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Green light-excitable naphthalenediimide acetylide-containing cyclometalated Ir(III) complex with long-lived triplet excited states as triplet photosensitizers for triplet–triplet annihilation upconversion†

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Naphthalenediimide (NDI) was connected to the ligand of a cyclometalated Ir(III) complex (**Ir-1**) *via* a C≡C triple bond to enhance the absorption in the visible region and to access long-lived triplet excited states. Ir(ppy)$_2$(bpy)[PF$_6$] (**Ir-2**, ppy = 2-phenylpyridine and bpy = 2,2′-bipyridine) was used as a model complex. The photophysical properties of the complexes were studied with steady state and time-resolved spectroscopy. **Ir-1** shows strong absorption in the visible region (ε = 11 000 M^{-1} cm^{-1} at 542 nm) and in comparison **Ir-2** shows typically weak absorption in the visible region (ε < 3000 M^{-1} cm^{-1} above 400 nm). Room temperature near IR emission at 732 nm (Φ_P = 0.1%) was observed for **Ir-1**, which is attributed to the NDI localized emissive triplet excited state, by transient absorption spectra and DFT calculations on the spin density surface. The lifetime of the NDI-localized triplet excited state is up to 130.0 μs, which is rarely reported for Ir(III) complexes. In comparison, **Ir-2** shows phosphorescence at 578 nm and the triplet state lifetime is a typical value of 0.3 μs. The complexes were used as triplet photosensitizers for triplet–triplet annihilation (TTA) upconversion and an upconversion quantum yield of 6.7% was observed with **Ir-1**. No upconversion was observed with **Ir-2** as the triplet photosensitizer at the same experimental conditions.

Introduction

Transition metal complexes, such as cyclometalated Ir(III) complexes,[1–9] have attracted much attention due to their applications in organic light-emitting diodes (OLED) and luminescence,[10] photocatalysis (*e.g.* H$_2$ production from water),[11–13] luminescent bioimaging,[14,15] molecular probes[16,17] and more recently triplet–triplet annihilation (TTA) upconversion.[18–23] However, conventional Ir(III) complexes show weak absorption of visible light and short triplet excited state lifetimes (a few μs).[2,3] These features are disadvantages for the application of Ir(III) complexes.

Concerning these aspects, transition metal complexes with rylene ligands have attracted much attention due to their unique photophysical properties, such as the strong absorption of visible light and long-lived triplet excited states, compared to analogues which are without rylene moieties.[22,24,25] For example, Pt(II) complexes with rylene acetylide ligands were reported to show long-lived triplet excited states.[24,26–28] Castellano *et al*. reported perylenebisimide (PBI) acetylide Pt(II) complexes which show strong absorption of visible light but interestingly, the lifetime of the triplet state is very short (0.246 μs).[29] A Re(I) complex was reported to show exceptionally long-lived triplet excited states (651 μs).[24b] Recently, we reported naphthalenediimide (NDI)- and coumarin-containing Pt(II) complexes,[28,30] naphthalimide (NI) Pt(II) and Ir(III) complexes,[27,31] which show long-lived triplet excited states.[32] However, the absorption of the Ir(III) complexes we prepared is limited to the blue region (<500 nm). Recently, diketopyrrolopyrrole (DPP)-containing Ir(III) complexes were reported to show absorption in the 500–600 nm range. The triplet excited state lifetime is 3 μs.[33] Therefore, much room is left for the preparation of Ir(III) complexes that show strong absorption of visible light and long-lived triplet excited states because these photophysical features are crucial for the application of Ir(III) complexes, such as in photocatalysis and photo upconversion.[11–13,32]

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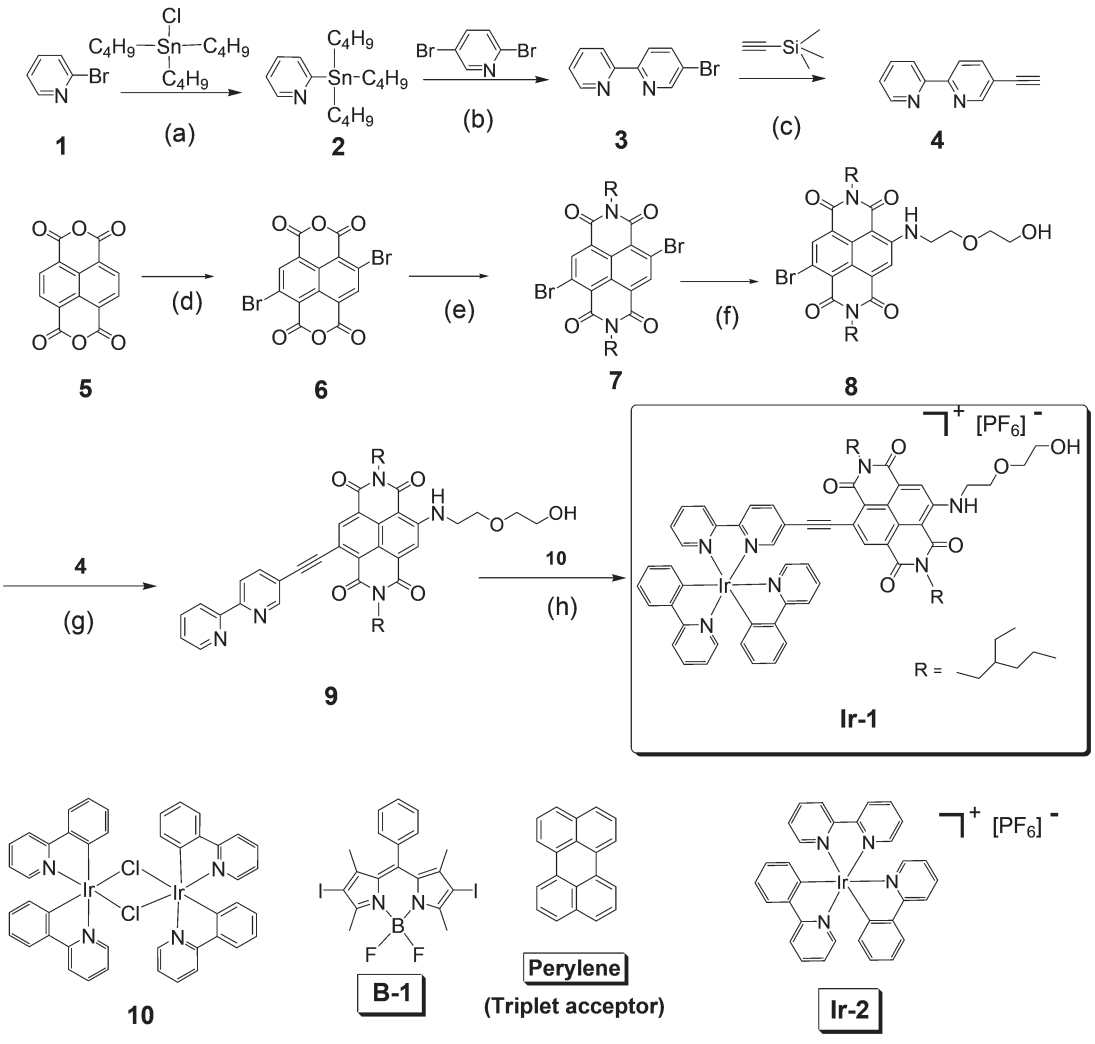
Naphthalenediimide (NDI) is a versatile chromophore for which the photophysical properties, such as the absorption wavelength, can be readily tuned by molecular structural modifications.[34–39] NDI has been widely used in fluorescence studies[35–39] but to the best of our knowledge, the application of NDI in phosphorescence or triplet excited states is rare.[40–42] The T_1 state energy level of NDI is high (*ca.* 2.0 eV) and thus it is suitable for use as a triplet photosensitizer (triplet energy donor) to initiate photophysical processes, such as TTA upconversion.[40] Previously, we studied the photophysical properties of bromo-substitued NDIs as well as the application of the compounds as triplet photosensitizers for TTA upconversion.[40] We used NDI for the preparation of a Pt(II) complex, which shows a moderate triplet excited state lifetime (22.3 μs).[28] NDI was also used for the preparation of a Ru(II) complex.[42*b*] However, to the best of our knowledge, NDI has never been used for the preparation of cyclometalated Ir(III) complexes.

Herein, for the first time, the NDI moiety was used for the preparation of cyclometalated Ir(III) complexes. Following the concept of maximizing the heavy atom effect by direct metalation of a chromophore,[28,30–32,43–46] the π-conjugated core of NDI is linked to the Ir(III) centre *via* C≡C triple bonds (**Ir-1**, Scheme 1). We did not use C=C double bonds because the triplet excited states may be quenched by the possible *cis*/*trans* isomerization of the C=C double bonds.[47] Strong absorption of visible light (ε = 11 000 M^{-1} cm^{-1} at 542 nm) and a long-lived triplet excited state (τ = 130.0 μs) were observed for **Ir-1**. These values are in stark contrast to conventional cyclometalated Ir(III) complexes,[1,2,48] such as **Ir-2** (Scheme 1), which show weak absorption of visible light and short-lived triplet excited states (τ = 0.3 μs). The complexes were used as triplet photosensitizers for TTA upconversion. We demonstrated that the triplet excited state of **Ir-1** is efficiently populated and that the performance of **Ir-1** is much better than **Ir-2**. Our results are useful for the design of new Ir(III) complexes that show



Scheme 1 Preparation of the Ir(III) complex **Ir-1**. The molecular structure of the model complex Ir(ppy)$_2$(bpy) (**Ir-2**) is also presented. Both complexes are cationic and the counter ion is $[PF_6]^-$. Reagents and conditions: (a) *n*-BuLi, DEE, −80 °C, 6 h; (b) Pd(PPh_3)$_4$, xylene, refluxed for 24 h; (c) Pd(PPh_3)$_2$$Cl_2$, PPh_3, CuI, Et_3N, refluxed for 8 h; (d) DBI, oleum (20% SO_3), 40 °C, 5 h; (e) 2-ethylhexylamine, 120 °C, under N_2, 2 h; (f) diglycolamine (DGA), 2-methoxyethanol, 120 °C, 8 h; (g) Pd(PPh_3)$_4$, CuI, Et_3N, reflux, 8 h; (h) CH_3CH_2OH–CH_2Cl_2 (v/v = 1 : 2), refluxed for 6 h.

strong absorption of visible light and long-lived triplet excited states. These complexes can be used for photocatalysis and TTA upconversion.

Experimental

Materials and reagents

All the chemicals were analytically pure and used as received. 2-Bromopyridine was purchased from Aladdin Co. The cyclometalated Ir^{III} chloro-bridged dimers[$\{Ir(ppy)_2Cl\}_2$],[49] **6**,[40] **7** and **8** were synthesized according to literature procedures (for characterization data, see the ESI†). Compounds **2** and **3** were synthesized according to a literature method.[50] 1,4,5,8-Naphthalenetetracarboxylic dianhydride (compound **5**) is a product of Aladdin Co. (China).

Analytical measurements

NMR spectra were recorded on a Bruker 400 MHz spectrometer ($CDCl_3$ as the solvent, TMS as the standard, δ = 0.00 ppm). High resolution mass spectra (HRMS) were determined on a MALDI micro MX. Luminescence spectra and the TTA upconversion were measured on a RF-5301PC spectrofluorometer (Shimadzu, Japan) or an adapted CRT970 spectrofluorometer. The nanosecond time-resolved transient difference absorption spectra were measured with a laser flash photolysis spectrometer (LP 920, Edinburgh Instruments, UK) and recorded on a Tektronix TDS 3012B oscilloscope. The lifetime values (by monitoring the decay trace of the transients) were obtained with the LP920 software. Luminescence quantum yields of the complexes were measured with **B-1** as the standard (Φ_F = 2.7% in CH_3CN). The emission spectra at 77 K were measured with an Oxford Optistat DN^{TM} cryostat (with liquid nitrogen filling) and a FLS920 spectrofluorometer (Edinburgh Instruments Ltd, UK).

Synthesis of 4

Under an argon atmosphere, compound **3** (300.0 mg, 1.283 mmol), $Pd(PPh_3)_2Cl_2$ (9.1 mg, 0.013 mmol), PPh_3 (6.8 mg, 0.026 mmol) and CuI (5.2 mg, 0.026 mmol) were dissolved in triethylamine (15 mL). After stirring, trimethylsilylacetylene (125.5 mg, 1.280 mmol) was added *via* a syringe. The mixture was then heated at 88 °C for 8 h. The solvent was removed under reduced pressure, water was added and the mixture was extracted with dichloromethane (4 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After the removal of the solvent, the crude product was purified with column chromatography (silica gel, CH_2Cl_2–hexane = 5 : 1, v/v) and a colourless liquid was obtained. Tetrabutylammonium fluoride (3.2 mL, 1 mol L^{-1}) was added to a solution of the above trimethylsilane protected intermediate (200 mg, 0.800 mmol) in THF (25 mL) and the solution was stirred at room temperature under argon for 3 h. CH_2Cl_2 (100 mL) and water (50 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous $MgSO_4$, filtered and then the solvent was removed. The residue was purified by passing it through a silica plug using CH_2Cl_2–hexane = 5 : 1 as the eluent to give a white solid (180.0 mg, yield: 78.3%). ^1H NMR (400 MHz, $CDCl_3$): 8.71 (d, 2H), 8.45 (t, 3H), 7.90 (t, 3H), 7.39 (s, 1H), 3.31 (s, 1H). MS-TOF EI$^+$: calcd ($C_{12}H_8N_2$) m/z = 180.0687, found m/z = 180.0689.

Synthesis of 9

Under an argon atmosphere, compounds **8** (50.0 mg, 0.074 mmol) and **4** (26.7 mg, 0.149 mmol) were dissolved in triethylamine (15 mL). Then $Pd(PPh_3)_4$ (8.6 mg, 0.0075 mmol) and CuI (5 mg, 0.026 mmol) were added. The mixture was refluxed for 8 h. The reaction mixture was cooled to room temperature (RT) and the solvent was removed under reduced pressure. Water was added and the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. After the removal of the solvent, the crude product was purified with column chromatography (silica gel, CH_2Cl_2–CH_3OH = 25 : 1 as eluent, v/v) to give a red solid **9** (30.0 mg, 52.6%). ^1H NMR (400 MHz, $CDCl_3$): 10.45 (s, 1H), 8.98 (s, 1H), 8.71 (d, 2H), 8.39 (d, 3H), 8.12 (s, 1H), 7.86 (s, 1H), 7.35 (s, 1H), 4.13 (d, 4H), 3.70 (t, 8H), 1.92–1.98 (m, 2H), 1.25–1.37 (m, 16H), 0.89–0.94 (m, 12H), MS-TOF LD$^+$: calcd ($[C_{40}H_{36}B_2F_4N_4]^+$), m/z = 772.4074, found, m/z = 772.4061.

Synthesis of Ir-1

A solution of compound **9** (30.0 mg, 0.039 mmol) and **10** (58.7 mg, 0.055 mmol) in CH_3OH–CH_2Cl_2 (15 mL, 1 : 2, v/v) was heated under reflux. After 6 h, the red solution was cooled to RT and then a 10-fold excess of ammonium hexafluorophosphate was added. The suspension was stirred for 1 h and then filtered to remove the insoluble inorganic salts. The solution was evaporated to dryness under reduced pressure to obtain a crude red solid. The crude product was purified by column chromatography (silica gel, CH_2Cl_2–CH_3OH = 30 : 1, v/v) and a red solid was obtained (35.0 mg, 45.5%). ^1H NMR (400 MHz, $CDCl_3$): 10.51 (s, 1H), 8.78 (s, 2H), 8.64 (s, 1H), 8.37 (s, 2H), 8.10 (d, 2H); 7.77–7.79 (m, 4H), 7.94 (s, 4H), 7.45–7.80 (m, 8H), 6.93 (d, 6H), 4.06–4.09 (s, 4H), 3.69 (t, 8H), 3.55 (s, 1H), 1.90 (s, 1H), 1.26–1.34 (m, 16H), 0.88 (s 12H), MS-TOF LD$^+$: calcd ($[C_{69}H_{56}N_8O_6S_2Ir\text{-}PF_6]^+$) m/z = 1272.4939, found m/z = 1272.5001.

Computational methods

The geometry optimizations were calculated using the B3LYP functional with the GENECP basis set with density functional theory (DFT). The excitation energy was calculated using the time-dependent DFT (TDDFT) method based on the optimized singlet ground state geometry. The spin density surfaces of the complexes were calculated with the energy minimized triplet state geometries. All the calculations were performed using Gaussian 09W (Gaussian, Inc.).[51]

TTA upconversions

A diode pumped solid state laser was used as the excitation source for the TTA upconversions. The samples were purged with N_2 or Ar for 15 min before the measurement. The upconversion quantum yields were determined with the fluorescence of **B-1** as the quantum yield standard (Φ = 0.027 in CH_3CN) and the quantum yields were calculated using eqn (1),

$$\Phi_{\mathrm{UC}} = 2\Phi\mathrm{std}\left(\frac{1-10^{-\mathrm{O.D.}}{}_{\mathrm{std}}}{1-10^{-\mathrm{O.D.}}{}_{\mathrm{sam}}}\right)\left(\frac{I_{\mathrm{sam}}}{I_{\mathrm{std}}}\right)\left(\frac{\eta_{\mathrm{sam}}}{\eta_{\mathrm{std}}}\right)^2 \tag{1}$$

where Φ_{UC}, $1\text{–}10^{-\mathrm{O.D.}}$, I_{sam} and η_{sam} represent the upconversion quantum yield, the absorbance correction factor, the integrated photoluminescence intensity and the refractive index of the solvents, respectively (sam means samples). The photographs of the upconversion were taken with a Samsung NV 5 digital camera. The exposure times are the default values of the camera.

Delayed fluorescence of the TTA upconverted emission

The delayed fluorescence of the TTA upconversion was measured with a nanosecond pulsed laser (Opolette™ 355II+UV nanosecond pulsed laser, typical pulse length: 7 ns; pulse repetition: 20 Hz; peak OPO energy: 4 mJ; the wavelength is tunable in the range of 210–355 nm and 410–2200 nm. OPOTEK, USA), which was synchronized to a FLS 920 spectrofluorometer (Edinburgh Instruments, UK). The decay kinetics of the upconverted fluorescence (delayed fluorescence) was monitored with a FLS 920 spectrofluorometer (synchronized to the OPO nanosecond pulse laser). The prompt fluorescence lifetime of the triplet acceptor DPA was measured with an EPL picosecond pulsed laser (405 nm) which was synchronized to the FLS 920 spectrofluorometer.

Time-resolved emission spectra

The nanosecond and the microsecond time-resolved emission spectra of the triplet photosensitizers alone and the TTA upconversion were recorded with a OPO nanosecond pulsed laser. The pulsed laser was synchronized to the FLS 920 spectrofluorometer (Edinburgh Instruments, UK).

Results and discussion

Design and synthesis of the complexes

The design of the complexes is based on a few rationalizations. First, the π-conjugated framework of NDI is linked to the coordination centre of the Ir(III) complexes *via* C≡C triple bonds to ensure an efficient heavy atom effect and thus ISC, otherwise the strong absorption of visible light will not result in efficient funneling of the energy to the triplet excited states.[52] Second, NDI alone gives a very weak absorption.[38,40] On introducing an amine substituent to the NDI core, the absorption in the visible range will be enhanced. Third, an ether chain was introduced to improve the solubility of the complex **Ir-1** (Scheme 1). A Sonogashira coupling reaction was used to connect the NDI to the bpy ligand. All the compounds were obtained in moderate to satisfactory yields.

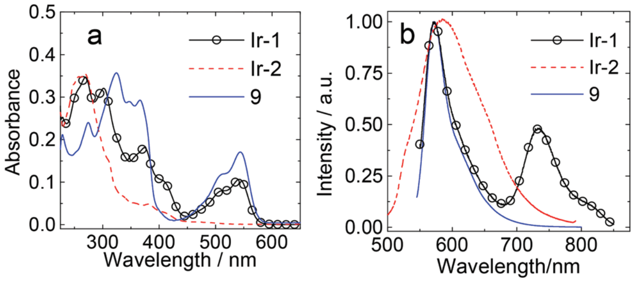


Fig. 1 The UV-Vis absorption and emission spectra of **Ir-1**, ligand **9** and **Ir-2**. (a) UV-Vis absorption. (b) Normalized emission spectra (with excitation at λ_{ex} = 542 nm, 542 nm, 400 nm respectively), 1.0×10^{-5} M, 20 °C.

UV-vis absorption and photoluminescence spectra of the complexes

The UV-Vis absorption of the complexes was studied with CH_2Cl_2 as the solvent (Fig. 1a). **Ir-2** shows the typical absorption of the normal Ir(III) complexes, *i.e.* a very weak absorption in the visible region.[53] The absorption maxima is at 269 nm (35 000 M^{-1} cm^{-1}). However, with the ethynyl NDI ligand, **Ir-1** shows a strong absorption at 542 nm (11 000 M^{-1} cm^{-1}). This absorption band can be attributed to the NDI ligand, which shows a similar absorption at 544 nm (Fig. 1a). Furthermore, we noticed a difference between the UV-Vis absorption of **Ir-1** and the NDI-conjugated bpy ligand (compound **9**, the free ligand) and therefore, we propose an electronic interaction between the NDI moiety and the Ir(III) coordination center.

To the best of our knowledge, this is the first time that the NDI moiety has been used to prepare cyclometalated Ir(III) complexes. Previously, we used the NI moiety to prepare Ir(III) complexes, but those complexes gave absorption in a much shorter wavelength range.[31,54] Furthermore, cyclometalated Ir(III) complexes showing strong absorption of visible light are rarely reported.[2,32] Previously, a bodipy-tethered Ir(III) complex was reported but a different, non-π-conjugated linker between the light-harvesting ligand and the coordination ligand was used.[55] We prepared Ir(III) complexes with a coumarin-containing ligand but these complexes show absorption in the relatively blue-shifted spectral region.[32]

The photoluminescence of the complexes was recorded (Fig. 1b). The model complex **Ir-2** shows the typical structureless emission band of the Ir(III) complexes at 578 nm (Φ_{P} = 4.3%). For **Ir-1**, two emission bands at 572 nm and 732 nm were observed. The luminescence lifetimes of **Ir-1** at 572 nm and 732 nm were determined as 5.0 ns and 220.3 μs, respectively (Table 1). The phosphorescence quantum yield of **Ir-1** (0.1%, Table 1) is much lower than **Ir-2**. Room temperature near IR emission has rarely been reported for Ir(III) complexes. Bodipy is a versatile chromophore and has been used for the preparation of Ir(III) complexes but no RT near IR emission was observed.[55] Recently, a DPP conjugated Ir(III) complex was

Table 1 Photophysical parameters of the Ir(III) complexes

	λ_{abs} [a] (nm)	ε [b]	λ_{em} [a] (nm)	τ_L [c]	Φ (%)	λ_{em} [e] (77 K)
Ir-1	542	1.11	572	5.0 ns[f]		574
			732	220.3 μs[g]	0.1[d]	724
Ir-2	269	3.47	578	0.3 μs	4.3[d]	585
9	544	1.71	578	9.8 ns[h]	76.2[i]	621

[a] In CH_2Cl_2 solution (1.0×10^{-5} mol L^{-1}). [b] Molar absorption coefficient at the absorption maxima. ε: 10^4 M^{-1} cm^{-1}. [c] Luminescence lifetime. $c = 1.0 \times 10^{-5}$ M in CH_2Cl_2 at RT. [d] Quantum yield of phosphorescence in CH_2Cl_2, **B-1** as the standard ($\Phi = 0.027$ in CH_3CN). [e] Luminescence maxima at 77 K, $c = 1.0 \times 10^{-5}$ M, EtOH–MeOH, (4 : 1, v/v). [f] Luminescence lifetime of 572 nm in nanoseconds. [g] Luminescence lifetime of 732 nm in microseconds. [h] Fluorescence lifetime with the decay monitored at 578 nm. [i] Quantum yield of the fluorescence with bodipy as the standard ($\Phi = 0.72$ in THF).

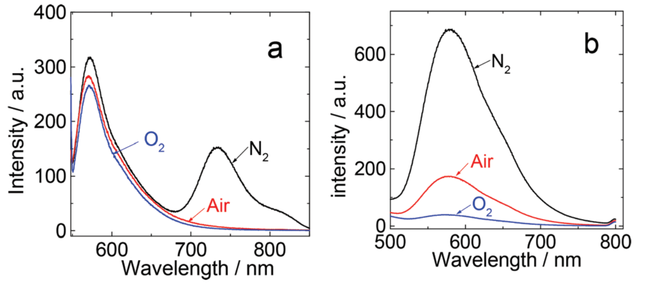


Fig. 2 Emission spectra of (a) **Ir-1** (λ_{ex} = 542 nm) and (b) **Ir-2** (λ_{ex} = 400 nm); $c = 1.0 \times 10^{-5}$ M in CH_2Cl_2, 20 °C.

reported, which shows absorption in the 500–600 nm region but near IR emission was only observed at low temperature (77 K).[33] Previously, we used NDI for a *N^N* Pt(II) bis(acetylides) complex, which shows emission at 784 nm.[28]

In order to investigate the singlet/triplet feature of the emission bands of the complexes, the emission sensitivity to oxygen (O_2) was studied (Fig. 2). For **Ir-2**, the emission can be quenched to a large extent in an aerated solution compared to that in a deaerated solution (Fig. 2b). Thus, the emission of **Ir-2** can be attributed to the triplet emission, *i.e.* phosphorescence. For **Ir-1**, the emission band at 732 nm is more sensitive to the presence of O_2 than that of **Ir-2**. For example, the emission was completely quenched in an aerated solution. The emission band at 732 nm shows structural features. Interestingly, the emission at 572 nm is not sensitive to O_2. Therefore, we concluded that the emission at 572 nm is fluorescence and the emission band at 732 nm can be assigned to phosphorescence. With the increased bulkiness of the ligand, transition metal complexes can demonstrate the residual fluorescence of the ligands.[33,56,57] Since the emission wavelength is significantly longer than the normal cyclometalated Ir(III) complexes, we therefore propose that the emission at 732 nm is due to the NDI-localized ^{3}IL state.[32,33,43] It should be noted that RT ligand-centered ^{3}IL emission has rarely been reported for cyclometalated Ir(III) complexes. For example, with bodipy, coumarin and DPP-containing ligands, no ligand-localized ^{3}IL emission has been observed at RT.[33,55]

In order to rule out any impurities responsible for the observation of the fluorescence band of **Ir-1**, the photoluminescence of **Ir-1** and ligand **9** at 77 K were compared to that at RT (Fig. S16 in the ESI†). For ligand **9**, the emission at 77 K (623 nm) is red-shifted compared to that at RT (583 nm). For **Ir-1**, however, the same emission maxima were observed for the solutions at 77 K (599 nm) and RT (597 nm) (in EtOH–MeOH, 4 : 1, v/v, Fig. S16 in the ESI†). Therefore, we propose that the fluorescence band of **Ir-1** is not due to any impurities, at least not due to the free ligand. This conclusion is supported by the different luminescence lifetimes of **Ir-1** and **9** at 540 nm (Table 1). The excitation spectra with the two emission maxima at 572 nm and 732 nm were measured (Fig. S18 in the ESI†). The two spectra are similar to each other, indicating that both emission bands at 572 nm and 732 nm originate from one species, that is, the emission band at 572 nm is not due to any impurities.

Nanosecond time-resolved transient difference absorption spectroscopy

In order to study the triplet excited state of the complexes, the nanosecond time-resolved transient difference absorption of the complexes was investigated (Fig. 3).[33] For **Ir-2**, no significant bleaching bands were observed in the visible region upon pulsed laser excitation (Fig. 3c), which is in agreement with the weak absorption of **Ir-2** in the visible region. The bleaching band at 620 nm is due to the phosphorescence of **Ir-2**. Positive transient absorption bands at 380 nm and 760 nm were observed. The lifetime of the transient was determined as 0.3 μs, which was further quenched to 67.7 ns in an aerated solution. Therefore, the triple feature of the transient species is verified.

Similarly, the transient absorption of **Ir-1** was studied (Fig. 3a). Upon pulsed laser excitation, bleaching bands at

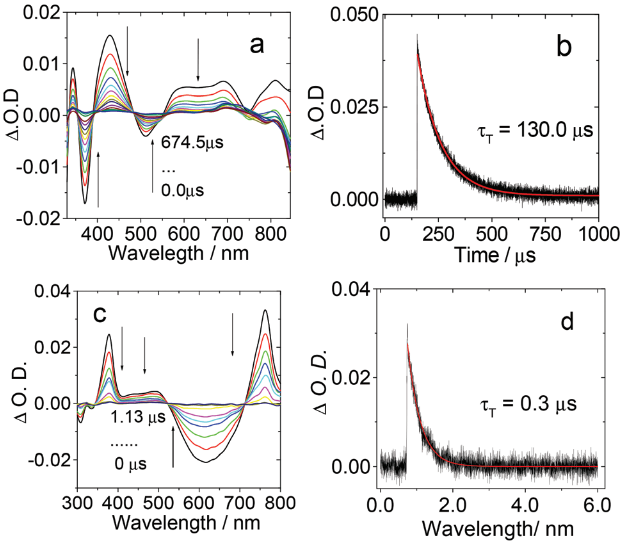


Fig. 3 Nanosecond time-resolved transient difference absorption spectra of (a) **Ir-1**. (b) Decay trace at 542 nm. (c) **Ir-2**. (d) Decay trace at 310 nm in deaerated CH_2Cl_2 after pulsed laser excitation (λ_{ex} = 355 nm), 2.0×10^{-5} M, 20 °C.

370 nm and 510 nm were observed. The minor bleaching band at 510 nm compared to that at 370 nm is in agreement with the fact that the steady-state molar absorption coefficient at 510 nm is much smaller than that at 370 nm. Positive transient absorptions in the 300–500 nm region and 600–700 nm region were found. Note that the bleaching and the positive absorption bands may be distorted by each other due to the overlap of the bleaching and the positive transient absorption bands. This situation may be responsible for the weak bleaching band at 542 nm and the lack of a bleaching band at 750 nm (due to the phosphorescence of **Ir-1**).

The triplet excited state lifetime of **Ir-1** was determined as 130.0 μs. Such a long-lived triplet excited state has rarely been reported for cyclometalated Ir(III) complexes.[2,33,54,55,58a,59,60] We prepared coumarin-containing Ir(III) complexes which show a triplet state lifetime of 75.5 μs.[59] With a bodipy-containing ligand, the triplet excited state lifetime is 25 μs.[55] With DPP-π-conjugated *N^N* Ir(III) complexes, the lifetime of the triplet excited state was determined as 3 μs.[33] With the ethynyl NI ligand, the lifetime of the triplet excited state of the cyclometalated Ir(III) complex was determined as 16.45 μs.[31] We also used NDI for the preparation of a *N^N* Pt(II) bis(acetylides) complex, which shows a much shorter T_1 state lifetime of 22.3 μs.[28] The photophysical properties of the complexes are listed in Table 1.

Spin density surfaces: assignment of the excited states

The triplet state of the complexes was studied from a point of view of theoretical calculations on the spin density surface of the complexes (Fig. 4).[32,43,58a,59,61] For **Ir-2**, the spin density surface was distributed on the bpy and ppy ligand as well as the Ir(III) metal center. This spin density distribution is in agreement with the known assignment of the triplet excited state of cylcometalated Ir(III) complexes as a MLCT/IL state.[59] For **Ir-1**, the spin density is mainly distributed on the NDI ligand, the Ir(III) center and the bpy ligands made no contribution to the spin density surface, which is in agreement with the long-lived IL triplet excited state of **Ir-1**. Therefore, the spin density surface analysis of the complexes confirmed that the T_1 triplet state of **Ir-1** is a ^{3}IL state, whereas the T_1 state of **Ir-2** is a ^{3}MLCT/^{3}IL state.

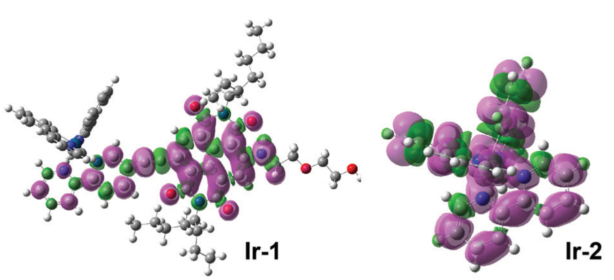


Fig. 4 Isosurfaces of the spin density of **Ir-1** and **Ir-2** at the optimized triplet state geometries (isovalue = 0.0004). CH_2Cl_2 was used as the solvent in the calculations. The calculations were performed at the B3LYP/6-31G(d)/LanL2DZ level with Gaussian 09W.

Triplet–triplet annihilation upconversion

TTA upconversion has attracted much attention due to the advantages of the requirement of low excitation power, strong absorption of photoexcitation energy, high quantum yields and readily changeable excitation and emission wavelengths.[18–23,62–69] TTA upconversion has been used for photocatalytic H_2 production,[70] solar cells,[71–73] luminescent bioimaging[74] and luminescent O_2 sensing.[75] The triplet photosensitizers are crucial for the TTA upconversion.[22] However, to date the triplet photosensitizers are limited to on-the-shelf compounds (which have been known for a long time) and few tailor-designed triplet photosensitizers have been used for TTA upconversion.[22,23] We developed a series of visible light-absorbing complexes that show a long-lived triplet excited state for TTA upconversion,[22] such as Pt(II) complexes,[28,30,44–46,76–78] Ir(III) complexes,[31,54,59,69] Ru(II) complexes,[52,61,79,80] and Re(I) complexes.[80] However, the Ir(III) complexes used for TTA upconversion are limited to those which show absorption in the blue range (<500 nm).[31,54,59,60] Therefore, much room is left for the preparation of Ir(III) complexes that show absorption in longer wavelength regions for TTA upconversion.

Ir-1 shows strong absorption of visible light and a long-lived triplet excited state, which is suitable for use as a triplet photosensitizer for TTA upconversion (Fig. 5). Upon 532 nm laser excitation, **Ir-1** gives a weak emission (Fig. 5a). In the presence of the triplet acceptor perylene, intensive blue emission in the 450–500 nm region was observed (Fig. 5b). The emission band is superimposable with the steady state fluorescence emission spectrum of perylene (Fig. S17 in the ESI†). Furthermore, excitation of **Ir-1** or perylene alone did not produce this emission band and therefore, the upconverted emission was proved.[22] For **Ir-2**, however, no TTA upconversion was observed due to the failure to excite **Ir-2** at 532 nm (the absorption of **Ir-2** in the visible region is very weak). To the best of our knowledge, this is the first time that a green light-excitable cyclometalated Ir(III) complex was used as a triplet photosensitizer for TTA upconversion. Previously, Ir(III) complexes used for TTA upconversion have only be excited at shorter wavelengths. For example, $Ir(ppy)_3$ was used as a

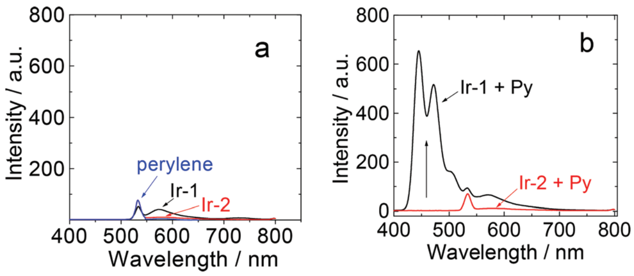


Fig. 5 Upconversions with **Ir-1** and **Ir-2** as the triplet photosensitizers. (a) Emission of the triplet photosensitizers or perylene (Py) alone, (b) emission of the sensitizers in the presence of perylene. Excited with a 532 nm laser (5.6 mW). c [**Ir-1** or **Ir-2**] = 1.0 × 10^{-5} M; c [perylene] = 1.3 × 10^{-5} M in deaerated CH_2Cl_2, 20 °C.

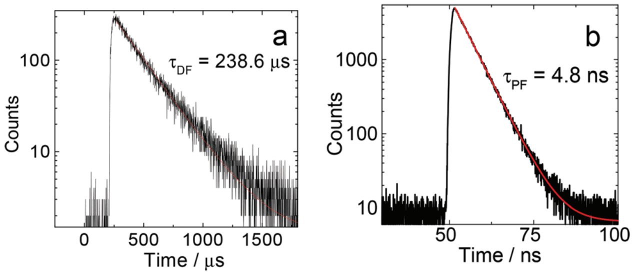


Fig. 6 (a) Delayed fluorescence observed in the TTA upconversion with **Ir-1** as the triplet photosensitizer and perylene as the triplet acceptor. DF stands for delayed fluorescence. Excited at 532 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and the decay trace was monitored at 470 nm. Under these circumstances, **Ir-1** was selectively excited and the emission is due to the upconverted emission of perylene. (b) Prompt fluorescence of perylene excited with an EPL picosecond laser (445 nm). PF stands for prompt fluorescence. In deaerated CH_2Cl_2. *c* [sensitizers] = 1.0 × 10^{-5} M; *c* [perylene] = 1.3 × 10^{-5} M; 20 °C.

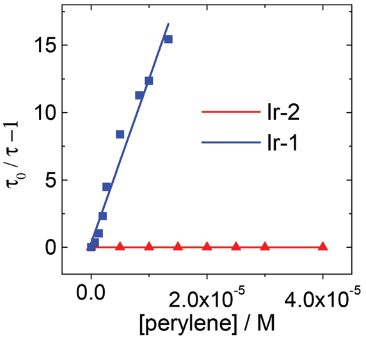


Fig. 7 Stern–Volmer plots generated from the triplet excited state lifetime (τ_T) quenching of compounds **Ir-1** (λ_{ex} = 532 nm) and **Ir-2** (λ_{ex} = 355 nm) measured as a function of perylene concentration. Measured with the nanosecond time-resolved transient absorption. *c* [sensitizers] = 2.0 × 10^{-5} M in deaerated CH_2Cl_2. 20 °C.

photosensitizer for upconversion but the excitation was at 445 nm.[81] Previously, we used coumarin-containing Ir(III) complexes for TTA upconversion with excitation in the blue range (445 nm or 473 nm).[31,54,59,60]

In order to prove the TTA upconversion, the luminescence lifetime of the upconversion was measured (Fig. 6a). It is known that the luminescence lifetime of the TTA upconverted emission is exceptionally long.[19,44,45,80,82] A lifetime of 238.6 μs was observed for the blue emission band of the **Ir-1**/perylene mixture. For the perylene alone, however, an emission lifetime of 4.8 ns was observed (Fig. 6b). Therefore, the TTA upconversion feature of the blue emission of the **Ir-1**/perylene mixture was unambiguously proved. The long-lived upconverted luminescence may be useful for time-resolved luminescent bioimaging or oxygen sensing.[74,75]

In order to reveal the effect of the triplet state lifetime on the TTA upconversion, the triplet–triplet-energy-transfer (TTET) efficiency was studied by a quenching experiment (Fig. 7), *i.e.* the quenching of the triplet excited state of the complexes by the triplet acceptor perylene was monitored by the variation of the triplet state lifetime of the Ir(III) complexes **Ir-1** and **Ir-2**. Much larger Stern–Volmer constants (1.0 × 10^6 M^{-1}) were observed for **Ir-1** than for **Ir-2**. Therefore, the TTET process of the **Ir-1**/perylene is much more efficient than that of **Ir-2**/perylene. This result indicates that the lifetime of the triplet excited state of triplet photosensitizers is important for their application. The photophysical parameters related to the TTA upconversion process are listed in Table 2. From Table 2, it is clear that the Stern–Volmer constants and the quenching constants of **Ir-1** are much larger than that of **Ir-2**. The enhanced TTET of **Ir-1** is due to its long-lived triplet excited state (130.0 μs). In comparison, **Ir-2** gives a much shorter triplet state lifetime (0. 3 μs).

The TTA upconversion is clearly visible to un-aided eyes (Fig. 8). For **Ir-1** alone, the emission is yellow. In the presence of the triplet acceptor perylene, intensive blue emission is observed (Fig. 8b). For **Ir-2**, however, no such emission

Table 2 Triplet excited state lifetimes (τ_T), Stern–Volmer constants (K_{SV}) and quenching constants (k_q) of the sensitizers. In a deaerated CH_2Cl_2 solution, 20 °C

	τ_T [a]/μs	K_{sv} [b]	k_q [c]	Φ_{UC} [d]/%	η [e]	τ_{DF} [f]/μs
Ir-1	130.0	1000	7692.3	6.7	7.4	238.6
Ir-2	0.3	0.001	3.3	0.0	0	—

[a] Triplet state lifetime. Determined with nanosecond time-resolved transient absorption spectroscopy. [b] Stern–Volmer constants. In 10^3 M^{-1}. [c] Bimolecular quenching constants. $k_q = K_{sv}/\tau_T$. In 10^6 M^{-1} s^{-1}. [d] Upconversion quantum yield. [e] $\eta = \varepsilon \times \Phi_{UC}$. In 10^2 M^{-1} cm^{-1}. [f] Lifetime of the delayed fluorescence (upconverted fluorescence).

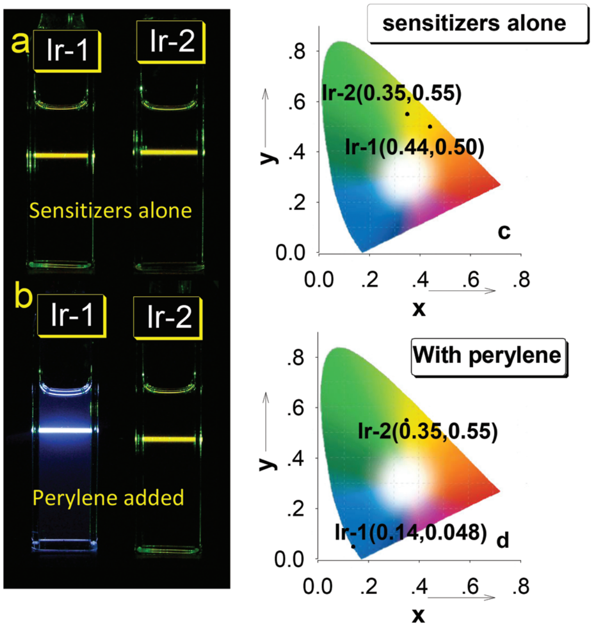


Fig. 8 (a) Photographs of the emission of the sensitizers alone and (b) the upconversion. (c) CIE diagram of the emission of the sensitizers alone and (d) in the presence of perylene (upconversion). *c* [**Ir-1** or **Ir-2**] = 1.0 × 10^{-5} M; *c* [perylene] = 1.3 × 10^{-5} M in deaerated CH_2Cl_2, λ_{ex} = 532 nm (5.6 mW); 20 °C.

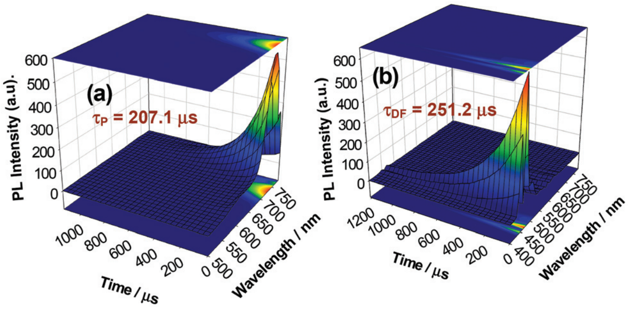
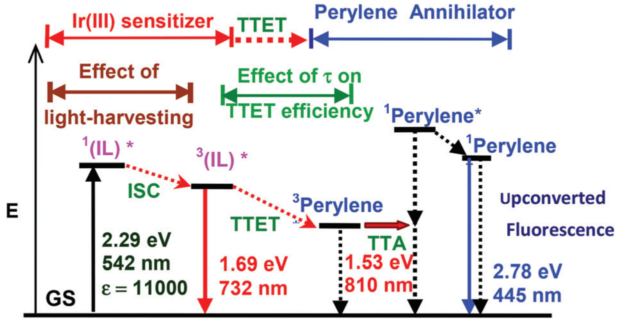


Fig. 9 Time-resolved emission spectra (TRES) of **Ir-1** alone and the TTA upconversion with perylene as the triplet acceptor. (a) The phosphorescence region was measured (500 nm–780 nm, τ_P = 207.1 μs), excited with a nanosecond pulsed laser (532 nm). (b) Upconverted emission in the range of 400 nm–800 nm (τ_{DF} = 252.1 μs) with nanosecond pulsed laser (532 nm) excitation. *c* [photosensitizers] = 1.0×10^{-5} M, *c* [perylene] = 1.3×10^{-5} M. In deaerated CH_2Cl_2; 20 °C.

color is observed, which is in agreement with the spectral results of the TTA upconversion (Fig. 6). The change in the emission color of the triplet photosensitizers with and without the triplet acceptor perylene were quantified with the CIE coordinates. For **Ir-1**, the CIE coordinates changed from (0.44, 0.50) to (0.14, 0.048). For **Ir-2**, no significant change was observed.

The upconversion was also studied with time-resolved emission spectra (TRES, Fig. 9). For complex **Ir-1** alone, a long-lived phosphorescence emission band was observed at 730 nm (τ_P = 207.1 μs). The lifetime is close to that obtained in the lifetime measurement (220.3 μs. Table 1). It should be pointed out that the short-lived fluorescence emission band of **Ir-1** cannot be recorded in the microsecond resolved TRES (the lifetime of the fluorescence band of **Ir-1** is 5.0 ns, Table 1). In the presence of the triplet acceptor perylene (Fig. 9b), the phosphorescence at 732 nm was diminished. However, strong emission in the blue region (460 nm) was observed. The lifetime of this long-lived emission band is 252.1 μs (Fig. 9b), which is very close to that obtained with different measuring modes (Fig. 6a, 238.6 μs). These results unambiguously confirmed the TTA upconversion of **Ir-1** in the presence of the triplet acceptor DPA as well as the kinetic feature of the emissions.

The photophysical processes involved in the TTA upconversion are presented in Scheme 2.[18] Upon visible light photoexcitation, first the ^{1}IL state of **Ir-1** was populated. Then direct ISC produces the NDI-localized ^{3}IL excited state. It should be pointed out that ^{1}IL→^{1}MLCT energy transfer is impossible due to the unmatched energy levels. The long-lived ^{3}IL excited state ensures efficient TTET process from **Ir-1** to perylene, the triplet energy acceptor in the TTA upconversion. Annihilation of the perylene triplet excited states produces the singlet excited state and the delayed fluorescence was observed. A notable feature of the present Ir(III) complex for TTA upconversion is the strong absorption of visible light (542 nm) and the exceptionally long-lived triplet excited states, these features are rarely reported for cyclometalated Ir(III) complexes.



Scheme 2 Jablonski diagram of the triplet–triplet-annihilation (TTA) upconversion with **Ir-1** as the triplet photosensitizer. GS stands for ground state (S_0); E is energy; ^{1}IL* is the intraligand singlet excited state (NDI localized); ISC is intersystem crossing; ^{3}IL* is the intraligand triplet excited state (NDI localized); TTET is triplet–triplet energy transfer; ^{3}Perylene* is the triplet excited state of perylene; TTA is triplet–triplet annihilation; ^{1}Perylene* is the singlet excited state of perylene. The emission bands observed in the TTA upconversion experiment is the delayed upconverted emission.

Conclusions

Naphthalenediimide (NDI) was connected to the coordination center of cyclometalated Ir(III) complexes *via* a π-conjugated linker (C≡C triple bonds. **Ir-1**). Strong absorption of visible light (542 nm, *ε* = 11 000 M^{-1} cm^{-1}) was observed for **Ir-1** compared to the model complex $Ir(ppy)_2(bpy)$ (**Ir-2**), which shows typical weak absorption of visible light. Room temperature near IR emission was observed for **Ir-1** (732 nm) compared to the normal emission at 578 nm for **Ir-2**. Furthermore, with nanosecond time-resolved transient absorption spectroscopy and DFT calculations on the spin density surfaces of the complex, we confirmed the long-lived triplet excited state (130.0 μs) of **Ir-1** is due to the NDI-localized intraligand triplet excited state (^{3}IL state). In comparison, the model complex shows a typical short lifetime of 0.3 μs. The complexes were used for triplet–triplet annihilation upconversion and an upconversion quantum yield of 6.7% was observed for **Ir-1** but no upconversion was observed with **Ir-2** under the same experimental conditions. Our method of preparing Ir(III) complexes shows that visible light-absorption and a long-lived triplet excited state will be useful for the development of Ir(III) complexes and for their applications in photocatalysis and upconversion.

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