Long-Lived Room-Temperature Deep-Red-Emissive Intraligand Triplet Excited State of Naphthalimide in Cyclometalated Ir^{III} Complexes and its Application in Triplet-Triplet Annihilation-Based Upconversion

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Abstract: Cyclometalated Ir^{III} complexes with acetylide ppy and bpy ligands were prepared (ppy=2-phenylpyridine, bpy = 2,2'-bipyridine) in which naphthal (Ir-2) and naphthalimide (NI) were attached onto the ppy (Ir-3) and bpy ligands (Ir-4) through acetylide bonds. $[Ir(ppy)_3]$ (Ir-1) was also prepared as a model complex. Room-temperature phosphorescence was observed for the complexes; both neutral and cationic complexes Ir-3 and Ir-4 showed strong absorption in the visible range ($\varepsilon = 39600 \,\mathrm{m}^{-1} \,\mathrm{cm}^{-1}$ at and $\varepsilon = 25100 \,\mathrm{m}^{-1} \,\mathrm{cm}^{-1}$ 402 nm at 404 nm, respectively), long-lived triplet excited states $(\tau_{\rm T} = 9.30 \ \mu s$ and 16.45 µs) and room-temperature red emission ($\lambda_{em} = 640 \text{ nm}, \Phi_p = 1.4\%$ and

Introduction

Cyclometalated Ir^{III} complexes have attracted much attention owing to their applications in electroluminescence,^[1-15] molecular sensing,^[1,16-23] and photocatalysis.^[24-29] The photophysics of these Ir^{III} complexes, such as UV/Vis absorption, phosphorescence, and the lifetimes of the triplet excited states (T₁), are pivotal for their applications. For example, cyclometalated Ir^{III} complexes have been used as photocatalysts in hydrogen (H₂) production^[24-28] and oxygen (O₂) sensing,^[18-21] and as luminescent molecular sensors.^[30] One of the main objectives in these applications is to prepare Ir^{III} complexes that show intense absorption of visible light, or to access the long-lived T₁ excited state. However, conventional cyclometalated Ir^{III} complexes typically show weak ab-

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201200224.

 $\lambda_{\rm em}$ =627 nm, $\Phi_{\rm p}$ =0.3%; cf. Ir-1: ε = 16600 m⁻¹ cm⁻¹ at 382 nm, $\tau_{\rm em}$ =1.16 µs, $\Phi_{\rm p}$ =72.6%). Ir-3 was strongly phosphorescent in non-polar solvent (i.e., toluene), but the emission was completely quenched in polar solvents (MeCN). Ir-4 gave an opposite response to the solvent polarity, that is, stronger phosphorescence in polar solvents than in non-polar solvents. Emission of Ir-1 and Ir-2 was not solvent-polarity-dependent. The T₁ excited states of Ir-2, Ir-3, and Ir-4 were identified as mainly intraligand triplet excited states

Keywords: density functional calculations • iridium • naphthalimide • photochemistry • upconversion

(³IL) by their small thermally induced Stokes shifts (ΔE_s), nanosecond timeresolved transient difference absorption spectroscopy, and spin-density analysis. The complexes were used as triplet photosensitizers for triplet-triplet annihilation (TTA) upconversion and quantum yields of 7.1% and 14.4% were observed for Ir-2 and Ir-3, respectively, whereas the upconversion was negligible for Ir-1 and Ir-4. These results will be useful for designing visible-light-harvesting transition-metal complexes and for their applications as triplet photosensitizers for photocatalysis, photovoltaics, TTA upconversion, etc.

sorption in the visible-light range,^[8-10,15,26,30-32] and only very few cyclometalated Ir^{III} complexes have shown intense visible-light absorption.^[7,18a,33] Moreover, the lifetimes of the T₁ excited states of the normal Ir^{III} complexes are short (usually less than 5.0 µs).^[1,8-12,15,18b,19,34,35] We proposed that these photophysical processes could be enhanced by the longlived T₁ excited states, as has been demonstrated in luminescent oxygen sensing^[36-45] and in triplet-triplet annihilation (TTA) upconversion.^[43-53] Thus, the preparation of cyclometalated Ir^{III} complexes with intense visible-light absorption and long-lived T₁ excited states is of great interest.

However, compared to Pt^{II} complexes and Ru^{II} complexes, the photophysics of cyclometalated Ir^{III} complexes that show intense visible-light absorption and long-lived T_1 excited state have been less investigated. The absorption and emission wavelengths, as well as the lifetimes of the T_1 excited states of Ru^{II} complexes, are readily tuned by ligand modification.^[38,54–56] However, for cyclometalated Ir^{III} complexes, the relationship between the molecular structure and photophysical properties is far from clear. For example, ligand modification is known to have a significant effect on the emission property of the Ir^{III} complexes, but sometimes the photophysics of the Ir^{III} coordination center and the chromophore have collapsed in their dyads. For example, boron dipyrromethene (BODIPY) was attached onto cyclo-



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metalated Ir^{III} complexes but the phosphorescence emission was completely quenched. $^{[33a]}$

Recently, by using a direct-cyclometalation strategy or the connection of a fluorophore to the transition-metal center through an ethynyl bond (C=C), we prepared cyclometalated Pt^{II} complexes with a naphthalimide (NI) ligand,^[36,52] and we found that the photophysical properties of the Pt^{II} complexes were tuned significantly by the NI moiety. For example, compared to the model complexes, intensified visiblelight absorption, red-shifted emission, and prolonged T₁ excited-state lifetimes were obtained for the NI-containing Pt^{II} complexes. We also obtained an exceptionally long T₁ excited-state lifetime with an N^N PtII bis-acetylide complex that contained NI acetylide ligands.^[37,57] Coumarin and BODIPY were incorporated into the Ir^{III} complexes and long-lived triplet excited states were observed.^[7a,18a,33a,49] However, to the best of our knowledge, the NI ligand has never been used for synthesis of the cyclometalated Ir^{III} complexes.

Herein, for the first time, the NI moiety was used for the preparation of both neutral (Ir-3) and cationic (Ir-4) cyclometalated Ir^{III} complexes. Cyclometalated neutral Ir^{III} complex with a naphthal ligand (Ir-2) and the model complex (Ir-1) were also prepared for comparison. By using steadystate absorption and -emission, 77 K emission, nanosecond time-resolved transient difference absorption spectroscopy, and density functional theory (DFT) and time-dependent DFT (TDDFT) calculations, we confirmed that the emissive excited states of complexes Ir-2, Ir-3, and Ir-4 were mainly intraligand triplet excited states (³IL), whereas for Ir-1, the T₁ excited state was mainly a metal-to-ligand-charge-transfer triplet excited state (³MLCT). These new complexes showed intense visible-light absorption and the lifetimes of the T₁ excited states were much longer than that of the model complex (Ir-1). The cyclometalated Ir^{III} complexes were used as triplet photosensitizers for TTA-based upconversion and an upconversion quantum yield of up to 14.4% was observed for Ir-3. Our complementary experimental and theoretical data will be useful for the design of visible-light-harvesting cyclometalated Ir^{III} complexes that show long-lived T₁ excited states, as well as for the application of these complexes in photovoltaics, photocatalysis, photodynamic therapies (PTD), and upconversion, etc.

Results and Discussion

Synthesis of the cyclometalated iridium (III) complexes: To enhance the UV/Vis absorption of these complexes and to access their long-lived ³IL excited states, our principle strategy was to extend the π -conjugation of the ppy or bpy ligands by adding arylacetylide ligands (Scheme 1).^[36,38] The aryl acetylides were judiciously selected to perturb the ³MLCT excited state of the parent coordination structure (e.g., **Ir-1**), thereby allowing access to the long-lived ³IL excited states.^[38,57-63] Arylacetylides are rarely used for the preparation of cyclometalated Ir^{III} complexes.^[33a] The NI and the naphthal moieties were connected to the ppy or bpy ligands on the Ir^{III} complex through acetylide bonds. This C=C linker assured efficient electronic communication between the NI moiety and the coordination center; thus, the T_1 excited state of the Ir^{III} coordination center could be drastically perturbed and it was more likely to attain the ³IL excited states because the ³IL excited state resided in a lower energy level than the ³MLCT excited state of the Ir^{III} coordination center.

4-Bromo-1,8-naphthalic anhydride (2) was used as the starting material and functionalized with alkylamines to prepare the *N*-alkyl NI moiety to improve the solubility of the final complexes (Scheme 1). Attachment of the NI moiety onto the ppy or bpy ligands was achieved with the Pd⁰-catalyzed Sonogashira coupling reactions. Complex **Ir-2**, which contained a naphthalene moiety, and parent complex **Ir-1** were also prepared for comparison of the photophysical properties. All of the complexes were obtained in moderate to satisfactory yields.

UV/Vis absorption of cyclometalated iridium (III) complexes: UV/Vis absorption spectra of the cyclometalated Ir^{III} complexes are shown in Figure 1. Ir-1 ($\varepsilon = 16\,600 \,\text{m}^{-1} \text{cm}^{-1}$ at 382 nm) and Ir-2 ($\varepsilon = 49\,100 \,\text{m}^{-1} \text{cm}^{-1}$ at 348 nm) showed



Figure 1. UV/Vis absorption spectra of complexes Ir-1, Ir-2, Ir-3, and Ir-4 (toluene, 1.0×10^{-5} M, 25 °C).

maxima in the UV range and only very weak absorption in the visible-light range. Strong absorption bands at 285 nm are typical for cyclometalated Ir^{III} complexes. For **Ir-3** and **Ir-4**, the absorption in the visible-light range was more-intense than that of **Ir-1** and **Ir-2**. For example, the molar extinction coefficient of **Ir-3** at 402 nm was $39600 \text{ m}^{-1} \text{ cm}^{-1}$, which was much larger than that of **Ir-1** and **Ir-2**. Ir-4 also showed strong absorption at 404 nm ($\varepsilon = 25100 \text{ m}^{-1} \text{ cm}^{-1}$). The absorption of **Ir-3** in the visible-light range was much stronger than the typical absorption of the Ir^{III} complexes.^[10,26,31,32,35]

Photoluminescence of the cyclometalated iridium (III) complexes: Room-temperature (RT) phosphorescence of the NI ligand: All of the Ir^{III} complexes were phosphorescent at room temperature, but the phosphorescence quantum yields varied dramatically (Figure 2 and Table 1). The phosphorescence quantum yields for Ir-1, Ir-2, Ir-3 and Ir-4 were $\Phi_{\rm P}$ = 0.726, 0.186, 0.014, and 0.003, respectively. The parent (un-



Scheme 1. Preparation of Ir^{III} complexes **Ir-1**, **Ir-2**, **Ir-3**, and **Ir-4**; the molecular structures of the triplet acceptor 9,10-diphenylanthracene (DPA) and ruthenium(II) complex $[Ru(dmb)_3][PF_6]_2$ (**Ru-1**), which was used as a standard in the upconversions, are also shown. a) 2-Phenylpyridine, silver triflate, 2-ethoxyethanol, Ar, 100°C, 18 h; b,e) [{Ir(ppy)_2Cl}_2], silver triflate, 2-ethoxyethanol, Ar, 100°C, 18 h; b,e) [{Ir(ppy)_2Cl}_2], silver triflate, 2-ethoxyethanol, Ar, 100°C, 18 h; c) 2-ethylhexylamine, EtOH, reflux, 6 h; d) 2-(4-ethynylphenyl)pyridine, [Pd(PPh_3)_2Cl_2], PPh_3, CuI, NEt_3, EtOH, Ar, reflux, 8 h; f) 5-ethynyl-2,2'-bipyridine, [Pd(PPh_3)_2Cl_2], PPh_3, CuI, NEt_3, EtOH, Ar, reflux, 8 h; g) [{Ir(ppy)_2Cl}_2], CH_2Cl_2/MeOH (2:1 v/v), Ar, reflux, 6 h.



Figure 2. Emission spectra of complexes Ir-1, Ir-2, Ir-3, and Ir-4: a) Comparison of the emission intensities of Ir-1, Ir-2, Ir-3, and Ir-4 under the same conditions; b) normalized emission spectra of Ir-3 and Ir-4. Ir-1: $\lambda_{ex} = 383$ nm; Ir-2: $\lambda_{ex} = 348$ nm; Ir-3: $\lambda_{ex} = 402$ nm; Ir-4: $\lambda_{ex} = 405$ nm (in deaerated toluene, 1.0×10^{-5} M, 25 °C).

substituted) complex **Ir-1** gave an intense emission at 510 nm. The emission band of **Ir-2** was red-shifted by 61 nm (571 nm). For **Ir-3**, a weak emission band was observed at 640 nm. However, the emission of cationic complex **Ir-4** was the weakest and was blue-shifted by 13 nm compared to the neutral complex (**Ir-3**, Figure 2b). We proposed that both **Ir-3** and **Ir-4** showed room-temperature phosphorescence of

the NI ligand. We noticed that the emission band of **Ir-1** was much-less structured than the other complexes. Typically, a structured emission band indicates a ³IL emission, whereas a structure-less emission band indicates that the emission is from a ³MLCT excited state.

Notably, the fluorescence of ligands L-2, L-3, and L-4 was completely quenched in complexes Ir-2, Ir-3, and Ir-4, respectively (for the emission of the ligands, see the Supporting Information), which indicated efficient intersystem crossing (ISC) from the singlet excited states to the triplet excited states. However, this ISC is not always the case for cyclometalated Ir^{III} complexes. For example, with a BODIPY fluorophore was attached to an Ir^{III} coordination center by using a similar approach, the fluorescence emission of the BODIPY could not be completely quenched; rather, the phosphorescence of the Ir^{III} coordination center was quenched instead.^[33a] Recently, cyclometalated Ir^{III} complexes with thiophene ligands were found to be fluorescence/phosphorescence dual emissive.^[64] Thus, the efficient ISC in Ir-2–Ir-4 may have been due to the direct connection

Table 1. Photophysical parameters of the ligands and cyclometalated Ir^{III} complexes (in toluene, 1.0×10^{-5} M, 25 °C).

	$\lambda_{abs} [nm]^{[a]}$	$arepsilon^{[b]}$	$\lambda_{em} [nm]^{[c]}$	Φ	$ au_{ m em}{}^{[{ m f}]}$	$ au_{\mathrm{T}} [\mu \mathrm{s}]^{\mathrm{[g]}}$	$ au_{\mathrm{T}} [\mathrm{ns}]^{[\mathrm{h}]}$
L2	235/334	53 400/47 700	427	0.826 ^[d]	0.90 ns	_[i]	_[i]
L3	382/402	48200/43300	428	$0.897^{[d]}$	1.74 ns	_[i]	_[i]
L4	379/400	37700/33700	418	$0.731^{[d]}$	1.47 ns	_[1]	_[i]
Ir-1	286/382	54600/16600	510	0.726 ^[e]	1.16 µs	1.34	29.4
Ir-2	286/348/363	48 300/49 100/46 300	571	$0.186^{[e]}$	6.98 µs	6.94	92.3
Ir-3	291/402	48 300/39 600	640	$0.014^{[e]}$	10.15 μs	9.30	313.7
Ir-4	291/383/404	21 000/28 300/25 100	627	0.003 ^[e]	16.36 µs	16.45	387.3

[a] Absorption maxima (in toluene, 1.0×10^{-5} M, 25 °C); [b] molar extinction coefficient at the absorption maxima (ε : M⁻¹cm⁻¹); [c] emission maxima; [d] fluorescence quantum yield with quinine sulfate as the standard ($\Phi_{\rm F}$ =0.547 in 0.05 M sulfuric acid); [e] phosphorescence quantum yield with complex [Ru(dmb)₃][PF₆]₂ as a standard ($\Phi_{\rm p}$ =0.073 in MeCN); [f] luminescence lifetimes; [g] triplet excited state lifetimes, measured by nanosecond time-resolved transient difference absorption in N₂; [h] triplet excited state lifetimes, measured by nanosecond time-resolved transient difference absorption in air; [i] not applicable.

of the π -core of the fluorophore to the coordination centers, which was not the case for some of the previous Ir^{III} complexes that contained a bulky organic chromophore.^[33a,64]

The emission of **Ir-3** was highly sensitive to the polarity of the solvent (Figure 3c). For example, the emission in toluene was relatively strong but it was completely quenched



Figure 3. Solvent-polarity-dependence of the emission of the complexes $(1.0 \times 10^{-5} \text{ m})$: a) **Ir-1**, $\lambda_{ex} = 383 \text{ nm}$; b) **Ir-2**, $\lambda_{ex} = 348 \text{ nm}$; c) **Ir-3**, $\lambda_{ex} = 402 \text{ nm}$; d) **Ir-4**, $\lambda_{ex} = 405 \text{ nm}$. The solutions were bubbled with N₂ for about 30 min before the measurements were taken, 25 °C.

in MeCN. However, the UV/Vis absorption of **Ir-3** was almost independent of solvent polarity (see the Supporting Information). The emission of cationic complex **Ir-4** also varied dramatically in different solvents but there was no clear trend with variation of the solvent polarity. For example, the emission of **Ir-4** was strongest in CH_2Cl_2 but it was weakest in toluene (Figure 3d). Unlike **Ir-3** and **Ir-4**, the emission of **Ir-1** and **Ir-2** was independent of solvent polarity (Figure 3a,b). It has been reported that the phosphorescence of a C^N Pt^{II} acac complex can be significantly quenched by a weak Lewis base, such as CH_2Cl_2 and MeCN; in this case, the quenching was due to the coordination of the solvent molecules to the electron-deficient Pt^{II}

center.^[65] These cyclometalated Ir^{III} complexes adopted octahedral geometries; thus the quenching of the emission of **Ir-3** was unlikely to have been caused by the coordination of solvent molecules to the Ir^{III} center.^[65] We proposed that the sensitivity of the emission of **Ir-3** and **Ir-4** to solvent polarity was due to the charge-transfer components of the $T_1 \rightarrow S_0$ transition (see below).

The photophysical properties of these complexes are summarized in Table 1. The T_1 excited

state lifetime of **Ir-4** was the longest (16.45 μ s). The phosphorescence lifetimes of **Ir-2**, **Ir-3**, and **Ir-4** were longer than those of **Ir-1** and other typical cyclometalated Ir^{III} complexes.^[1,10,12,19,22,23,25,31,32,35,66-68] Thus, we proposed that the T₁ excited states of **Ir-2**, **Ir-3**, and **Ir-4** were mainly due to ³IL excited states. Usually, emission from ³IL states gives low phosphorescent quantum yields.^[69,70] Furthermore, the T₁ excited-state lifetimes of all of the complexes in air-saturated solutions were much shorter than those in N₂-saturated solutions; thus, these results confirmed that the long-lived excited states were T₁ states (see the Supporting Information).

The photophysical properties of the complexes were compared with known Ir^{III} complexes that contained ligands with extended π -conjugation frameworks.^[33] The BODIPYcontaining cyclometalated Ir^{III} complex showed no RT phosphorescence,^[33a] whereas an Ir^{III} complex with styryl-tpy ligands showed much-shorter phosphorescence lifetimes (<2 µs) and lower phosphorescence quantum yields.^[33b]

Emission spectra of the complexes at 77 K: To study the emissive excited states of these IrIII complexes, their emissions at 77 K and RT were compared (Figure 4).^[34,71] Basically, the vibration progression of the emission spectra became more significant at 77 K. The emission of Ir-1 at 77 K was blue-shifted by 19 nm compared to that at RT; thus, the thermally induced Stokes shift (ΔE_s) of Ir-1 was 755 cm⁻¹. However, for Ir-2, Ir-3, and Ir-4, the ΔE_s values were 31, 148, and 156 cm⁻¹, respectively, which were much smaller than that of Ir-1. A large ΔE_s value is an indication of a ³MLCT emissive state, whereas small $\Delta E_{\rm S}$ values usually indicate a ³IL excited state.^[34,57,71] Based on the emission spectra at 77 K and RT, we proposed that the emission of Ir-2, Ir-3, and Ir-4 were due to ³IL emissive states, whereas the emissive state of Ir-1 was characterized by a more-significant ³MLCT state.

Nanosecond time-resolved transient difference absorption of the Ir^{III} complexes: Assignment of the emissive excited state: To study the T_1 excited states of the Ir^{III} complexes, nanosecond time-resolved transient difference absorption spectroscopy was performed (Figure 5). For Ir-1 (Figure 5 a),

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Figure 4. Normalized emission intensity of the Ir^{III} complexes at RT (25°C) and 77 K in 2-methyltetrahydrofuran $(1.0 \times 10^{-5} \text{ M})$: a) Ir-1, $\lambda_{ex} = 400 \text{ nm}$; b) Ir-2, $\lambda_{ex} = 410 \text{ nm}$; c) Ir-3, $\lambda_{ex} = 402 \text{ nm}$; d) Ir-4, $\lambda_{ex} = 405 \text{ nm}$. The solutions were purged with N₂ for about 15 min before the measurements were taken.



Figure 5. Nanosecond time-resolved transient difference absorption spectra of a) **Ir-1**; b) **Ir-2**; c) **Ir-3**; and d) **Ir-4** (in deoxygenated toluene, 1.0×10^{-5} M, 25 °C). Arrows indicate the elapsed time after a 355 nm laser flash.

a transient absorption was observed at 320 nm. The significant bleaching at 525 nm was due to the strong phosphorescence emission of the complex (Φ_P =0.726). However, for **Ir-3**, a notably different transient profile was observed (Figure 5 c): Significant bleaching was observed at 405 nm and 380 nm, which were due to bleaching of the ground state; this bleaching was consistent with the strong UV/Vis absorption of the complex in this range (Figure 1). Furthermore, strong transient absorption of **Ir-3** was found at 620 nm and 658 nm, which was characteristic of an NI-localized T₁ excited state.^[57] Thus, we concluded that the T₁ excited state in **Ir-3** was an NI-localized ³IL excited state. **Ir-2** and **Ir-4** also showed similar transient absorption (Figure 5b, d). From the



Figure 6. Electron-density maps of the frontier molecular orbitals of **Ir-1**; based on the optimized ground-state geometry calculated by DFT calculations at the B3LYP/6-31 g(d)/LanL2DZ level with Gaussian 09W.

transient absorption spectra, we concluded that the emissive excited states of **Ir-3** and **Ir-4** were ³IL emissive excited states, whilst that of **Ir-1** was characterized by a more-significant ³MLCT state.

TDDFT calculations: Assignment of the UV/Vis absorption and emissive excited states: TDDFT calculations have been used to rationalize the photophysics of transition-metal complexes.^[8,12,30,66,72-74] Previously, we have used TDDFT calculations to explain the UV/Vis absorption and emission properties of Pt^{II}–bis-acetylide complexes, polyimine Ru^{II} complexes, and phosphorescent molecular probes.^[36-53,75,76] Herein, we carried out TDDFT calculations to rationalize the UV/Vis absorption and phosphorescence emission properties of the Ir^{III} complexes.

The vertical excitations (i.e., UV/Vis absorption) of **Ir-1** are listed in Table 2. The calculations predicted weak transitions at 428, 398, 387, and 361 nm. The calculated data were in agreement with the experimental results (Figure 1). The Ir^{III} atom contributed to the transitions, which could be assigned as MLCT or LLCT transitions (Figure 6).

The T_1 excited state of **Ir-1** was calculated and the major $S_0 \rightarrow T_1$ transition was a HOMO \rightarrow LUMO transition, which could be assigned as LLCT or MLCT; this result was in agreement with the photophysics of the typical cyclometalated Ir^{III} complexes. The calculated $S_0 \rightarrow T_1$ energy gap was 2.64 eV (470 nm), which was in good agreement with the observed RT phosphorescence emission at 510 nm (Figure 2a and Table 1).

The excitations of **Ir-2** were also studied by TDDFT calculations (Table 3 and Figure 7), and the UV/Vis absorption bands could be assigned as MLCT, IL, or LLCT. The calculated excitations were in good agreement with the experimental data (Figure 1). The $S_0 \rightarrow T_1$ energy gap was calculated to be 590 nm, which was close to the experimentally observed RT phosphorescence emission of **Ir-2** (571 nm, Figure 2a). Based on the components of the T_1 excited states, the transitions were assigned as LLCT/MLCT/IL. Noticeably, the ³IL that was localized on the naphthalene-ppy

Table 2. Electronic excitation energies [eV], oscillator strengths [f], main configurations, and CI coefficients of the low-lying electronic excited states of **Ir-1**; calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ based on the optimized ground-state geometries.

		T	TDDFT//B3LYP/6-31G(d)		
Electronic transition	Energy ^[a] [eV/nm]	<i>f</i> ^[b]	Composition ^[c]	$CI^{[d]}$	Character
$S_0 \rightarrow S_1$	2.90/428	0.0006	$H \! \rightarrow \! L$	0.6963	LLCT/MLCT
$S_0 \rightarrow S_5$	3.11/398	0.0225	$H{-}2{\rightarrow}L$	0.6482	MLCT/LLCT
			$H-2\rightarrow L+2$	0.1521	LLCT
			$H-1\rightarrow L+1$	0.1607	LLCT/MLCT
$S_0 \rightarrow S_8$	3.20/387	0.0540	$H-2\rightarrow L+1$	0.4371	LLCT/MLCT
			$H{-}1{\rightarrow}L$	0.2384	LLCT
			$H-1\rightarrow L+1$	0.1517	LLCT/MLCT
			$H-1\rightarrow L+2$	0.4369	LLCT/MLCT
$S_0 \rightarrow S_{10}$	3.43/361	0.0478	$H-2\rightarrow L+2$	0.3343	LLCT
			$H-1\rightarrow L+1$	0.3316	LLCT/MLCT
$S_0 \rightarrow T_1$	2.64/470	$0.0000^{[e]}$	$H-2\rightarrow L+1$	0.1519	LLCT/MLCT
			$H-1\rightarrow L+1$	0.1803	LLCT/MLCT
			$H-1\rightarrow L+2$	0.1598	LLCT/MLCT
			$H \! \rightarrow \! L$	0.5557	LLCT/MLCT

[a] Only selected low-lying excited states are presented; [b] oscillator strengths; [c] only the main configurations are presented; [d] the CI coefficients are in absolute values; [e] no spin-orbital coupling effect was considered, thus the f value was zero.

Table 3. Electronic excitation energies [eV], oscillator strengths [f], main configurations, and CI coefficients of the low-lying electronic excited states of **Ir-2**; calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ based on the optimized ground-state geometries.

TDDFT/		DDFT//B3LYP/6-3	T//B3LYP/6-31G(d)		
Electronic transition	Energy ^[a] [eV/nm]	<i>f</i> ^[b]	Composition ^[c]	$CI^{[d]}$	Character
$S_0 \rightarrow S_1$	2.70/459	0.0399	$H{-}3{\rightarrow}L$	0.1123	MLCT/ILCT
			$H{-}2{\rightarrow}L$	0.1606	MLCT/ILCT
			$H \! \rightarrow \! L$	0.6536	MLCT/ILCT
$S_0 \rightarrow S_8$	3.19/389	0.7678	$H{-}3{\rightarrow}L$	0.5182	MLCT/ILCT
			$H{-}2{\rightarrow}L$	0.2008	MLCT/ILCT
			$H-2\rightarrow L+2$	0.1283	LLCT/MLCT
			$H-1\rightarrow L+2$	0.1840	LLCT/MLCT
			$H \rightarrow L$	0.1539	MLCT/ILCT
$S_0{\rightarrow}S_{10}$	3.27/379	0.1319	$H{-}3{\rightarrow}L$	0.1364	MLCT/ILCT
			$H - 3 \rightarrow L + 2$	0.2204	LLCT/MLCT
			$H-2\rightarrow L+1$	0.1236	LLCT/MLCT
			$H-2\rightarrow L+2$	0.1173	LLCT MLCT
			$H{-}1{\rightarrow}L{+}1$	0.1208	MLCT/ILCT
			$H-1\rightarrow L+2$	0.3833	LLCT/MLCT
			$H \! \rightarrow \! L$	0.1149	MLCT/ILCT
$S_0{\rightarrow}T_1$	2.10/590	$0.0000^{[e]}$	$H{-}3{\rightarrow}L$	0.2726	MLCT/ILCT
			$H{-}2{\rightarrow}L$	0.1816	MLCT/ILCT
			$H{-}1{\rightarrow}L$	0.3629	ILCT
			$H{\rightarrow}L$	0.4007	MLCT/ILCT

[a] Only selected low-lying excited states are presented; [b] oscillator strength; [c] only the main configurations are presented; [d] the CI coefficients are in absolute values; [e] no spin-orbital coupling effect was considered, thus the f value was zero.

ligand was clearly recognizable (Figure 7). Thus, we proposed that the T_1 excited state was a ³IL state to some extent, which was consistent with the long-lived T_1 excited state of **Ir-2** (τ =6.94 µs, Table 1) and it was in agreement with the 77 K emission spectrum (Figure 4b) and the transient difference absorption spectrum (Figure 5b). The lifetime of **Ir-2** was longer than those of typical Ir^{III} complexes.^[1,8–12,15,18b,19,34,35]

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The calculated UV/Vis absorption of Ir-3 was in good agreement with the experimental results (Table 4 and Figure 1). The weak absorption band at 537 nm was attributed to the HOMO→LUMO and HOMO→LUMO+1 transitions. Based on the calculated frontier molecular orbitals (Figure 8), these transitions were mixed LLCT/MLCT (ppy \rightarrow NI-ppy and Ir→ppy-NI) states. The intense absorption at 433 nm was assigned to the IL transition (HOMO $-3 \rightarrow$ LUMO). This result showed that the intensified absorption at 433 nm was due to the NIppy ligand (for the UV/Vis absorption of NI-ppy). The absorption at 390 nm was assigned to HOMO-2 \rightarrow LUMO+1, HOMO $-2 \rightarrow LUMO+2$, HOMO-2 \rightarrow LUMO+3 transitions, etc., with mixed IL/MLCT/LLCT states.

The calculated $S_0 \rightarrow T_1$ energy gap was 671 nm (1.85 eV), which was close to the experimentally observed RT phosphorescence emission of **Ir-3** (640 nm, Figure 2a). Based on the components of the T_1 excited state (HOMO-3 \rightarrow LUMO, HOMO-2 \rightarrow LUMO, HOMO \rightarrow LUMO, etc.; Table 4), the major components of the transitions were assigned as NI-localized. Thus, we proposed that the T_1 excited state was in a ³IL state, which was consistent with the long-lived T_1 excited state of **Ir-3** (τ_T =9.3 µs, Table 1).

The calculated UV/Vis absorption of **Ir-4** (see the Supporting Information) was similar to that of **Ir-3**, which was in good agreement with the experiment results (Table S1 in the Supporting Information and Figure 1). The calculated $S_0 \rightarrow T_1$ energy gap was 663 nm (1.85 eV), which was close to the experimentally observed RT phosphorescence emission of **Ir-4** (627 nm, Figure 2). The T_1 excited state of **Ir-4** was also in the ³IL state, which was consistent with the long-lived T_1 excited state of **Ir-4** (τ =16.45 µs, Table 1).

The difference between complexes **Ir-2**, **Ir-3**, and **Ir-4** was that the Ir^{III} center in **Ir-2** was more involved in the transitions than in **Ir-3** and **Ir-4**; that is, the IL feature of the excitation transitions of **Ir-2** was less than those of **Ir-3** and **Ir-4**.

Spin-density surfaces of the triplet excited states: To support the assignment of the T_1 excited states of the Ir^{III} complexes from a theoretical perspective, we studied the spin-density surfaces of the triplet states of the complexes (Figure 9). For **Ir-1**, the

spin-density was distributed on the Ir^{III} atom and on the ppy ligand. This result was in agreement with the LLCT/MLCT assignment of **Ir-1**. For **Ir-2**, **Ir-3**, and **Ir-4**, only the acetylide-linked ppy-naphthalene, bpy-naphthalene, or ppy-NI moieties contributed to the triplet excited states. Thus, ³IL T₁ excited states were assigned for **Ir-2**, **Ir-3** and **Ir-4**.^[74]

The 77 K emission spectra, nanosecond time-resolved transient difference spectra, and DFT calculations suggested



Figure 7. Electron-density maps of the frontier molecular orbitals of **Ir-2**; based on the optimized ground-state geometry calculated by TDDFT calculations at the B3LYP/6-31 g(d)/LanL2DZ level with Gaussian 09W.

Table 4. Electronic excitation energies [eV], oscillator strengths [f], main configurations, and CI coefficients of the low-lying electronic excited states of **Ir-3**; calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ based on the optimized ground-state geometries.

		Т	TDDFT//B3LYP/6-31G(d)		
Electronic transition	Energy ^[a] [eV/nm]	$f^{[b]}$	Composition ^[c]	$CI^{[d]}$	Character
$S_0 \rightarrow S_1$	2.31/537	0.0251	$H{ ightarrow}L$	0.6845	LLCT/MLCT
			$H \rightarrow L+1$	0.1552	MLCT/LLCT
$S_0 \rightarrow S_4$	2.86/433	0.9062	$H{-}3{\rightarrow}L$	0.6823	LLCT/MLCT
$S_0 \rightarrow S_{10}$	3.19/390	0.0542	$H-2 \rightarrow L+1$	0.5229	MLCT/IL
			$H-2\rightarrow L+2$	0.1282	MLCT/ILCT
			$H-1\rightarrow L+2$	0.2925	MLCT/ILCT
$S_0 \rightarrow T_1$	1.85/671	$0.0000^{[e]}$	$H{-}3{\rightarrow}L$	0.1721	MLCT/ILCT
			$H{-}2{\rightarrow}L$	0.5440	ILCT
			$H{-}1{\rightarrow}L$	0.2919	MLCT/ILCT
			$H{\rightarrow}L$	0.1124	LLCT/MLCT





Figure 8. Electron-density maps of the frontier molecular orbitals of **Ir-3**; based on the optimized ground-state geometry calculated by TDDFT calculations at the B3LYP/6-31 g (d)/LanL2DZ level with Gaussian 09W.

that the T_1 excited states of **Ir-2**, **Ir-3**, and **Ir-4** were intraligand triplet excited states (³IL), whilst the T_1 excited state of **Ir-1** was mainly a ³MLCT state. The long-lived ³IL states are significant for the application of these Ir^{III} complexes.

Application of the visible-light-harvesting and long-lived T_1 excited states for TTA upconversion: Next, we used the enhanced visible-light absorption and the long-lived T_1 excited states of Ir-2, Ir-3, and Ir-4 in photophysical processes that

required T₁ excited states for sensitization. We chose to study TTA upconversion. Among the various upconversion schemes,^[77,78] TTA upconversion was of particular interest owing to its low excitation power (0.1 W cm^{-2} , the same scale as terrestrial solar radiation).^[46,79–82] Furthermore, the excitation and the emission wavelength of the TTA upconversion could be readily tuned by independent selection of the triplet sensitizers and the acceptors/emitters, two components of the TTA upconversion.

The basic TTA-upconversion mechanism was the photoexcitation of the triplet photosensitizer (e.g., $S_0 \rightarrow S_1$), followed by population of the T_1 excited state by ISC. Triplettriplet energy-transfer (TTET) from the sensitizer to the acceptor would produce the T_1 excited state of the acceptor. Collision of the triplet acceptors would produce the singlet

excited state of the acceptor, with an overall probability of at least 11.1%, as determined by the spin statistical law.^[79,83]

Currently, the typical triplet photosensitizers for TTA upconversion are Pt^{II}/Pd^{II} porphyrin complexes.^[79,81,84] Previously, the cyclometalated Ir^{III} complex [Ir(ppy)₃] was used as a triplet sensitizer for TTA upconversion but the lifetime of the complex was short (τ =1.34 µs) and the excitation had to be performed in the UV range; the upconversion quantum yield was not provided.^[85] Because Ir-2, Ir-3, and Ir-4 showed intense absorption in the visible-light range, these complexes with long-lived T₁ excited states could be used as triplet photosensitizers for the TTA upconversion (for the Jablonski diagram of the TTA upconversion, see Scheme 2).

9,10-Diphenylanthracene (DPA) was used as the triplet acceptor owing to its appropriate T_1 excited-



Figure 9. Isosurfaces of the spin density of Ir^{III} complexes **Ir-1**, **Ir-2**, **Ir-3**, and **Ir-4** (in toluene) at the optimized triplet-state geometry; calculated at the B3LYP/6-31G/LANL2DZ level with Gaussian 09W.

state energy level (1.77 eV, 700 nm).^[86] Upon laser excitation at 445 nm, the complexes showed different phosphorescence emission intensities (Figure 10a): **Ir-1** gave the strongest emission owing to its high phosphorescence quantum yield. **Ir-2** gave a similar ε value at 445 nm, but its emission was much weaker than **Ir-1. Ir-3** gave very weak emission, whilst



Scheme 2. Qualitative Jablonski diagram that shows the sensitized TTA process between the Ir^{III} complexes (exemplified by **Ir-3**) and the triplet acceptor DPA; the effect of visible-light-harvesting ability and the luminescence lifetime of the Ir^{III} sensitizer on the efficiency of TTA-based upconversion is also shown. *E* is energy; GS is the ground state (S₀); ¹MLCT* is the Ir^{III}-based metal-to-ligand charge-transfer singlet excited state; ISC is intersystem crossing; ³IL* is the intraligand triplet excited state (NI localized); TTET is triplet-triplet energy transfer; ³DPA* is the triplet excited state of DPA. The emission band for the sensitizer alone is the ³IL emissive excited state. The emission bands in the TTA experiment are the simultaneous ³IL* emission (phosphorescence) and the ¹DPA* emission (fluorescence).



Figure 10. Upconversion with Ir^{III} complexes as triplet sensitizers and DPA as triplet acceptors (in deaerated toluene): a) The emission of the complexes alone (laser excitation: 445 nm); b) upconversion emission spectra of mixtures of the sensitizers and DPA upon selective excitation of the sensitizers at 445 nm. Note the residual phosphorescence of the sensitizers; [sensitizers] = 1.0×10^{-5} M, [DPA] = 6.0×10^{-5} M, 25 °C.

Ir-4 gave almost no emission because the absorption band of Ir-4 in the visible-light range was very narrow and the absorption at 445 nm was weak ($\varepsilon = 1128 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$, Figure 1). However, we considered that this property did not necessarily mean that the efficiency of the $S_1 \rightarrow T_1$ ISC was low. In other words, the low phosphorescence quantum yields of Ir-**3** and Ir-4 should not necessarily negate their application in photophysical processes that are sensitized with triplet excited states. To confirm this concept, and to explore the application of visible-light harvesting, as well as the long-lived T_1 excited states of Ir-3 and Ir-4, the complexes were used as triplet sensitizers for TTA-based upconversion (Figure 10).

In the presence of DPA, blue emission in the range 380– 550 nm was observed for **Ir-2** and **Ir-3**, which was due to the upconverted fluorescence of DPA (Figure 10b). Laser irradiation of DPA alone at 445 nm failed to produce the emission at 380–550 nm; thus, the blue emission of the mixed **Ir-2**/DPA and **Ir-3**/DPA solutions was due to TTA upconversion. However, for **Ir-1**, no upconverted emission was observed in the range 380–550 nm, which indicated that **Ir-1** was not efficient at sensitizing the TTA upconversion under these experimental conditions because of its poor absorption at 445 nm (ε =4559 M⁻¹ cm⁻¹, Figure 1) and short T₁ excited-state lifetime ($\tau_{\rm T}$ =1.34 µs, Table 1). Because excitation of **Ir-4** at 445 nm was not suitable, **Ir-4** could not be excited efficiently, and no upconversion was observed (Figure 10b), although the lifetime of the T₁ excited state was long ($\tau_{\rm T}$ = 16.45 µs, Table 1).

The variation in the emission of the sensitizers with increasing DPA concentration was investigated (Figure 11). The emission of **Ir-1** was partially quenched in the presence of DPA, but no upconverted emission of DPA was observed (Figure 11a). We proposed that the lack of upconversion was due to the poor absorption of **Ir-1** at 445 nm and to the short-lived T₁ excited state (τ_T =1.34 µs). However, for **Ir-2**, the upconverted fluorescence of DPA was observed with quenching of the phosphorescence of **Ir-2** (Figure 11b). Similar to **Ir-1**, **Ir-2** also showed weak absorbance at 445 nm; however, the T₁ excited-state lifetime of **Ir-2** (τ_T =6.94 µs) was much longer than that of **Ir-1**. The upconversion quantum yield with **Ir-2** as the triplet sensitizer was 7.1% (Table 5). Because excitation at 445 nm was not suitable for



Figure 11. Upconverted fluorescence of DPA and the residual phosphorescence of the Ir^{III} complexes with increasing DPA concentration (selective excitation at 445 nm): a) **Ir-1**; b) **Ir-2**; c) **Ir-3**; d) **Ir-4** (in deaerated toluene, 1.0×10^{-5} M, 25 °C).

Table 5. Upconversion-related parameters of the complexes.^[a]

	$\Phi_{ m uc}{}^{ m [b]}$ [%]	$K_{\rm sv}^{\rm [c]}$ (×10 ³) [m ⁻¹]	$K_{\rm q}^{\rm [d]} (imes 10^9) [{ m M}^{-1}{ m S}^{-1}]$			
Ir-1	0.0	5.2	4.50			
Ir-2	7.1	24.1	3.46			
Ir-3	14.4	25.8	2.54			
Ir-4	0.0	30.9	1.89			
Ru-1	1.6	3.9	5.30			

[a] Measured in toluene, 1.0×10^{-5} M, 25 °C; [b] upconversion quantum yields, measured with [Ru(dmb)₃][PF₆]₂ as a standard ($\Phi_p = 0.073$ in CH₃CN); [c] Stern–Volmer quenching constants (K_{sv}) of the quenching of phosphorescence of Ir^{III} complexes by triplet acceptor DPA; [d] bimolecular quenching constants (k_q), $K_{sv} = K_q$.

Ir-4, neither the phosphorescence of Ir-4 nor the upconverted fluorescence of DPA could be observed (Figure 11 d), despite the longest T₁ excited lifetime (τ_T =16.45 µs, Table 1). For Ir-3, a more-significant upconversion was observed (Figure 11 c), which was attributed to the intense absorbance at 445 nm compared to that of Ir-1, Ir-2, and Ir-4 (Figure 1). Furthermore, the T₁ excited-state lifetime of Ir-3 (τ_T =9.30 µs) was longer than that of Ir-1 and Ir-2. The upconversion quantum yield with Ir-3 as the triplet sensitizer was up to 14.4%.

Interestingly, the peak area of the upconverted fluorescence was much larger than the diminished quenched phosphorescence peak area; this result was apparently inconsistent the photophysics of the TTA upconversion with phosphorescent triplet photosensitizers (Scheme 2).^[79] We proposed that the **Ir-3** molecules at the T_1 excited state that were otherwise non-phosphorescent were involved the TTET process, which was a key step in the cascade photophysical process of TTA upconversion (Scheme 2). Thus, we expect that weakly phosphorescent or even non-phosphorescent complexes can be used as triplet sensitizers for TTA upconversion, as long as the T_1 excited state of the complexes can be populated upon photoexcitation.^[48]

The efficiency of the TTET process of TTA upconversion was quantitatively studied by investigating the quenching of the phosphorescence emission of the Ir^{III} complexes by DPA (Figure 12). Stern–Volmer curves are shown in Figure 13. Ir-2, Ir-3, and Ir-4 showed similar quenching effects in the presence of DPA with similar quenching constants (Table 5). However, for Ir-1, the quenching curve had a much shallower slope and the quenching constant was much smaller $(K_{\rm SV}=5.22 \times 10^3 \,{\rm m}^{-1})$ than those of Ir-2 $(K_{\rm SV}=2.41 \times 10^4 \,{\rm m}^{-1})$, Ir-3 $(K_{\rm SV}=2.58 \times 10^4 \,{\rm m}^{-1})$, and Ir-4 $(K_{\rm SV}=3.09 \times 10^4 \,{\rm m}^{-1})$; Table 5).

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Figure 13. Stern–Volmer plots that were generated from the quenching of the photoluminescence intensity of the Ir^{III} complexes as a function of DPA concentration in toluene: Ir-1 (λ_{ex} =445 nm); Ir-2 (λ_{ex} =460 nm); Ir-3 (λ_{ex} =445 nm); Ir-4 (λ_{ex} =425 nm). [complex]= 1.0×10^{-5} M in deaerated toluene, 25 °C.

Next, the upconversion quantum yields were determined (Table 5). For **Ir-3**, the upconversion quantum yield was 14.4%. For **Ir-2**, the upconversion quantum yield was 7.1%. The upconversion quantum yields with **Ir-1** and **Ir-4** as the sensitizers were almost zero. We attributed the high upconversion quantum yield of **Ir-3** to its intense absorption at the excitation wavelength and to the long-lived T_1 excited state. Previously, the theoretical limit of the TTA upconversion quantum yield was predicted to be 11.1%. However, examples that exceeded this limit have been reported.^[79]

The upconversion was visible to the naked eye (Figure 14). The emission color changes were characterized by CIE coordinates (Figure 14c,d). For **Ir-1**, no upconversion was observed; thus, only the green emission of **Ir-1** was observed (laser excitation at 445 nm) and there was almost no change in the CIE coordinates. For **Ir-2**, a yellow emis-



Figure 12. Phosphorescence emission spectra of the Ir^{III} complexes with increasing DPA concentration in deaerated toluene: a) Ir-1, $\lambda_{ex} = 445$ nm); b) Ir-2, $\lambda_{ex} = 460$ nm; c) Ir-3, $\lambda_{ex} = 445$ nm; d) Ir-4, $\lambda_{ex} = 425$ nm (in toluene, 1.0×10^{-5} M, 25 °C).



Figure 14. a) Photographs of the emission of the sensitizers alone and b) photographs of the upconversion (mixed solution with triplet acceptor DPA); c) CIE diagram of the emissions of the sensitizers alone and d) CIE diagram of the emissions in the presence of DPA (upconversion). The data of **Ir-4** are not shown owing to the weak emission; $\lambda_{ex} = 445$ nm (5 mW), in deaerated toluene, 1.0×10^{-5} M, 25 °C.

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sion was observed for the sensitizer alone. White emission (CIE coordinates of 0.40, 0.36) was observed for **Ir-2** in the presence of DPA, owing to the upconverted fluorescence emission of DPA in the blue region and to the residual phosphorescence emission of **Ir-2** at 571 nm (Figure 14b, d). For **Ir-3**, a red emission was observed without DPA (Figure 14a). In the presence of DPA, a blue emission was observed, owing to the upconversion (Figure 14b). There was a notable change in the CIE coordinates of **Ir-3** (Figure 14c, d). For **Ir-4**, there was no emission and no upconverted fluorescence was observed. The weak blue light in **Ir-4** was after laser excitation at 445 nm (Figure 14a,b).

We noticed a slow upconversion process in the upconversion with **Ir-3** as the triplet sensitizer, that is, the upconversion was weak at the beginning of the laser irradiation and it became more significant with prolonged irradiation (see the Supporting Information). We tentatively attributed the slow kinetics to the consumption of trace amounts of O₂ in the solution. Previously, we observed a similar phenomenon for the TTA upconversion with Ru^{II}–polyimide complexes that showed long-lived ³IL excited states.^[47,48]

The photophysics of TTA with the Ir^{III} complexes as triplet sensitizers and DPA as the triplet acceptor are summarized in Scheme 2. The principle processes that were involved in the cascade photophysical processes of TTA upconversion were: photoexcitation of the sensitizer and population of the T₁ excited state by ISC and TTET, which led to population of the acceptor DPA at the T₁ excited state. Collision and annihilation of two DPA molecules at the T1 excited state produced the S₁ excited states and the unconverted fluorescence emanate from the S_1 excited state of DPA. Note that a few processes were crucial for the upconversion efficiency; that is, the light-harvesting ability of the triplet sensitizer, the efficiency of ISC, and the lifetimes of the T₁ excited state of the sensitizer, as well as the energy level of the T_1 excited state of the sensitizer. These processes could be enhanced by the light-harvesting ability, the heavy-atom effect. Ir-3 fulfilled these requirements; therefore, the upconversion quantum yield with Ir-3 as the triplet sensitizer was as high as 14.4%. It should be pointed out that this quantum yield was far beyond that of the model Ir(III) complexes (Ir-1, whose upconversion quantum yields was almost zero). We are now actively working along these lines to prepare new cyclometalated Ir^{III} complexes that showed strong absorption in the visible-light range, and long-lived triplet excited states to enhance the application of these complexes for photocatalysis, photovoltaics, photodynamic therapy (PDT), and TTA upconversions.

Conclusion

We have prepared Ir^{III} complexes with ethynylated ppy and bpy ligand (ppy=2-phenylpyridine, bpy=2,2'-bipyridine). Naphthal acetylide (**Ir-2**) and NI acetylide (**Ir-3** and **Ir-4**) were attached to the ppy or bpy ligands of the Ir^{III} complexes. Unsubstituted [Ir(ppy)₃] was studied as a model com-

plex (Ir-1). RT phosphorescence was observed for all of the Ir^{III} complexes. Ir-3 showed intense absorption in the visiblelight range ($\varepsilon = 39600 \text{ m}^{-1} \text{ cm}^{-1}$ at 402 nm), RT deep-red emission (640 nm, $\Phi_p = 1.4\%$), and a long-lived T₁ excited state ($\tau_{\rm T}$ = 9.30 µs). The phosphorescence of **Ir-3** was strongly dependent on the polarity of the solvent: it was strongly phosphorescent in non-polar solvents, such as toluene, but the emission was completely quenched in polar solvents, such as MeCN. Complexes Ir-1 and Ir-2 showed solvent-polarity-independent emission. The T₁ excited states of Ir-2, Ir-3, and Ir-4 were assigned as a ³IL state from the emission spectra at 77 K (small thermally induced Stokes shifts), nanosecond time-resolved transient difference absorption spectra, and by TDDFT calculations (spin density of the triplet states). These complexes were used for TTA-based upconversion and upconversion quantum yields of 7.1% and 14.4% were observed for Ir-2 and Ir-3, respectively, whereas the TTA upconversion was negligible for Ir-1 and Ir-4 under the same conditions. The high upconversion quantum yield of Ir-3 was attributed to the strong absorption of the complex at the excitation wavelength and to the long-lived T₁ excited state. Our results will be useful for the design of visible-light-harvesting transition-metal complexes that show long-lived triplet excited states and for their applications as triplet sensitizers for various photophysical processes, such as TTA upconversion, photovoltaics, photocatalysis, etc.

Experimental Section

All of the chemicals were analytical pure and used as received. The solvents were dried and distilled. 2-(4-Ethynylphenyl)pyridine,^[36] 1-ethynylnaphthalene,^[36] 2-ethylhexyl-4-bromo-1,8-naphthalimide,^[36] ligand L-2,^[36] the cyclometalated Ir^{III} chloro-bridged dimers [{Ir(ppy)₂Cl}₂],^[87] and 5-ethynyl-2,2'-bipyridine^[88] were synthesized according to literature procedures (for characterization data, see the Supporting Information).

¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova NMR spectrophotometer at 400 and 100 MHz, respectively, with total proton decoupling. Mass spectra were recorded on Q-TOF Micro and MALDI micro MX spectrometers. UV/Vis absorption spectra were measured on a HP8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded on a RF-5301 PC or on a Sanco 970 CRT spectrofluorometer (modified for the upconversion experiments). Fluorescence quantum yields were measured with quinine sulfate as a standard (Φ_F =0.547 in 0.05 M sulfuric acid). Phosphorescence quantum yields were measured with [Ru(dmb)₃]-[PF₆]₂ (Φ_p =7.3%, in deaerated MeCN) as a reference. Fluorescence lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument. The emission spectra at 77 K were measured on an Oxford Optistat DN cryostat (filled with liquid N₂) and a FLS920 fluorospectrometer (Edinburgh Instruments Ltd. U.K.).

Synthesis: Ligands L3 and L4 were synthesized according to a modified literature procedure.^[36]

L3: 2-ethylhexyl-4-bromo-1,8-naphthalimide (1.08 g, 2.78 mmol), 2-(4-ethynylphenyl)pyridine (497.7 mg, 2.78 mmol), dry EtOH (40 mL), and triethylamine (12 mL) were mixed together. Then, [Pd(PPh₃)₂Cl₂] (0.139 mmol, 97.6 mg, 5 mol%), PPh₃ (0.139 mmol, 97.6 mg, 5 mol%), and CuI (26.5 mg, 0.139 mmol, 5 mol%) were added. The reaction mixture was heated to reflux and stirred under an argon atmosphere for 8 h. After completion of the reaction, the mixture was cooled to RT, the yellow precipitate was collected by filtration, and the crude product was purified by column chromatography on silica gel (CH₂Cl₂) to give the

product as a yellow solid (984.6 mg, 72.8 %). ¹H NMR (400 MHz, CDCl₃): δ =8.73–8.77 (m, 2H), 8.64 (d, 1H, *J*=7.2 Hz), 8.56 (d, 1H, *J*=7.7 Hz), 8.10 (d, 2H, *J*=8.3 Hz), 7.99 (d, 1H, *J*=7.6 Hz), 7.87 (t, 1H, *J*=7.8 Hz), 7.79 (d, 4H, *J*=7.8 Hz), 7.27–7.30 (m, 1H), 4.07–4.18 (m, 2H), 1.92–2.00 (m, 1H), 1.30–1.44 (m, 8H), 0.86–0.95 ppm (m, 6H); HRMS (ESI): *m/z* calcd for [C₃₃H₃₁N₂O₂]⁺: 487. 2386; found: 487.0323.

L4: Yellow solid (350.4 mg, 71.9%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.96$ (s, 1H), 8.75–8.47 (m, 6H), 8.10–8.01 (m, 2H), 7.90–7.85 (m, 2H), 7.37 (t, 1H, J = 5.5 Hz), 4.19–4.08 (m, 2H), 1.97–1.93 (m, 1H), 1.43–1.26 (m, 8H), 0.96–0.87 ppm (m, 6H); HRMS (ESI): m/z calcd for [C₃₂H₃₀N₃O₂]⁺: 488.2338; found: 488. 2326.

Complexes Ir-1, Ir-2, and Ir-3 were synthesized according to a modified literature procedure.^[19]

Ir-1: 2-phenylpyridine (46.5 mg, 0.3 mmol), [[Ir(ppy)₂Cl]₂] (64.3 mg, 0.06 mmol), and silver triflate (30.7 mg, 0.12 mmol) were dissolved in 2-ethoxyethanol (10 mL) and heated at 100 °C in an oil bath under an argon atmosphere overnight. The deep-yellow solution was cooled and gravity-filtered to remove the gray AgCl precipitate. The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH₂Cl₂/*n*-hexane =2:1, v/v) to afford the product as a yellow solid (66.9 mg, 85.1 %). ¹H NMR (400 MHz, CDCl₃): δ =7.96 (d, 3 H, *J*=8.0 Hz), 7.59–7.71 (m, 9 H), 6.76–6.97 ppm (m, 12 H); HRMS (MALDI): *m*/*z* calcd for [C₃₃H₂₄IrN₃]⁺: 655.1600; found: 655.1634; elemental analysis calcd (%) for [C₃₃H₂₄IrN₃+0.05 C₆H₁₄]: C 60.68, H 3.78, N 6.38; found: C 60.75, H 3.76, N 6.36.

Ir-2: Column chromatography on silica gel (CH₂Cl₂/*n*-hexane, 1:1 v/v) afforded the product as a yellow solid (95.3 mg, yield: 59.2 %). ¹H NMR (400 MHz, CDCl₃): δ =8.30 (s, 1 H), 6.88–7.87 ppm (m, 29 H); ¹³C NMR (100 MHz, CDCl₃): δ =166.82, 166.00, 160.83, 160.56, 160.33, 147.16, 147.06, 146.93, 144.40, 143.63, 140.15, 137.38, 137.18, 135.95, 133.46, 133.21, 129.92, 128.08, 126.56, 126.17, 125.15, 124.12, 123.91, 123.46, 122.16, 121.82, 120.05, 119.93, 119.17, 118.90, 118.75, 96.70 ppm; HRMS (MALDI): *m/z* calcd for [C₄₅H₃₀IrN₃+0.15 C₆H₁₄]: C 67.40, H 3.96, N 5.14; found: C 67.61, H 3.81, N 5.06.

Ir-3: Column chromatography on silica gel (CH₂Cl₂/*n*-hexane, 4:1 v/v) afforded the product as a red solid (56.9 mg, 57.7%). ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.48-8.61$ (m, 3H), 7.90 (t, 3H, J = 8.1 Hz), 7.83 (d, 1H, J = 7.6 Hz), 7.76 (t, 1H, J = 7.8 Hz), 7.52–7.71 (m, 9H), 7.20 (t, 2H, J = 8.1 Hz), 6.87–6.99 (m, 9H), 4.06–4.16 (m, 2H), 1.89–1.97 (m, 1H), 1.30–1.43 (m, 8H), 0.86–0.95 ppm (m, 6H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.89$, 165.83, 164.71, 164.42, 160.94, 160.59, 160.33, 147.49, 147.19, 145.71, 143.81, 140.64, 137.32, 136.26, 132.93, 131.88, 131.62, 130.60, 130.24, 130.09, 128.52, 128.26, 127.33, 124.26, 124.11, 123.69, 122.97, 122.78, 122.08, 121.65, 120.24, 119.58, 119.15, 119.02, 102.09, 86.85, 44.34, 38.10, 30.93, 28.87, 24.23, 23.22, 14.22, 10.80 ppm; HRMS (MALDI): m/z calcd for [C₅₅H₄₅IrN₄O₂+0.09C₆H₁₄]: C 67.11, H 4.69, N 5.64; found: C 67.05, H 4.43, N 5.42.

Ir-4: Ir-4 was synthesized according to our previously reported procedure.^[49] [{Ir(ppy)₂Cl}₂] (53.6 mg, 0.05 mmol) and L4 (60.0 mg, 0.12 mmol) were dissolved in CH2Cl2/MeOH (12 mL, 2:1, v/v). The mixture was heated at reflux for 6 h under an Ar atmosphere. The reaction mixture turned an orange color. After completion of the reaction, the mixture was cooled to RT and a 10-fold excess of ammonium hexafluorophosphate was added. The suspension was stirred for 15 min and then filtered to remove the insoluble inorganic salts. The solution was evaporated to drvness under reduced pressure to obtain a crude orange solid. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/MeOH=15:1, v/v) to afford the product as an orange solid (72.4 mg, 73.3 %). ¹H NMR (CDCl₃, 400 MHz): $\delta = 9.89$ (d, 1H, J =7.6 Hz), 9.65 (d, 1 H, J=7.9 Hz), 8.65 (d, 1 H, J=7.1 Hz), 8.53 (d, 2 H, J= 7.6 Hz), 8.42 (d, 1 H, J=8.3 Hz), 8.28 (t, 1 H, J=7.7 Hz), 8.07 (s, 1 H), 7.99-7.70 (m, 9H), 7.58 (d, 1H, J=5.3 Hz), 7.51 (d, 1H, J=5.2 Hz), 7.44 (t, 1H, J=6.4 Hz), 7.15-6.93 (m, 6H), 6.39-6.30 (m, 2H), 4.17-4.06 (m, 2H), 2.03 (d, 1H), 1.39–1.26 (m, 8H), 0.95–0.86 ppm (m, 6H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 167.89$, 164.18, 163.91, 155.73, 155.59, 155.44, 152.01, 150.15, 149.77, 148.63, 143.61, 143.43, 142.62, 140.39, 138.44, J. Zhao et al.

127.72, 127.18, 125.13, 125.01, 123.76, 123.53, 123.13, 122.89, 120.05, 119.89, 93.44, 92.89, 44.34, 37.96, 30.77, 28.73, 24.08, 23.14, 14.19, 10.70 ppm; HRMS (ESI): m/z calcd for $[C_{54}H_{45}IrN_5O_2]^+$: 988.3203; found: 988.3183; elemental analysis calcd (%) for $[C_{54}H_{45}F_6IrN_5O_2P+0.02 C_6H_{14}]$: C 57.28, H 4.02, N 6.17; found: C 57.15, H 4.11, N 6.34.

TTA upconversion: A diode pumped laser was used for the upconversions. The laser power was measured with a phototube. A mixed solution of the complex (triplet photosensitizer) and 9,10-diphenylanthracene (DPA, triplet acceptor) was degassed for at least 15 min with N2 or Ar before the measurements were taken. The absorption of DPA at 445 nm was very weak, thus the triplet acceptor could not be excited with 445 nm laser irradiation (only the sensitizers, that is, the IrII complexes, were selectively excited). The upconversion quantum yields were determined with $[Ru(dmb)_3][PF_6]_2$ ($\Phi_p = 0.073$ in MeCN) and 2-iodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoro-4-bora-3a-azonia-4a-aza-s-indacene ($\Phi_{\rm F}$ = 3.6% in aerated MeCN) as the standards.^[53] It was important to keep the concentration of [Ru(dmb)₃][PF₆]₂ low, otherwise the upconversion quantum yield would be overestimated (self-quenching was observed for [Ru- $(dmb)_3][PF_6]_2$ in highly concentrated solutions, such as at 2.0×10^{-5} M). The quantum yields were calculated by using Equation (1), where Φ_{unk} , A_{unk} , I_{unk} , and η_{unk} represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the samples, respectively.^[79a] The photography of the upconversion were taken with a Samsung NV 5 digital camera.

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

Nanosecond time-resolved transient difference absorption spectroscopy: Nanosecond time-resolved transient difference absorption spectra were recorded on a LP 920 laser flash photolysis spectrometer (Edinburgh Instruments, Livingston, UK). The samples were purged with N_2 or Ar for 30 min before any measurements were taken. The samples were excited with a 355 nm laser and the transient signals were recorded on a Tektronix TDS 3012B oscilloscope.

TDDFT computational methods: Geometry optimizations were calculated by using the B3LYP functional with the 6-31G(d)/LanL2DZ basis set. The vertical excitation energy was calculated with the TDDFT method based on the singlet ground-state geometry. The spin-density of the triplet excited state was calculated with their energy-minimized triplet geometries.^[89] The solvents were used in the calculations (CPCM model). All calculations were performed with the Gaussian 09W software (Gaussian, Inc.).

Acknowledgement

We thank the NSFC (20972024 and 21073028), the Fundamental Research Funds for the Central Universities (DUT10ZD212), the Royal Society (UK), the NSFC (China) (China-UK Cost-Share Program, 21011130154), the Ministry of Education (SRFDP-200801410004 and NCET-08–0077), the Education Department of Liaoning Province (2009T015), the State Key Laboratory of Fine Chemicals (KF0802), and the Dalian University of Technology for financial support.

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Received: January 20, 2012 Published online: May 21, 2012

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