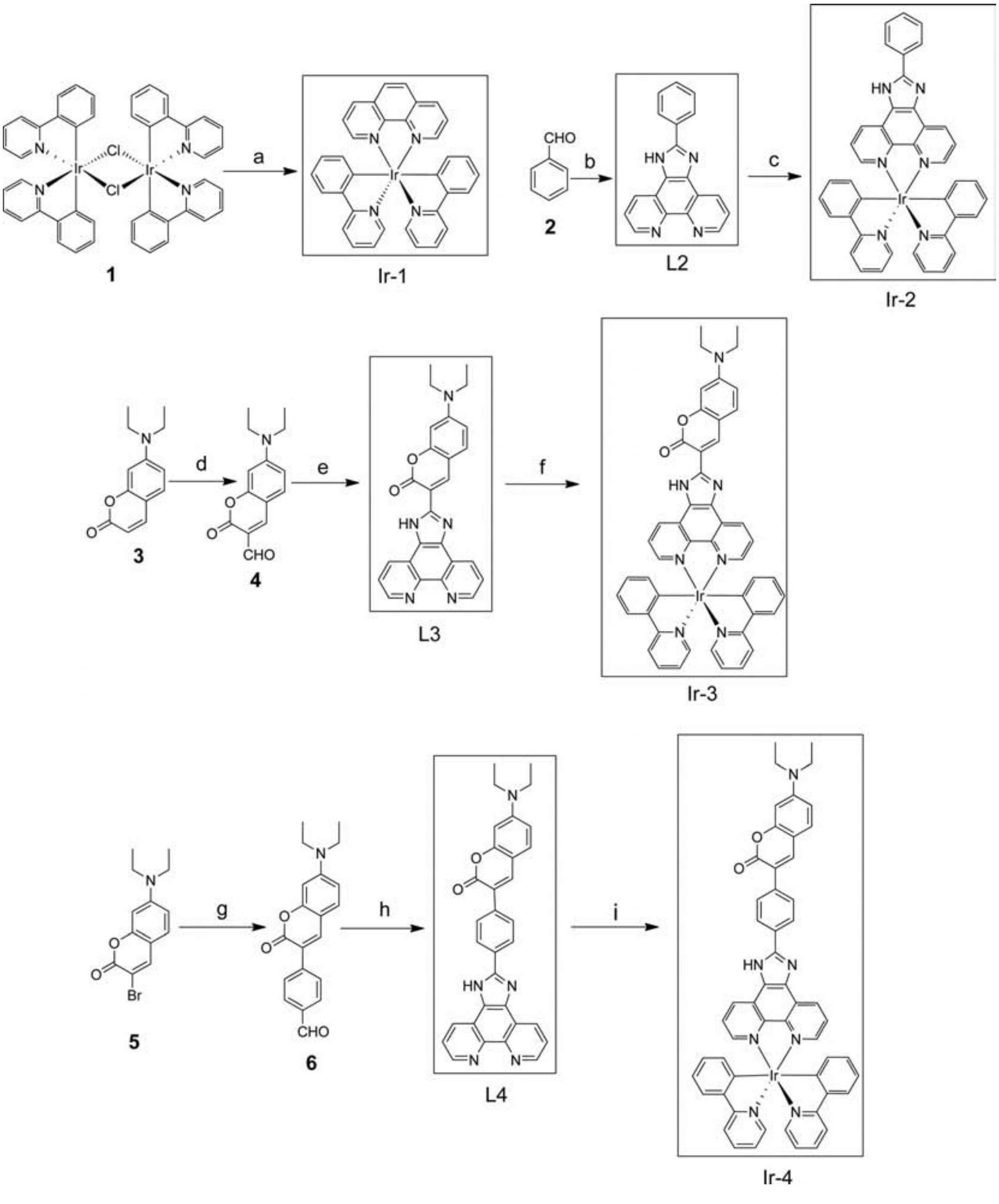
and a triplet excited state that has a lifetime over 25 times longer than those of ruthenium analogues. The dyads are weakly phosphorescent ($\Phi_P$ = 0.6%); however, we proved that the triplet excited states of the $Ir^{III}$ complexes are efficiently populated upon photoexcitation, by using the complexes as triplet sensitizers for triplet–triplet annihilation upconversion.[21–24] Upconversion quantum yields ($\Phi_{UC}$) of up to 23.4% were observed, whereas $\Phi_{UC}$ = 0.0% for Ir-1 and Ir-2 (two complexes without the visible-light harvesting effect) under the same experimental conditions.

## Results and Discussion

### Design of the Light-Harvesting Complexes

Coumarin is well known for its intense absorption. Thus coumarin units were incorporated in $Ir^{III}$ complexes Ir-3 and Ir-4 to enhance its UV/Vis absorption. We used an imidazole scaffold to assemble the $Ir^{III}$–coumarin dyads (Scheme 1; see Supporting Information for the details of the characterization). An extra phenyl linker is present in Ir-4



Scheme 1. Preparation of $Ir^{III}$–coumarin arrays Ir-1, Ir-2, Ir-3, and Ir-4. (a) 1,10-Phenanthroline, $CH_2Cl_2$/MeOH (2:1 v/v), Ar, reflux, 5–6 h; (b, e, and h) 1,10-phenanthroline-5,6-dione, $CH_3COONH_4$, $CH_3COOH$, Ar, reflux, 6 h; (c, f, and i) $[Ir(ppy)_2Cl]_2$, $CH_2Cl_2$/MeOH (2:1 v/v), Ar, reflux, 5–6 h; (d) $POCl_3$, DMF, 0–5 °C; (g) 4-formylphenylboronic acid, $Pd(PPh_3)_4$, toluene/EtOH/water (1:1:2 v/v), Ar, reflux, 5 h.

between the coumarin unit and the imidazole-Phen unit, to investigate the potential effect of the intramolecular hydrogen bond in the ligand of Ir-3. The compounds were obtained in satisfying yields.

### Steady State Spectroscopic Properties

The UV/Vis absorptions of the ligands (Figure 1a) demonstrate the visible-light-harvesting effect in L3 and L4, which have a coumarin unit, whereas L2, which does not have a coumarin unit, has a much lower absorption in the visible range. The ligands have blue to green emissions (Figure 1b), with drastically different fluorescence quantum yields (Table 1).

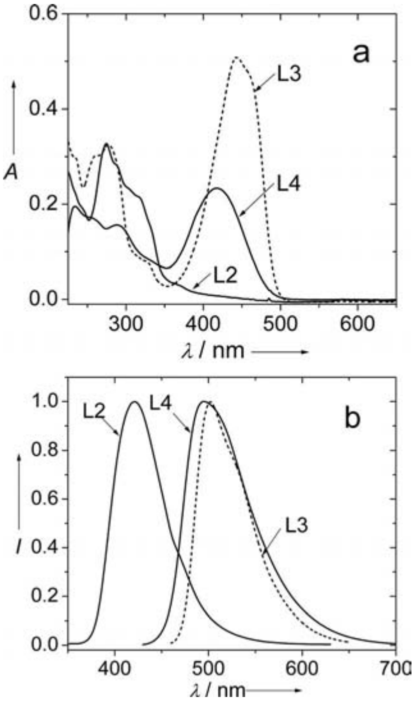


Figure 1. (a) UV/Vis absorption and (b) fluorescence emission spectra of ligands L2 ($\lambda_{ex}$ = 319 nm), L3 ($\lambda_{ex}$ = 450 nm), and L4 ($\lambda_{ex}$ = 414 nm); $1.0 \times 10^{-5}$ M in $CH_2Cl_2$, 20 °C.

Ir-1 and Ir-2 have weak absorption beyond 400 nm, with $\varepsilon < 10000$ M$^{-1}$cm$^{-1}$ (Figure 2a). Intense absorption in the range 250–300 nm was observed for all the complexes ($\varepsilon$ up to 60000 M$^{-1}$cm$^{-1}$), which is due to the ligand-localized $S_0 \rightarrow {}^1IL$ transition. For Ir-3 and Ir-4, however, intense absorption in the visible region (466 nm for Ir-3) was found, with $\varepsilon$ up to 70920 M$^{-1}$cm$^{-1}$, which is due to the coumarin ligand. It is notable that the $\varepsilon$ values of Ir-3 and Ir-4 are comparable to those of the well-known organic dyes that show intense absorption in the visible region, such as boron-dipyrromethene (BODIPY).[25] The blueshifted absorption of Ir-4 relative to that of Ir-3 may be due to the lack of the intramolecular hydrogen bond; the absorption profiles of the complexes are similar to those of the free ligands (Figure 1a).

Table 1. Photophysical parameters of the ligands and the Ir$^{III}$ complexes in $CH_2Cl_2$ (ligands) or $CH_3CN$ (complexes); $1.0 \times 10^{-5}$ M solution; 20 °C.

| | $\lambda_{abs}$[a] | $\varepsilon$[b] | $\lambda_{em}$[c] | $\Phi$ | $\tau_L$[f] | $\tau_T$[g] |
|---|---|---|---|---|---|---|
| L-2 | 275 | 31 650 | 421 | 0.102[d] | 4.8 ns | –[h] |
| L-3 | 442 | 50 830 | 502 | 0.373[d] | 2.6 ns | –[h] |
| L-4 | 418 | 2 380 | 495 | 0.050[d] | 2.9 ns | –[h] |
| Ir-1 | 371 | 7 030 | 584 | 0.492[e] | 0.81 μs | 0.77 μs |
| Ir-2 | 385 | 8 870 | 585 | 0.556[e] | 0.66 μs | 0.68 μs |
| Ir-3 | 466 | 70 920 | 603 | 0.006[e] | 71.3 μs | 75.5 μs |
| Ir-4 | 418 | 64 170 | 608 | 0.007[e] | 68.3 μs | 73.6 μs |

[a] Absorption maxima in nm. [b] Molar extinction coefficient at the absorption maxima ($\varepsilon$ in M$^{-1}$cm$^{-1}$). [c] Emission wavelength in nm. [d] Luminescence quantum yields. Quinine sulfate was used as standard ($\Phi_F$ = 0.547 in 0.05 M sulfuric acid). [e] [Ru(phen)(bpy)$_2$]-[PF$_6$]$_2$ was used as standard ($\Phi_p$ = 0.06 in $CH_3CN$). [f] Luminescence lifetimes. [g] Triplet state lifetimes, measured by time-resolved transient absorption at 20 °C. [h] Not applicable.

Ir-1 and Ir-2 emit strongly, but the emissions of Ir-3 and Ir-4 are much weaker, upon excitation at their respective absorption maxima (Figure 2b). The fluorescence of the coumarin ligand is completely quenched in the Ir$^{III}$ complexes, indicating an efficient internal conversion (IC) from the light-harvesting antenna ($^1$IL) to the Ir$^{III}$ coordination center ($^1$MLCT), or efficient ISC from the singlet excited state to the triplet excited state ($^1MLCT \rightarrow {}^3IL$). We propose that the weak emission of Ir-3 and Ir-4 is due to the $^3$IL excited states localized on the coumarin ligand (see Supporting Information for the energy levels of the ligands). A similar effect has been reported for Ru$^{II}$ polyimine com-

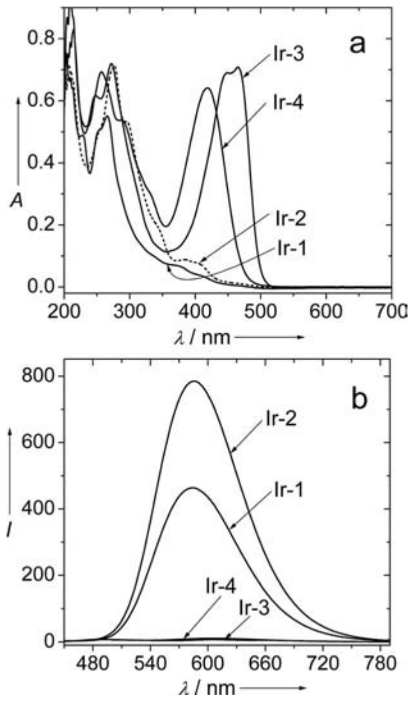


Figure 2. (a) UV/Vis absorption of Ir-1, Ir-2, Ir-3, and Ir-4 measured in $CH_3CN$ ($1.0 \times 10^{-5}$ M) at 20 °C. (b) Emission spectra of the Ir$^{III}$ complexes. Ir-1: $\lambda_{ex}$ = 386 nm, Ir-2: $\lambda_{ex}$ = 407 nm, Ir-3: $\lambda_{ex}$ = 462 nm, Ir-4: $\lambda_{ex}$ = 421 nm; in deaerated $CH_3CN$ ($1.0 \times 10^{-5}$ M) at 20 °C.

plexes, for example, $^3$IL/$^3$MLCT excited state equilibrium usually leads to weak emission, especially when the $^3$IL state is lower in energy than the $^3$MLCT state.[17,19,26,27] Phosphorescence lifetimes (room temp.) of 71.3 and 68.3 μs were observed for Ir-3 and Ir-4, respectively (Table 1). To the best of our knowledge, these are the longest phosphorescence lifetimes reported for C^N cyclometalated Ir$^{III}$ complexes.[1] For Ir-1 and Ir-2, however, much shorter phosphorescence lifetimes were found (less than 1 μs, Table 1). Previously a cyclometalated Ir$^{III}$ complex with a BODIPY subunit was reported, in which the phosphorescence of Ir$^{III}$ coordination subunit was quenched, the lifetime of the $^3$IL excited state was 25 μs.[16] A directly cyclometalated C^N Ir$^{III}$ (acac) complex with coumarin was reported but its $\tau$ was only 13 μs.[10b] Recently, a cyclometalated Ir$^{III}$ dipyrrin complex was found to show intense absorption of visible light and $^3$IL emission, but the $\varepsilon$ (38300 $\text{M}^{-1}\,\text{cm}^{-1}$ at 483 nm) value is smaller than that of Ir-3 and the lifetime is shorter (12.7 μs).[28]

Superimposable excitation and UV/Vis absorption spectra for the dyads are shown in the Supporting Information, indicating that the intense absorption at 466 nm is efficient enough to produce the emissive triplet excited state.[29]

### Assignment of the $^3$IL Excited States of the Complexes by DFT Calculations

In order to elucidate the T$_1$ states of the complexes from a theoretical perspective, the spin density isosurfaces were studied by DFT calculations (Figure 3).[28] The isosurface of the spin density of Ir-1 is localized on the ppy and phen ligands and the Ir$^{III}$ ion. A similar result was found for Ir-2. This is in agreement with the known MLCT/LLCT excited state of cyclometalated Ir$^{III}$ complexes.[2,30] For Ir-3 and Ir-4, however, the spin density isosurfaces are exclusively localized on the coumarin/imidazole/phen moiety. The Ir$^{III}$ atom contributes much less to the spin density than it does in Ir-1 and Ir-2. Thus, the lowest-lying triplet excited state is the $^3$IL excited state (ligand-localized) for Ir-3 and Ir-4.

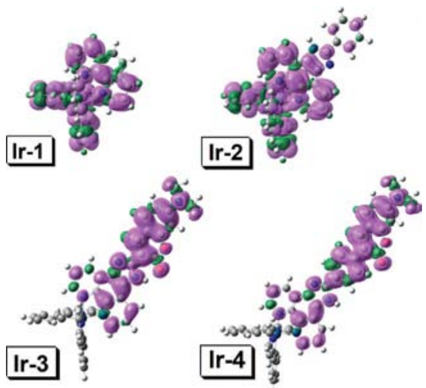


Figure 3. Isosurfaces of the spin density of the Ir$^{III}$ complexes at the optimized T$_1$ state geometry (isovalue: ±0.0004) calculated at B3LYP/6-31G/LANL2DZ level with Gaussian 09W.

### Nanosecond Time-Resolved Transient Difference Absorption Spectra

The accessible $^3$IL excited states of Ir-2 and Ir-4 upon excitation were unambiguously proved by nanosecond time-resolved transient difference absorption spectroscopy (Figure 4). For Ir-2, weak bleaching at 400 nm (MLCT band) was observed upon excitation. The bleaching at 620 nm is due to the emission of the complex. For Ir-3, however, intense bleaching at 441 nm and 466 nm was observed upon excitation, clearly due to the depletion of the ground state of the coumarin ligand. Thus, the $^3$IL excited state can be assigned for Ir-3, which is in agreement with the spin density isosurfaces (Figure 3). Similar IL bleaching was also found for Ir-4 (Supporting Information). Triplet excited state lifetimes of 75.5 and 73.6 μs were observed for Ir-3 and Ir-4, respectively, by monitoring the decay kinetics of the bleaching. These values are identical to the lifetimes determined by the phosphorescence method (Table 1), thus the phosphorescence in Ir-3 and Ir-4 is due to the emissive $^3$IL excited states.

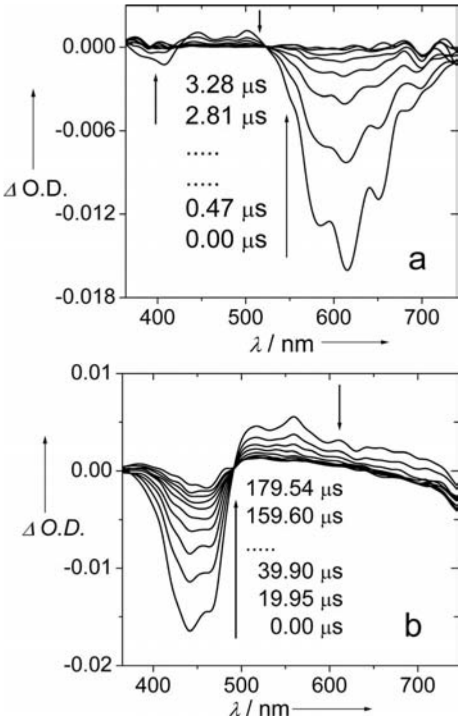


Figure 4. Nanosecond time-resolved transient difference absorption spectra, in deaerated CH$_3$CN at 20 °C, for (a) Ir-2 and (b) Ir-3. Arrows indicate the elapsed time after the 355 nm laser flash.

### Emission Spectra at 77 K

The emission spectra of the complexes at 77 K and room temperature were compared (Figure 5). Complex Ir-2 shows a significantly blueshifted emission band relative to the emission at room temperature, the thermally induced Stokes shift ($\Delta E_S$) is as high as 2282 cm$^{-1}$. Furthermore, the emission bands at both room temperature and 77 K are broad and do not have a distinct structure. All these features propose a $T_1$ state with significant charge-transfer character ($^3$MLCT).[2e] A similarly large value was observed for Ir-1 (see Supporting Information). For Ir-3, however, the emission at 77 K does not show any blueshift, and the emission band becomes more structured; all these features indicate an emissive $T_1$ state for Ir-3 with significant $^3$IL character. A similar result was observed for Ir-4 (see Supporting Information). This assignment is in line with the spin density analysis and the time-resolved transient difference absorption (Figures 3 and 4).

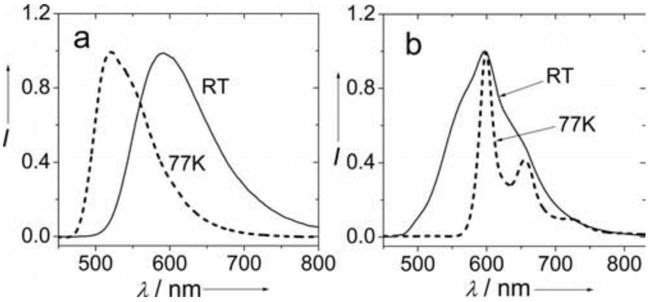
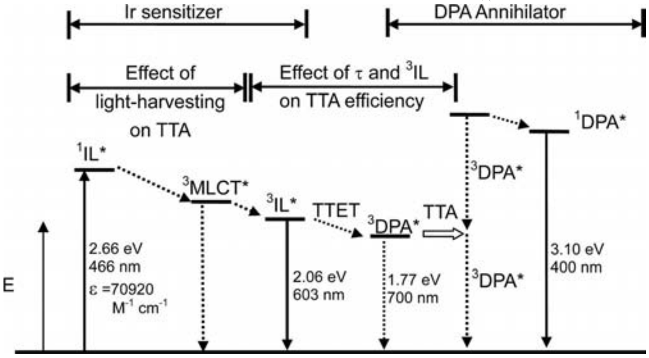


Figure 5. Emission of complexes (a) Ir-2 and (b) Ir-3 at room temperature and 77 K. At both temperatures, the concentration of the complexes was $1.0 \times 10^{-5}$ M in an EtOH/MeOH mixed solution (4:1 v/v); $\lambda_{ex}$ = 410 nm for Ir-2 and $\lambda_{ex}$ = 470 nm for Ir-3. The solution was purged with $N_2$ for about 15 min before measurement.

### Triplet–Triplet-Annihilation Upconversion

The visible-light harvesting and the long-lived $^3$IL excited state of dyads Ir-3 and Ir-4 inspired us to employ these novel complexes as triplet sensitizers to initiate a photophysical process. Herein we selected upconversion based on triplet–triplet-annihilation (TTA),[21–24] which requires triplet sensitizers to harvest excitation light and transfer the energy to a triplet acceptor (see Jablonski diagram, Scheme 2, for photophysical details).[21]

Upconversion (UC) is important for photovoltaics, photocatalysis, and nonlinear photonics.[24,31,32] Among UC applications, such as two-photon absorption dyes, nonlinear optical crystals, or rare earth metal materials,[33] TTA upconversion is particularly interesting, because of its low excitation power (can be lower than the energy of solar light) and its readily adjustable excitation/emission wavelengths.[21–24] However, we note the limitations facing the current development of TTA upconversion, such as the limited availability of triplet sensitizers, which are currently limited to Ru$^{II}$ polyimine complexes[34] and Pt$^{II}$/Pd$^{II}$ porphyrin complexes.[21,24] It is very difficult for these complexes to be chemically modified to optimize their photophysical properties, such as excitation wavelength and lifetime and energy level of the $T_1$ state, etc (all these properties are important for TTA upconversion), for upconversion purposes. Ir-3 and Ir-4 show intense absorption in the visible range and long-lived $^3$IL excited states, making these dyads perfect candidates as triplet sensitizers for TTA upconversion.



Scheme 2. Qualitative Jablonski diagram illustrating the sensitized TTA upconversion process between Ir$^{III}$ complexes (exemplified by Ir-3) and DPA. The effect of the light-harvesting ability and the luminescence lifetime of the Ir$^{III}$ sensitizer on the efficiency of the TTA upconversion is also shown. *E* is energy. GS is ground state ($S_0$). $^1$IL* is intraligand singlet excited state (coumarin-localized). IC is internal conversion. ISC is intersystem crossing. $^3$MLCT* is the Ir$^{III}$-based metal-to-ligand-charge-transfer triplet excited state. $^3$IL* is intraligand triplet excited state (coumarin-localized). TTET is triplet–triplet energy transfer. $^3$DPA* is the triplet excited state of DPA. TTA is triplet–triplet annihilation. $^1$DPA* is the singlet excited state of DPA. The emission bands observed for the sensitizers alone is the $^3$IL emissive excited state. The emission bands observed in the TTA experiment is the simultaneous $^3$IL* emission (phosphorescence) and the $^1$DPA* emission (fluorescence).

9,10-Diphenylanthracene (DPA) was used as the triplet acceptor. Its $T_1$ state lies at an energy level of 1.77 eV, which is lower than the levels of the $T_1$ states of Ir-3 and Ir-4 (ca. 2.06 eV, approximated by the room-temperature phosphorescence wavelength). A higher $T_1$ energy level for the sensitizer than that for the acceptor is a prerequisite for the triplet–triplet energy-transfer process (TTET), a critical step in TTA upconversion.[35]

In the presence of DPA, the phosphorescence of Ir-3 and Ir-4 was quenched, and upconverted fluorescence of DPA from 400 to 550 nm was observed (Figure 6a). Irradiation of DPA alone at 445 nm does not produce any emission, which proves the upconversion with Ir-3 and Ir-4. The anti-Stokes shift is 0.21 eV. The upconversion quantum yields with Ir-3 and Ir-4 as the sensitizers were determined to be 21.3 and 23.4 %, respectively (Table 2). For Ir-1 and Ir-2, however, no upconversion was observed. We propose that this is due to the low concentration of the sensitizer molecules at excited triplet excited states, resulting from the poor absorption of Ir-1 and Ir-2 at the excitation wavelength, as also demonstrated by our recent upconversion with Ru$^{II}$ and Pt$^{II}$ complexes.[36] Furthermore, the lifetimes of the $T_1$ states of Ir-1 and Ir-2 are much shorter than those of Ir-3 and Ir-4. The significant upconversion demonstrated that the triplet excited states of Ir-3 and Ir-4 were efficiently populated. We noted that a cyclometalated Ir$^{III}$ complex, Ir(ppy)$_3$ (ppy = 2-phenylpyridine, $\tau$ = 2.0 μs),[1] has been used for TTA upconversion.[37] However, without the light-harvesting effect, the absorption maximum of that complex is centered at 390 nm, and molar extinction coefficients are much smaller than those of Ir-3 and Ir-4.[37]

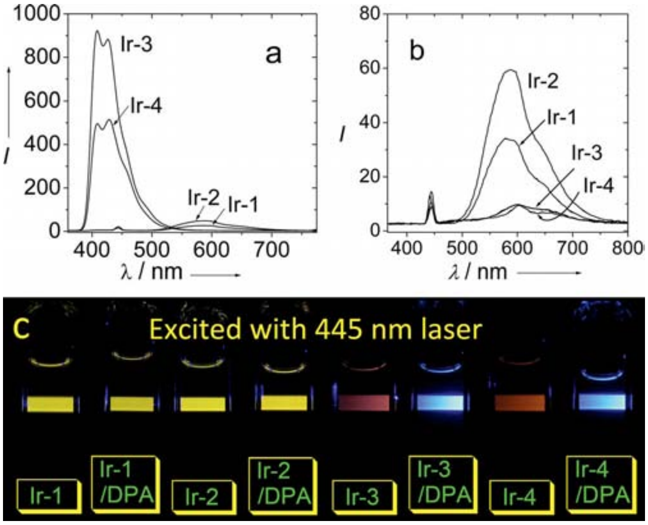


Figure 6. Upconversion with $Ir^{III}$ complexes as the triplet sensitizers and DPA as the triplet acceptor in deaerated $CH_3CN$ at 20 °C. (a) Upconversion emission spectra of the mixtures of Ir-1, Ir-2, Ir-3, and Ir-4 ($1.0 \times 10^{-5}$ M) with DPA ($8.0 \times 10^{-5}$ M). (b) Phosphorescence of sensitizers alone ($\lambda_{ex}$ = 445 nm, 5 mW). (c) Photographs of the upconversion.

Table 2. Upconversion-related parameters of the $Ir^{III}$ complexes.[a]

| | Ir-1 | Ir-2 | Ir-3 | Ir-4 |
|---|---|---|---|---|
| $\Phi_{UC}$[b] | –[e] | –[e] | 21.3% | 23.4% |
| $K_{SV}$ /$M^{-1}$ [$10^3$][c] | 17.1 | 6.57 | 551.0 | 317.7 |
| $k_q$ /$M^{-1}$ $s^{-1}$ [$10^9$][d] | 21.1 | 9.95 | 7.73 | 4.65 |

[a] Measured in $CH_3CN$. [b] Upconversion quantum yields measured with $[Ru(dmb)_3][PF_6]_2$ as the standard ($\Phi_P$ = 0.073 in $CH_3CN$). [c] Stern–Volmer quenching constants. [d] Bimolecular quenching constants. $K_{SV} = k_q\tau$. [e] Not applicable.

The upconversion is visible unaided with the eye (Figure 6c). For complexes Ir-1 and Ir-2, yellow emissions were observed, either for the complexes alone or in the presence of DPA. For Ir-3 and Ir-4, the phosphorescence is red, and the emissions turn to blue in the presence of DPA, due to the significant upconversion.

The Stern–Volmer quenching constants of the emission of the $Ir^{III}$ triplet sensitizers quenched by DPA were studied (Figure 7). Much larger slopes were observed for Ir-3 and Ir-4 than for Ir-1 and Ir-2. This is in line with the phosphorescence lifetimes of the complexes. Larger quenching constants indicate more efficient triplet–triplet energy transfer (TTET), a critical step in TTA upconversion (Scheme 2).

Upconversion with Ir-3 and Ir-4 is significant, despite the weak phosphorescence of the complexes. Upconversion without any quenched phosphorescence is against the conventional understanding of the TTA upconversion mechanism (Scheme 2), which states that the upconverted fluorescence must be accompanied by quenching of the phosphorescence of the sensitizer (band areas in ratios of at least 2:1 of quenched phosphorescence to upconverted fluorescence), because the triplet excited state of the sensitizer must be quenched by the triplet acceptor (DPA) in the TTET step (Scheme 2).[21] We propose that the sensitizer molecules at the $^3$IL state that were otherwise nonemissive were involved in TTET. This is clearly demonstrated by Ir-3 (Figure 8). With increasing DPA concentration, the upconverted fluorescence emission intensity increased significantly, with no phosphorescence at all to be quenched.

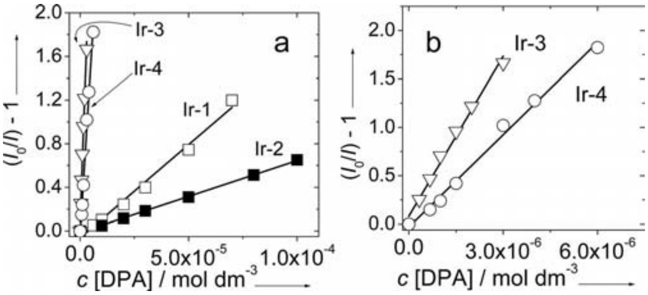


Figure 7. Stern–Volmer plots generated from intensity-quenching of complexes Ir-1 ($\lambda_{ex}$ = 386 nm), Ir-2 ($\lambda_{ex}$ = 410nm), Ir-3 ($\lambda_{ex}$ = 475 nm), and Ir-4 ($\lambda_{ex}$ = 425 nm). (a) Comparison of the four complexes and (b) complexes Ir-3 and Ir-4. Phosphorescence measured as a function of DPA concentration in $1.0 \times 10^{-5}$ M $CH_3CN$ at 20 °C.

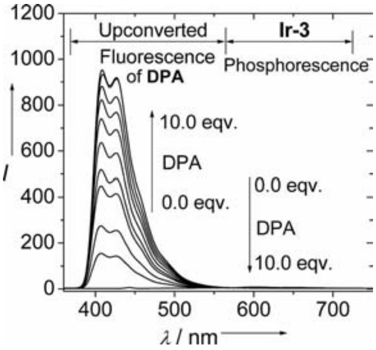


Figure 8. Change in upconverted DPA fluorescence with DPA concentration with Ir-3 as sensitizer in deaerated $CH_3CN$ ($1.0 \times 10^{-5}$ M) at 20 °C; $\lambda_{ex}$ = 445 nm.

This is the first time that sensitizers at excited states that are otherwise nonemissive are proposed to be responsible for TTA upconversion. Currently, all transition metal complexes that are used as triplet sensitizers for TTA upconversion are phosphorescent. However, we propose that the phosphorescence of triplet sensitizers is actually detrimental to TTA upconversion, because the radiative decay of the $T_1$ state of the triplet sensitizers competes with TTET (Scheme 2). Thus, nonphosphorescent transition metal complexes can be used as triplet sensitizers for TTA upconversion, as long as the triplet excited states of the sensitizers can be populated upon photoexcitation. This new concept will greatly increase the availability of the triplet sensitizers for TTA upconversion. We believe that this new concept can be used for other photophysical applications where the phosphorescence of the sensitizer is not required.

## Conclusions

We prepared coumarin-containing cyclometalated iridium(III) complexes that show intense absorption in the visible range ($\varepsilon = 70920\ \text{M}^{-1}\ \text{cm}^{-1}$ at 466 nm). Room-temperature phosphorescence was observed and is attributed to the $^3$IL excited state (ligand-localized), which is supported by data obtained by nanosecond time-resolved transient absorption spectroscopy, emission at 77 K, and the spin density isosurface of the $T_1$ excited state. Greatly prolonged room-temperature triplet excited state lifetimes of 75.5 and 73.6 µs were observed for the two light-harvesting complexes. The visible-light harvesting ability and the long-lived $^3$IL states were employed for triplet–triplet-annihilation (TTA) upconversion. Upconversion quantum yields up to 23.4% were observed. We propose that weakly phosphorescent or nonphosphorescent transition metal complexes can be used as triplet sensitizers for TTA upconversion. Currently triplet sensitizers are limited to those that are phosphorescent, but the phosphorescence of the triplet sensitizers is detrimental to the upconversion. Our design of visible-light-harvesting Ir$^{III}$–chromophore molecular arrays that have long-lived $^3$IL excited states and the application of the weakly phosphorescent complexes as sensitizers for TTA upconversion will be helpful for photovoltaics, photocatalysis, upconversion, molecular probes, and so on.

## Experimental Section

**Materials:** All the chemicals were analytically pure and were used as received. Solvents were dried and distilled for synthesis. $IrCl_3 \cdot 3H_2O$ was purchased from Xi'an Catalyst Chemical Co., Ltd. The cyclometalated Ir$^{III}$ chlorido-bridged dimers $[Ir\text{-}(ppy)_2Cl]_2$ (**1**),[38] 1,10-phenanthroline-5,6-dione (**2**),[39] 7-(diethylamino)-2*H*-chromen-2-one (**3**),[40] 7-diethylamino-2-oxo-2*H*-chromene-3-carboxyldehyde (**4**),[40] and 3-bromo-7-aminocoumarin (**5**)[41] were synthesized according to literature methods (see Supporting Information for molecular structure characterization data).

**Compound 6:** Compound **5** (296.2 mg, 1.0 mmol) and 4-formylphenylboronic acid (300.0 mg, 2.0 mmol) were dissolved in EtOH/toluene/$H_2O$ (1:1:2, v/v; 24 mL) in a 50 mL two-neck round-bottom flask. Under an argon atmosphere, the mixture was deoxygenated for about 30 min. $Pd(PPh_3)_4$ (60.0 mg, 5%) and $K_2CO_3$ (552.0 mg) were added. Then, the mixture was heated at reflux for 5 h under an argon atmosphere. After completion of the reaction, the mixture was cooled to room temperature. There was a precipitate that separated out. The precipitate was filtered and dissolved in $CH_2Cl_2$. The crude product was further purified by column chromatography (silica gel; dichloromethane/methanol = 100:1), and a yellow solid was obtained (270.4 mg, 84.1% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 10.03 (s, 1 H), 7.92 (m, 4 H), 7.81 (s, 1 H), 7.36 (d, $J$ = 9.0 Hz, 1 H), 6.63 (d, $J$ = 8.5 Hz, 1 H), 6.54 (s, 1 H), 3.48–3.42 (m, 4 H), 1.24 (t, $J$ = 7.0 Hz, 6 H) ppm.

**Compound L2:** Benzaldehyde (63.7 mg, 0.6 mmol), 1,10-phenanthroline-5,6-dione (104.1 mg, 0.5 mmol), and ammonium acetate (805.4 mg, 11.3 mmol) were dissolved in glacial acetic acid (13 mL) in a 25 mL double-neck, round-bottomed flask. The mixture was heated at reflux for 6 h under argon. The reaction system turned orange. After completion of the reaction, the mixture was cooled to room temperature, and concentrated $NH_3 \cdot H_2O$ was added until the pH of the mixture was tuned to about 7.0 to give a pink precipitate. The precipitate was filtered, then washed with water, and then dried in vacuo overnight. The crude product was further purified by column chromatography (silica gel; dichloromethane/methanol = 8:1), an ivory-white solid was obtained (108.4 mg, 73.2% yield). $^1$H NMR (400 MHz, [D$_4$]MeOH): $\delta$ = 8.74 (d, $J$ = 3.9 Hz, 1 H), 8.59–8.32 (m, 1 H), 7.98 (d, $J$ = 7.8 Hz, 1 H), 7.48–7.41 (m, 3 H), 4.87 (m, 5 H) ppm. $^{13}$C NMR (100 MHz, [D$_4$]MeOH): $\delta$ = 151.42, 147.42, 143.14, 129.77, 129.63, 128.81, 126.47, 123.10 ppm. ESI-HRMS: calcd. for $C_{19}H_{13}N_4$ $[M + H]^+$ 297.1140; found 297.1135.

**Compound L3:** The synthetic procedure was the same as that for L2 except that 7-diethylamino-2-oxo-2*H*-chromene-3-carboxyldehyde (**4**) (127.9 mg, 0.68mmol), which replaced benzaldehyde, was used. The product was a yellow precipitate, which was purified by column chromatography (silica gel; dichloromethane/methanol = 10:1). Yield: 166.9 mg, 68.5%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.16 (d, $J$ = 4.2 Hz, 2 H), 8.99 (s, 1 H), 8.78 (d, $J$ = 5.8 Hz, 2 H), 7.72–7.69 (m, 2 H), 7.48 (d, $J$ = 8.0 Hz, 1 H), 6.66–6.63 (m, 1 H), 6.50 (d, $J$ = 2.3 Hz, 1 H), 3.48–3.43 (m, 4 H), 1.26 (t, $J$ = 7.0 Hz, 6 H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 162.12, 156.41, 151.70, 148.29, 146.89, 144.36, 141.52, 130.13, 129.44, 122.89, 110.02, 108.68, 107.68, 96.78, 45.06, 12.52 ppm. ESI-HRMS: calcd. for $C_{26}H_{22}N_5O_2$ $[M + H]^+$ 436.1774; found 436.1767.

**Compound L4:** The synthetic procedure was same as that for L2, except that compound **6** (160.7 mg, 0.50mmol), which replaced benzaldehyde, was used. The product was a brown solid, which was purified by column chromatography (silica gel; dichloromethane/methanol = 10:1). Yield: 165.5 mg, 64.7%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.25 (m, 2 H), 9.04 (m, 2 H), 8.32 (m, 2 H), 8.04–7.91 (m, 4 H), 7.46 (t, $J$ = 9.3 Hz, 2 H), 6.74 (d, $J$ = 8.0 Hz, 1 H), 6.57 (d, $J$ = 8.2 Hz, 1 H), 3.51–3.48 (m, 4 H), 1.24 (t, $J$ = 6.8 Hz, 6 H) ppm. ESI-HRMS: calcd. for $C_{32}H_{26}N_5O_2$ $[M + H]^+$ 512.2087; found 512.2090.

**Complex Ir-1:** Complex Ir-1 was synthesized by a modified literature procedure.[2b] $[Ir\text{-}(ppy)_2Cl]_2$ (107.2 mg, 0.1 mmol) and 1,10-phenanthroline (36.0 mg, 0.2 mmol) were dissolved in $CH_2Cl_2$/MeOH (2:1 v/v; 12 mL). Then the mixture was heated at reflux for 5–6 h under argon. The reaction system turned orange. After completion of the reaction, the mixture was cooled to room temperature, and a 10-fold excess of ammonium hexafluorophosphate was added. The suspension was stirred for 15 min and then filtered to remove insoluble inorganic salts. The solution was concentrated to dryness under reduced pressure to obtain a crude orange solid. The crude product was further purified by column chromatography (silica gel; dichloromethane/methanol = 20:1). An orange solid was obtained (90.4 mg, 54.6% yield). $^1$H NMR (400 MHz, [D$_6$]-DMSO): $\delta$ = 8.89–8.91 (d, $J$ = 8.3 Hz, 2 H), 8.39 (s, 2 H), 8.20–8.27 (m, 4 H), 8.04–8.07 (m, 2 H), 7.94–7.96 (d, $J$ = 7.6 Hz, 2 H), 7.85–7.89 (t, $J$ = 8.0 Hz, 2 H), 7.45–7.46 (d, $J$ = 5.7 Hz, 2 H), 7.05–7.08 (t, $J$ = 7.3 Hz, 2 H), 6.94–7.00 (m, 4 H), 6.29–6.31 (d, $J$ = 7.5 Hz, 2 H) ppm. ESI-HRMS: calcd. for $[M - PF_6]^+$ 681.1630; found 681.1635. $C_{34}H_{24}F_6IrN_4P$ (825.76): calcd. C 49.45, H 2.93, N 6.78; found C 49.61, H 2.78, N 6.51.

**Complex Ir-2:** The synthetic procedure was the same as that for Ir-1, except that compound L2 (25.7 mg, 0.087mmol), which replaced phenanthroline, was used. The product was a yellow solid, which was purified by column chromatography (silica gel; dichloromethane/methanol = 10:1). Yield: 41.7 mg, 60.5%. $^1$H NMR (400 MHz, $CDCl_3/CD_3OD$): $\delta$ = 9.24 (s, 2 H), 8.26–8.29 (t, $J$ = 5.2 Hz, 4 H), 7.89–8.00 (m, 4 H), 7.74–7.79 (m, 4 H), 7.55–7.64 (m, 3 H), 7.36–7.38 (d, $J$ = 6.9 Hz, 1 H), 7.10–7.13 (t, $J$ = 7.4 Hz, 2 H), 6.98–7.02

(t, $J$ = 7.5 Hz, 2 H), 6.86–6.90 (t, $J$ = 6.4 Hz, 2 H), 6.41–6.43 (d, $J$ = 7.5 Hz, 2 H), 5.33 (s, 1 H) ppm. $^{13}$C NMR (100 MHz, [D$_6$]acetone): $\delta$ = 167.82, 150.41, 149.48, 149.04, 144.27, 138.56, 132.18, 131.77, 130.37, 129.17, 126.83, 126.61, 124.92, 123.50, 122.54, 119.83 ppm. ESI-HRMS: calcd. for [M – PF$_6$]$^+$ 797.2005; found 797.2007. $C_{41}H_{28}F_6IrN_6P$ (941.88): calcd. C 52.28, H 3.00, N 8.92; found C 52.58, H 3.14, N 8.69.

**Complex Ir-3:** The synthetic procedure was same as that for Ir-1, except that compound L3 (53.6 mg, 0.1 mmol), which replaced phenanthroline, was used. The product was a brown solid, which was purified by column chromatography (silica gel; dichloromethane/methanol = 15:1). Yield: 81.6 mg, 75.5%. $^1$H NMR (400 MHz, $CDCl_3/CD_3OD$): $\delta$ = 9.21–9.23 (d, $J$ = 7.9 Hz, 2 H), 8.98 (s, 1 H), 8.28–8.29 (d, $J$ = 4.9 Hz, 2 H), 7.99–8.01 (d, $J$ = 8.3 Hz, 2 H), 7.89–7.92 (m, 2 H), 7.75–7.80 (t, $J$ = 8.1 Hz, 4 H), 7.60–7.62 (d, $J$ = 9.0 Hz, 1 H), 7.36–7.40 (t, $J$ = 5.7 Hz, 2 H), 7.10–7.14 (t, $J$ = 7.3 Hz, 2 H), 6.99–7.02 (t, $J$ = 7.5 Hz, 2 H), 6.87–6.91 (t, $J$ = 7.0 Hz, 2 H), 6.79–6.82 (m, 1 H), 6.61 (s, 1 H), 6.41–6.43 (d, $J$ = 7.4 Hz, 2 H), 3.52–3.57 (m, 4 H), 1.27–1.32 (m, 6 H) ppm. $^{13}$C NMR (100 MHz, [D$_6$]acetone): $\delta$ = 167.87, 160.37, 156.72, 152.26, 150.61, 150.44, 149.75, 149.59, 149.48, 149.10, 148.51, 144.95, 144.50, 144.25, 142.54, 138.59, 137.04, 132.41, 132.16, 131.74, 130.68, 130.44, 126.68, 126.42, 126.22, 124.94, 123.62, 122.56, 122.05, 119.86, 109.99, 108.27, 106.96, 96.09, 44.61 ppm. ESI-HRMS: calcd. for [M – PF$_6$]$^+$ 936.2485; found 936.2502. $C_{48}H_{37}F_6IrN_7O_2P$ (1081.03): calcd. C 53.33, H 3.45, N 9.07; found C 53.29, H 3.48, N 9.13.

**Complex Ir-4:** The synthetic procedure was same as that for Ir-1, except that compound L4 (61.4 mg, 0.12mmol), which replaced phenanthroline, was used. The product was a brown solid, which was purified by column chromatography (silica gel; dichloromethane/methanol = 15:1). Yield: 85.5 mg, 73.9%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 9.05–9.28 (d, $J$ = 91.2 Hz, 2 H), 8.25–8.26 (d, $J$ = 5.3 Hz, 4 H), 7.98–8.00 (d, $J$ = 7.8 Hz, 2 H), 7.73–7.82 (m, 9 H), 7.35–7.48 (t, $J$ = 8.6 Hz, 3 H), 6.91–7.15 (m, 6 H), 6.63–6.65 (d, $J$ = 8.3 Hz, 1 H), 6.38–6.47 (t, $J$ = 31.6 Hz, 3 H), 3.42–3.44 (d, $J$ = 6.8 Hz, 4 H), 1.20–1.23 (t, $J$ = 6.6 Hz, 6 H) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 161.69, 156.27, 153.13, 151.12, 150.07, 148.79, 144.60, 143.90, 141.56, 138.13, 137.77, 132.47, 131.80, 130.68, 129.49, 128.46, 126.56, 126.27, 124.87, 123.28, 122.72, 119.77, 109.50, 108.95, 96.38, 44.86 ppm. ESI-HRMS: calcd. for [M – PF$_6$]$^+$ 1012.2951; found 1012.2921. $C_{54}H_{41}F_6IrN_7O_2P$ (1157.13): calcd. C 56.05, H 3.57, N 8.47; found C 55.90, H 3.60, N 8.31.

### Physical Measurements

NMR spectra were recorded with a 400 MHz Varian Unity Inova NMR spectrometer. Carbon NMR spectra were recorded with the same instrument at 100 MHz with total proton decoupling. Mass spectra were recorded with a Q-TOF Micro MS spectrometer. UV/Vis absorption spectra were measured with a HP8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded with a JASCO FP-6500 or a Sanco 970 CRT spectrofluorometer (modified for the upconversion experiments). Fluorescence quantum yields were measured with Ru(bpy)$_2$(Phen) as the reference ($\Phi$ = 6.0%, in $CH_3CN$, under deaerated conditions). Fluorescence lifetimes were measured with a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument. Nanosecond time-resolved transient absorption spectroscopy was performed with a LP-920 pump-probe spectrometer (Edinburgh Instruments). The emission spectra at 77 K were measured with an Oxford Optistat DN$^{TM}$ cryostat (with liquid nitrogen filling) and a FS920 spectrofluorometer (Edinburgh Instruments Ltd.).

A diode-pumped solid-state laser (DPSSL) with 445 nm output was used as the excitation source for the upconversion experiments. The laser power was measured with a phototube. The variation of the laser power was less than ±5% over eight hours. The mixed solution of the complex (triplet sensitizer) and 9,10-diphenylanthracene (DPA, triplet acceptor) was degassed for at least 30 min with $N_2$ or Ar. The upconverted fluorescence of DPA was measured with a spectrofluorometer. Note that the absorption of DPA at 445 nm is weak, thus the triplet sensitizer can be excited with 445 nm laser irradiation (only the sensitizers, i.e. the Ir$^{III}$ complexes, were selectively excited). The upconversion quantum yields were calculated with the following equation, where $\Phi_{UC}$, $A_{unk}$, $I_{unk}$, and $\eta_{unk}$ represent the quantum yield, absorbance, integrated photoluminescence intensity, and refractive index of the samples and the solvents [Equation (1)]. The equation is multiplied by two in order to make the maximum quantum yield to be equal to unity.[35]

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

DFT calculations were used for optimization of the ground-state geometries, for both singlet states and triplet states. The energy levels of the $T_1$ states (energy gap between $S_0$ and $T_1$) were calculated with time-dependent DFT (TDDFT), on the basis of optimized triplet state geometries. All the calculations were carried out with Gaussian 09W.[42]

**Supporting Information** (see footnote on the first page of this article): Additional characterization and photophysical data; results of DFT calculations.

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[1] a) L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Top. Curr. Chem.* **2007**, *281*, 143–203; b) S. Ladouceur, D. Fortin, E. Zysman-Colman, *Inorg. Chem.* **2010**, *49*, 5625–5641.

[2] a) J. Zhang, P. Du, J. Schneider, P. Jarosz, R. Eisenberg, *J. Am. Chem. Soc.* **2007**, *129*, 7726–7727; b) C. Dragonetti, L. Falciola, P. Mussini, S. Righetto, D. Roberto, R. Ugo, A. Valore, *Inorg. Chem.* **2007**, *46*, 8533–8547; c) S. C. Lo, R. E. Harding, C. P. Shipley, S. G. Stevenson, P. L. Burn, I. D. W. Samuel, *J. Am. Chem. Soc.* **2009**, *131*, 16681–16688; d) M. Felici, P. C.-Carballada, Y. Vida, J. M. M. Smits, R. J. M. Nolte, L. De Cola, R. Williams, M. C. Feiters, *Chem. Eur. J.* **2009**, *15*, 13124–13134; e) M. G. Colombo, A. Hauser, H. U. Gudel, *Inorg. Chem.* **1993**, *32*, 3088–3092.

[3] C. S. K. Mak, D. Pentlehner, M. Stich, O. S. Wolfbeis, W. K. Chan, H. Yersin, *Chem. Mater.* **2009**, *21*, 2173–2175.

[4] a) Z. W. Liu, M. Guan, Z. Q. Bian, D. B. Nie, Z. L. Gong, Z. B. Li, C. H. Huang, *Adv. Funct. Mater.* **2006**, *16*, 1441–1448; b) B. Du, L. Wang, H. Wu, W. Yang, Y. Zhang, R. Liu, M. Sun, J. Peng, Y. Cao, *Chem. Eur. J.* **2007**, *13*, 7432–7442; c) M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal Jr., G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712–5719; d) J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G. G. Malliaras, *J. Am. Chem. Soc.* **2004**, *126*, 2763–2767.

[5] a) Y. Chi, P. T. Chou, *Chem. Soc. Rev.* **2010**, *39*, 638–655; b) B.-S. Du, C.-H. Lin, Y. Chi, J.-Y. Hung, M.-W. Chung, T.-Y. Lin, G.-H. Lee, K.-T. Wong, P.-T. Chou, W.-Y. Hung, H.-C. Chiu, *Inorg. Chem.* **2010**, *49*, 8713–8723.

[6] L. H. Fischer, M. I. J. Stich, O. S. Wolfbeis, N. Tian, E. Holder, M. Schäferling, *Chem. Eur. J.* **2009**, *15*, 10857–10863.

[7] a) C. Yang, X. W. Zhang, H. You, L. Y. Zhu, L. Q. Chen, L. N. Zhu, Y. T. Tao, D. G. Ma, Z. G. Shuai, J. G. Qin, *Adv. Funct. Mater.* **2007**, *17*, 651–661; b) L. He, J. Qiao, L. Duan, G. F. Dong, D. Q. Zhang, L. D. Wang, Y. Qiu, *Adv. Funct. Mater.* **2009**, *19*, 2950–2960.

[8] a) J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510; b) M. S. Lowry, S. Bernhard, *Chem. Eur. J.* **2006**, *12*, 7970–7977.

[9] a) Q. Zhao, F. Li, S. Liu, M. Yu, Z. Liu, T. Yi, C. Huang, *Inorg. Chem.* **2008**, *47*, 9256–9264; b) E. C.-H. Kwok, M.-Y. Chan, K. M.-C. Wong, W. H. Lam, V. W.-W. Yam, *Chem. Eur. J.* **2010**, *16*, 12244–12254; c) L. Q. Xiong, Q. Zhao, H. L. Chen, Y. B. Wu, Z. S. Dong, Z. G. Zhou, F. Y. Li, *Inorg. Chem.* **2010**, *49*, 6402–6408.

[10] a) M. S. Lowry, W. R. Hudson, R. A. J. Pascal, S. Bernhard, *J. Am. Chem. Soc.* **2004**, *126*, 14129–14135; b) S. M. Borisov, I. Klimant, *Anal. Chem.* **2007**, *79*, 7501–7509.

[11] Z. G. Xie, L. Q. Ma, K. E. DeKrafft, A. Jin, W. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 922–923.

[12] R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, C. E. Housecroft, E. C. Constable, *J. Am. Chem. Soc.* **2010**, *132*, 5978–5980.

[13] a) T. Hofbeck, H. Yersin, *Inorg. Chem.* **2010**, *49*, 9290–9299; b) J. H. Palmer, A. C. Durrell, Z. Gross, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2010**, *132*, 9230–9231; c) K. T. Prasad, B. Therrien, K. Mohan Rao, *J. Organomet. Chem.* **2010**, *695*, 1375–1382.

[14] J. S. Y. Lau, P. K. Lee, K. H. K. Tsang, C. H. C. Ng, Y. W. Lam, S. H. Cheng, K. K. W. Lo, *Inorg. Chem.* **2009**, *48*, 708–718.

[15] a) K. K.-W. Lo, C.-K. Chung, N. Zhu, *Chem. Eur. J.* **2003**, *9*, 475–483; b) J. C. Araya, J. Gajardo, S. A. Moya, P. Aguirre, L. Toupet, J. A. G. Williams, M. Escadeillas, H. L. Bozece, V. Guerchais, *New J. Chem.* **2010**, *34*, 21–24; c) A. Rizzo, O. Inganäs, N. Solin, *Chem. Eur. J.* **2010**, *16*, 4190–4195; d) K. K.-W. Lo, K. Y. Zhang, C.-K. Chung, K. Y. Kwok, *Chem. Eur. J.* **2007**, *13*,7110–7120; e) S. P.-Y. Li, H.-W. Liu, K. Y. Zhang, K. K.-W. Lo, *Chem. Eur. J.* **2010**, *16*, 8329–8339.

[16] A. A. Rachford, R. Ziessel, T. Bura, P. Retailleau, F. N. Castellano, *Inorg. Chem.* **2010**, *49*, 3730–3736.

[17] a) N. Armaroli, *ChemPhysChem* **2008**, *9*, 371–373; b) W. Wu, W. Wu, S. Ji, H. Guo, P. Song, K. Han, L. Chi, J. Shao, J. Zhao, *J. Mater. Chem.* **2010**, *20*, 9775–9786; c) H. Guo, S. Ji, W. Wan, W. Wu, J. Shao, J. Zhao, *Analyst* **2010**, *135*, 2832–2840; d) S. Ji, H. Guo, X. Yuan, X. Li, H. Ding, P. Gao, C. Zhao, W. Wu, W. Wu, J. Zhao, *Org. Lett.* **2010**, *12*, 2876–2879.

[18] N. D. McClenaghan, Y. Leydet, B. Maubert, M. T. Indelli, S. Campagna, *Coord. Chem. Rev.* **2005**, *249*, 1336–1350.

[19] X. Y. Wang, A. D. Guerzo, R. H. Schmehl, *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 55–77.

[20] a) M. Chen, K. P. Ghiggino, S. H. Thang, G. J. Wilson, *Angew. Chem.* **2005**, *117*, 4442–4446; *Angew. Chem. Int. Ed.* **2005**, *44*, 4368–4372; b) T. Akasaka, T. Mutai, J. Otsuki, K. Araki, *Dalton Trans.* **2003**, 1537–1544; c) M. Chen, K. P. Ghiggino, A. Launikonis, A. W. H. Mau, E. Rizzardo, W. H. F. Sasse, S. H. Thang, G. J. Wilson, *J. Mater. Chem.* **2003**, *13*, 2696–2700.

[21] A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, F. Meinardi, *Phys. Rev. B* **2008**, *78*, 195112/1–195112/5.

[22] A. Monguzzi, R. Tubino, F. Meinardi, *Phys. Rev. B* **2008**, *77*, 155122/1–155122/4.

[23] T. N. S. Rachford, A. Haefele, R. Ziessel, F. N. Castellano, *J. Am. Chem. Soc.* **2008**, *130*, 16164–16165.

[24] S. Baluschev, S. Yakutkin, T. Miteva, Y. Avlasevich, S. Chernov, S. Aleshchenkov, G. Nelles, A. Cheprakov, A. Yasuda, K. Müllen, G. Wegner, *Angew. Chem.* **2007**, *119*, 7837–7840; *Angew. Chem. Int. Ed.* **2007**, *46*, 7693–7696.

[25] G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem.* **2008**, *120*, 1202–1219; *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201.

[26] S. Ji, W. Wu, W. Wu, P. Song, K. Han, Z. Wang, S. Liu, H. Guo, J. Zhao, *J. Mater. Chem.* **2010**, *20*, 1953–1963.

[27] D. S. Tyson, F. N. Castellano, *J. Phys. Chem. A* **1999**, *103*, 10955–10960.

[28] K. Hanson, A. Tamayo, V. V. Diev, M. T. Whited, P. I. Djurovich, M. E. Thompson, *Inorg. Chem.* **2010**, *49*, 6077–6084.

[29] F. N. Castellano, *Inorg. Chem.* **1999**, *38*, 4382–4383.

[30] F. Neve, M. L. Deda, A. Crispini, A. Bellusci, F. Puntoriero, S. Campagna, *Organometallics* **2004**, *23*, 5856–5863.

[31] H. C. Chen, C. Y. Hung, K. H. Wang, H. L. Chen, W. S. Fann, F. C. Chien, P. Chen, T. J. Chow, C. P. Hsu, S. S. Sun, *Chem. Commun.* **2009**, *27*, 4064–4066.

[32] P. E. Keivanidis, S. Baluschev, T. Miteva, G. Nelles, U. Scherf, A. Yasuda, G. Wegner, *Adv. Mater.* **2003**, *15*, 2095–2098.

[33] a) H. M. Kim, B. R. Cho, *Acc. Chem. Res.* **2009**, *42*, 863–872; b) W. Niu, S. Wu, S. Zhang, L. Li, *Chem. Commun.* **2010**, *46*, 3908–3910; c) J. Grimm, E. Beurer, P. Gerner, H. U. Güdel, *Chem. Eur. J.* **2007**, *13*, 1152–1157.

[34] R. R. Islangulov, D. V. Kozlov, F. N. Castellano, *Chem. Commun.* **2005**, *29*, 3776–3778.

[35] T. N. S. Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.

[36] a) S. Ji, W. Wu, W. Wu, H. Guo, J. Zhao, *Angew. Chem. Int. Ed.* **2011**, *50*, 1626–1629; b) W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *Dalton Trans.* **2011**, *40*, 5953–5963; c) Y. Liu, W. Wu, J. Zhao, X. Zhang, H. Guo. *Dalton Trans.* **2011**, DOI: 10.1039/c1dt10679a; d) H. Sun, H. Guo, W. Wu, X. Liu, J. Zhao. *Dalton Trans.* **2011**, DOI: 10.1039/cldt10490j.

[37] W. Zhao, F. N. Castellano, *J. Phys. Chem. A* **2006**, *110*, 11440–11445.

[38] S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653.

[39] Y. Sun, D. A. Lutterman, C. Turro, *Inorg. Chem.* **2008**, *47*, 6427–6434.

[40] D. Ray, P. K. Bharadwaj, *Inorg. Chem.* **2008**, *47*, 2252–2254.

[41] D. N. Lee, G. J. Kim, H. J. Kim, *Tetrahedron Lett.* **2009**, *50*, 4766–4768.

[42] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09W Revision A.1*, Gaussian Inc., Wallingford CT, **2009**.

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