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Rhenium(I) tricarbonyl polypyridine complexes showing strong absorption of visible light and long-lived triplet excited states as a triplet photosensitizer for triplet–triplet annihilation upconversion[†]

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The preparation of rhenium(1) tricarbonyl polypyridine complexes that show a strong absorption of visible light and long-lived triplet excited state and the application of these complexes as triplet photosensitizers for triplet–triplet annihilation (TTA) based upconversion are reported. Imidazole-fused phenanthroline was used as the *N*^N coordination ligand, on which different aryl groups were attached (Phenyl, **Re-0**; Coumarin, **Re-1** and naphthyl, **Re-2**). **Re-1** shows strong absorption of visible light ($\varepsilon = 60\ 800\ M^{-1}\ cm^{-1}$ at 473 nm). Both **Re-1** and **Re-2** show long-lived T₁ states (lifetime, τ_{T} is up to 86.0 µs and 64.0 µs, respectively). These properties are in contrast to the weak absorption of visible light and short-lived triplet excited states of the normal rhenium(1) tricarbonyl polypyridine complexes, such as **Re-0** ($\varepsilon = 5100\ M^{-1}\ cm^{-1}$ at 439 nm, $\tau_{T} = 2.2\ \mu$ s). The photophysical properties of the complexes were fully studied with steady state and time-resolved absorption and emission spectroscopes, as well as DFT calculations. The intra-ligand triplet excited state is proposed to be responsible for the exceptionally long-lived T₁ states of **Re-1** and **Re-2**. The Re(1) complexes were used as triplet photosensitizers for TTA based upconversion and an upconversion quantum yield up to 17.0% was observed.

Introduction

Rhenium(I) tricarbonyl polypyridine complexes have attracted much attention due to their tunable photophysical properties and applications in luminescent biological molecular probes, photovoltaics and photocatalysis, etc.¹⁻⁶ For example, rhenium(1) tricarbonyl polypyridine complexes have been used for luminescent bio-labeling, DNA probes and luminescent materials.^{3,5,7–9} However, similar to the conventional Pt(II) and Ir(III) complexes,^{11,12} the rhenium(I) tricarbonyl polypyridine complexes show weak absorption in the visible range, which is a disadvantage for the application of these rhenium(1) complexes as luminescent molecular probes.^{1,3,5,8,9} Visible light-harvesting rhenium(I) tricarbonyl complexes with dipyrrinato or porphyrin ligands have been prepared,¹³ but none of these complexes have been used to sensitize a photophysical process.¹³ Previously Re(I) complexes were used for the photosensitizing of singlet oxygen $({}^{1}O_{2})$, but the complex showed weak absorption in the visible range.¹⁰ Furthermore, the phosphorescent Re(1) complexes usually show short luminescence times of a few

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microseconds $(\tau, \mu s)$. It is clear that much room is left for the development of new rhenium(1) tricarbonyl complexes that show a *visible light-harvesting* effect and *long-lived triplet excited states*.

On the other hand, a recent application of transition metal complexes as triplet photosensitizers for triplet–triplet annihilation (TTA) upconversion have attracted much attention.^{14–19} However, *no* rhenium(1) tricarbonyl polypyridine complexes have been used as triplet photosensitizers in TTA upconversion.^{15–17} Concerning this aspect, the rhenium(1) tricarbonyl polypyridine complexes are of particular interest because these complexes give intense phosphorescence emission, indicating that the non-radiative decay is inhibited and efficient intersystem crossing (ISC) occurs, which are beneficial for the triplettriplet-energy-transfer (TTET), a crucial step for TTA upconversions and other photophysical processes.^{15–17}

In order to prepare rhenium(1) tricarbonyl complexes that show strong absorption of visible light, and to utilize these complexes in a practical photophysical process, herein we used a coumarin-containing imidazole $N^{\Lambda}N$ ligand for the preparation of new rhenium(1) tricarbonyl complexes (**Re-1**, **Re-0** and **Re-2** as control compounds, Scheme 1). Previously a similar ligand was used for the preparation of visible light-harvesting Ru(11) and Ir(111) complexes,^{20,21} but these ligands have not been used for the preparation of Re(1) complexes. **Re-2** shows strong absorption in visible range. All the complexes are phosphorescent at room temperature (RT). **Re-1** and **Re-2** show long-lived triplet excited state ($\tau_{\rm T}$ are 86.0 µs and 64.0 µs, *vs.* the normal

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 $[\]dagger$ Electronic supplementary information (ESI) available: The synthesis and the structure characterization data of the Re(1) complexes, the details of TTA upconversion and DFT calculation information. See DOI: 10.1039/c2dt30804e



Scheme 1 Synthesis of Re-0, Re-1 and Re-2. (a) NaIO₄, RuCl₃·3H₂O; (b) POCl₃, DMF, 0-5 °C; (c) CH₃COOH, Ar, NH₄OAc, reflux, 12 h; (d) toluene, reflux, 1 h.

lifetime of the triplet states of Re(1) complex of a few μ s).¹ The complexes were used as triplet photosensitizers for TTA upconversions.

Experimental

Materials and reagents

All the chemicals were analytically pure and were used as received. Solvents were dried and distilled for synthesis. Re(CO)₅Cl was purchased from Sigma-Aldrich.

Analytical measurements

NMR spectra were recorded on a 400 MHz Varian Unity Inova NMR spectrophotometer. Mass spectra were recorded with Q-TOF Micro MS spectrometer. UV-Vis absorption spectra were measured with a HP8453 UV-vis spectrophotometer. Fluorescence spectra were recorded on Shimadzu 5301 PC spectrofluorometer. Upconversion was carried out on a customized Sanco 970 CRT spectrofluorometer. Phosphorescence quantum yields were measured with [Ru(dmb)₃(PF₆)₂] as the standard (Φ = 7.3% in acetonitrile, dmb = 4,4'-dimethyl-2,2'-bipyridine). Luminescence lifetimes were measured on a OB920 luminescence lifetime spectrometer (Edinburgh Instruments, UK) and FLS920 spectrofluorometer (Edinburgh Instruments, UK).

Synthesis of L-1

7-Diethylamino-2-oxo-2H-chromene-3-carboxyldehyde (128 mg, 0.68 mmol), 1,10-phenanthroline-5,6-dione (104 mg, 0.5 mmol), and ammonium acetate (805 mg, 11.3 mmol) were dissolved in glacial acetic acid (13 mL). The mixture was heated and refluxed for 6 h under Ar atmosphere. The color of the mixture turned to orange. After completion of the reaction, the mixture was cooled to room temperature, and concentrated NH₃·H₂O was added until the pH of the mixture was brought to about 7.0 to give a yellow precipitate. The precipitate was filtered, washed with water, and then dried under vacuum overnight. The crude product was further purified by column chromatography (silica gel, CH_2Cl_2 -methanol = 10:1, v/v). Yield: 167 mg, 77%. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.16$ (d, J = 4.2 Hz, 2H), 8.99 (s, 1H), 8.78 (d, J = 5.8 Hz, 2H), 7.72–7.69 (m, 2H), 7.48 (d, J = 8.0 Hz, 1H), 6.66–6.63 (m, 1H), 6.50 (d, J = 2.3 Hz, 1H), 3.48–3.43 (m, 4H), 1.26 (t, J = 7.0 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 162.1$, 156.4, 151.7, 148.3, 146.9, 144.4, 141.5, 130.1, 129.4, 122.9, 110.0, 108.7, 107.7, 96.8, 45.1, 12.5 ppm. ESI-HRMS: calcd ($[C_{26}H_{22}N_5O_2 + H]^+$): m/z =436.1774, found, *m*/*z* = 436.1767.

Synthesis of L-0

The synthetic procedure is similar to that of L-1, except that benzaldehyde (72 mg, 0.68 mmol) was used. The crude product was purified by column chromatography (silica gel, CH₂Cl₂-methanol = 8:1, v/v). Yield: 105 mg, 71%. ¹H NMR (400 MHz, methanol-d₄): δ = 8.74 (d, 1H, *J* = 3.9 Hz), 8.59–8.32 (m, 1H), 7.98 (d, 1H, *J* = 7.8 Hz), 7.48–7.41 (m, 3H), 4.87 (m, 5H) ppm. ¹³C NMR (100 MHz, methanol-d₄): δ = 151.42, 147.42, 143.14, 129.77, 129.63, 128.81, 126.47, 123.10 ppm. ESI-HRMS: calcd ([C₁₉H₁₂N₄ + H]⁺): *m/z* = 297.1140, found, *m/z* = 297.1135.

Synthesis of L-2

The synthetic procedure is similar to that of **L-1** except that 1-naphthaldehyde (63.7 mg, 0.6 mmol) was used. The crude product was purified with column chromatography (silica gel, dichloromethane-methanol = 8 : 1, v/v), and a pink solid was obtained. Yield: 128.5 mg, 74.3%. ¹H NMR (400 MHz, methanol-d₄): δ = 9.02 (d, 2H, *J* = 4.0 Hz), 8.87 (m, 1H), 8.79 (m, 1H), 8.59 (d, 1H, *J* = 8.1 Hz), 8.08 (d, 1H, *J* = 8.2 Hz), 8.00–7.95 (m, 2H), 7.78–7.75 (m, 2H), 7.67–7.56 (m, 3H) ppm. ESI-HRMS: calcd ([C₂₃H₁₅N₄ + H]⁺): *m*/*z* = 347.1297, found, *m*/*z* = 347.2496.

Synthesis of Re-0

Re(CO)₅Cl (25 mg, 0.07 mmol) and **L-0** (21 mg, 0.07 mmol) were dissolved in dry toluene and heated to 110 °C, and stirred under Ar for 1 h. The solvent was then removed under reduced pressure, and the product was obtained as a yellow solid by column chromatography (silica gel, CH₂Cl₂). Yield: 39 mg, 93%. M.p. > 250 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 9.39 (d, 2H, *J* = 4.6 Hz); 9.29 (d, 2H, *J* = 8.4 Hz); 8.32 (m, 6H); 8.14–8.22 (m, 2H); 7.64–7.68 (m, 2H); 7.57–7.60 (m, 1H) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ = 203.5, 197.8, 152.6, 151.4, 143.7, 136.3, 132.9, 130.4, 129.7, 129.3, 126.8, 126.5, 125.6 ppm. ESI-HRMS: calcd ([C₂₂H₁₂N₄O₃ClRe + Na]⁺): *m/z* = 625.0053, found, *m/z* = 625.0047. IR (KBr, cm⁻¹) *v*: 2025 (s), 1894 (s), 1622 (m), 1545 (w), 1514 (w), 1458 (m), 1406 (w), 1366 (w), 807 (m), 726 (m), 697 (m).

Synthesis of Re-1

The synthetic procedure was the same as that for **Re-0** except that **L-1** (31 mg, 0.07 mmol) was used. The product was obtained as a red solid by column chromatography (silica gel, CH₂Cl₂–CH₃OH = 25 : 1, v/v). Yield: 46 mg, 88%. M.p. > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.39 (d, 2H, *J* = 4.6 Hz); 9.29 (d, 2H, *J* = 8.4 Hz); 8.32 (m, 6H); 8.14–8.22 (m, 2H); 7.64–7.68 (m, 2H); 7.57–7.60 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 197.5, 189.8, 162.3, 157.2, 152.6, 151.3, 150.7, 149.5, 145.2, 143.2, 137.2, 132.3, 131.4, 131.0, 125.9, 121.1, 110.7, 108.9, 106.9, 106.8, 97.2, 45.4, 12.7 ppm. ESI-HRMS: calcd ([C₂₉H₂₁N₅O₅ClRe + Na]⁺): *m/z* = 764.0687, found, *m/z* = 764.0673. IR (KBr, cm⁻¹) *v*: 2978 (w), 2927 (w), 2871 (w), 2020 (s), 1917 (s), 1718 (m), 1619 (s), 1590 (s), 1521 (s), 1424 (m), 1358 (m), 1263 (s), 1188 (m), 1133 (m), 1078 (w), 811 (m), 775 (w).

Synthesis of Re-2

The synthetic procedure is similar to that of **Re-0** except that **L-2** (24 mg, 0.07 mmol) was used. The product was obtained as a

red solid after column chromatography (silica gel, CH₂Cl₂– CH₃OH = 25 : 1, v/v). Yield: 41 mg, 89%. M.p. > 250 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 9.41 (d, 2H, *J* = 5.0 Hz); 9.31 (d, 2H, *J* = 8.2 Hz); 9.10 (d, 1H, *J* = 8.4 Hz); 8.14–8.19 (m, 4H); 8.08 (d, 1H, *J* = 8.0 Hz); 7.62–7.77 (m, 3H) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ = 197.8, 190.1, 152.5, 151.4, 143.8, 133.6, 132.9, 130.7, 128.5, 128.3, 127.4, 126.6, 126.0, 125.3 ppm. ESI-HRMS: calcd ([C₂₆H₁₄N₄O₃ClRe + Na]⁺): *m/z* = 675.0210, found, *m/z* = 675.0216. IR (KBr, cm⁻¹) *v*: 2022 (s), 1909 (s), 1622 (w), 1541 (w), 1455 (m), 1406 (m), 1261 (m), 1093 (m), 807 (m), 726 (m).

Nanosecond time-resolved transient difference absorption spectroscopy

The nanosecond time-resolved transient absorption spectra were measured on LP 920 laser flash photolysis spectrometer (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 LP900 software. All samples in flash photolysis experiments were deaerated with argon for *ca.* 15 min before measurement and the argon gas flow was kept during the measurement.

Triplet-triplet annihilation upconversions

A diode pumped solid state (DPSS) continuous laser (473 nm) was used as the excitation source for the upconversions. The diameter of the laser spot was *ca.* 3 mm. The power of the laser beam was measured with a VLP-2000 pyroelectric laser power meter. For the upconversion experiments, the mixed solution of the compound (triplet sensitizer) and 9,10-diphenylanthracene (DPA) was degassed with N_2 or Ar for at least 15 min (note the upconversion can be significantly quenched by O_2). Then the solution was excited with laser. The upconverted fluorescence of DPA was observed with a spectrofluorometer. In order to repress the scattered laser, a black box was put behind the fluorescent cuvette to trap the laser beam.

The upconversion quantum yields ($\Phi_{\rm UC}$) were determined with the prompt fluorescence of coumarin-6 ($\Phi_{\rm F} = 78\%$ in C₂H₅OH). The upconversion quantum yields were calculated with the following equation, where $\Phi_{\rm UC}$, $A_{\rm sam}$, $I_{\rm sam}$ and $\eta_{\rm sam}$ represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the solvents (eqn (1), where the subscript "std" is for the standard used in the measurement of the quantum yield and "sam" for the samples to be measured). The equation is multiplied by a factor of 2 in order to make the maximum quantum yield be unity.¹⁵ All these data were independently measured three times (with different solutions samples).

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

The CIE coordinates (x, y) of the emission of the sensitizers alone and the emission of the upconversion were derived from the emission spectra with the software of CIE color Matching Linear Algebra.

Delayed fluorescence

The delayed fluorescence feature of the upconversion was measured with a nanosecond pulsed laser (OpolettTM 355II+ UV nanosecond pulsed laser, typical pulse length: 7 ns, pulse repetition: 20 Hz, peak OPO energy: 4 mJ, wavelength is tunable in the range of 210–355 nm and 410–2200 nm, OPOTEK, USA), which is synchronized to a FLS920 spectrofluorometer (Edinburgh, U.K.). The pulsed laser is sufficient to sensitize the TTA upconversion. The decay kinetics of the upconverted fluorescence (delayed fluorescence) was monitored with a FLS920 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 is synchronized to the FLS 920 spectrofluorometer.

DFT calculations

The density functional theory (DFT) calculations were used for optimization of both singlet states and triplet states. The energy level of the T_1 state (energy gap between S_0 state and T_1 state) were calculated with the time-dependent DFT (TDDFT), based on the optimized singlet ground state geometries (S_0 state). All the calculations were performed with Gaussian 09W.²²

Results and discussion

Design and synthesis of complexes

Imidazole fused phenanthroline was used as the N^N ligand for the preparation of the Re(1) complexes (Scheme 1). Different aryl units can be introduced on to the imidazole moieties to tune the photophysical properties of the complexes. Previously a similar strategy was used for the preparation of Ir(III) complexes and Ru(II) complexes.^{20,21} However, this method has not been used for the preparation of visible light-harvesting Re(1) complexes.¹ A coumarin unit was attached to the imidazole unit (Re-1). The intramolecular hydrogen bond will enhance the absorption. Re-2 was prepared as a control complex, in which the naphthalene unit was attached to the imidazole moiety. All the compounds were obtained in moderate to satisfying yields. The molecular structures of the compounds were fully characterized with ¹H NMR, ¹³C NMR and HR MS spectroscopy. Notably all the Re(I) complexes show the characteristic C≡O stretchings at 2020 cm^{-1} and 1900 cm^{-1} in the IR spectra.

Absorption and emission spectra

The UV-vis absorption of the complexes and the ligand were studied (Fig. 1). The model complex **Re-0** gives weak absorption in the visible range ($\varepsilon = 5100 \text{ M}^{-1} \text{ cm}^{-1}$ at 439 nm). The absorption maximum is at 288 nm ($\varepsilon = 46646 \text{ M}^{-1} \text{ cm}^{-1}$). The control compound **Re-2** also gives weak absorption in the visible range ($\varepsilon = 5300 \text{ M}^{-1} \text{ cm}^{-1}$ at 447 nm). This absorption property is typical for the normal Re(1) tricarbonyl complexes.^{1,2,5,7–9,23,24} Interestingly, **Re-1** gives strong absorption in the visible range ($\varepsilon = 60800 \text{ M}^{-1} \text{ cm}^{-1}$ at 473 nm). This strong absorption is comparable to some typical organic fluorescent dyes, such as



Fig. 1 UV-Vis absorption of Re(1) complexes and the ligand L-1. $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C.



Fig. 2 The emission spectra of Re(1) complexes under different atmosphere. (a) Re-0 ($\lambda_{ex} = 439$ nm) (b) Re-1 ($\lambda_{ex} = 472$ nm). $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C.

bodipy.^{25–27} The strong absorption of **Re-1** is similar to the Re(1) complexes with a dipyrrinato ligand.¹³ Previously a Re(1) tricarbonyl diimine complex with napthalimide appendent was prepared which showed much weaker absorption in the visible range ($\varepsilon = 11\ 980\ M^{-1}\ cm^{-1}$ at 408 nm).²⁸

Ligand L-1 gives weak absorption in the visible range ($\varepsilon = 23344 \text{ M}^{-1} \text{ cm}^{-1}$). Thus metalation of the *N*^*N* ligand gives enhanced absorption. This red-shifted and enhanced absorption of the complex compared to the free ligand indicate that the electronic interaction of the coumarin unit with the Re(1) coordination center is strong at the ground state.

The emission of the complexes were studied (Fig. 2). All the complexes give RT phosphorescence (see ESI[†] for the results of **Re-2**). However, different emission properties were found for the complexes. For **Re-0** and **Re-2**, broad and structureless emission bands were observed, thus the emission is basically an MLCT feature.^{7,8,29} For **Re-1**, however, the emission band shows significant vibrational progression.^{9a} Furthermore, the sensitivity of the phosphorescence intensity to O₂ is different for the complexes. The phosphorescence emission intensity of **Re-1** and **Re-2** are more significantly quenched in an aerated solution than that of **Re-0**. Thus we propose that the lifetime of the triplet excited states of **Re-1** and **Re-2** are longer than that of **Re-0**. All these results indicated that the emissive triplet excited states of **Re-1** and **Re-2** are different from each other.

The luminescence lifetimes and the luminescence quantum yields of the complexes were studied and the data are listed in Table 1. The model complex **Re-0** gives intense phosphorescence emission ($\Phi_P = 23.4\%$) and a short luminescence

Table 1	Photophysical	parameters	of Re-0 ,	Re-1	and 1	Re-2
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	$\lambda_{ m abs}{}^a$	$e^{a}_{ m s} = \varepsilon^{b}$			$ au_{ ext{P}}^{e}(\mu ext{s})$		$ au_{\mathrm{T}}^{f}(\mu \mathrm{s})$	
			$\lambda_{ m em}{}^c$	${\pmb{\varPhi}_{ extsf{L}}}^d$	77 K	298 K	Air	N_2
Re-0	439	0.51	554	23.4%	5.14 µs	0.1 µs	0.14	2.2
Re-1	473	6.08	605	0.03%	63.1 ms	70.4 μs	0.43	86.0
Re-2	447	0.53	552	3.3%	1.4 ms	80.1 µs	0.34	64.0

^{*a*} In toluene, $c = 1.0 \times 10^{-5}$ M. ^{*b*} Molar extinction coefficient at the absorption maxima. ε : $10^4/M^{-1}$ cm⁻¹. ^{*c*} In toluene. ^{*d*} Luminescence quantum yield. In toluene, with [Ru(dmb)₃(PF₆)₂] ($\boldsymbol{\Phi} = 0.073$ in acetonitrile) as the standards. ^{*e*} Luminescence lifetime, at RT (20 °C) and 77 K (in C₂H₅OH–CH₃OH = 4 : 1). ^{*f*} Triplet state lifetime, measured by time-resolved transient absorption. $c = 1.0 \times 10^{-5}$ M in aerated and de-aerated toluene.

lifetime ($\tau_{\rm P} = 0.1 \ \mu$ s). For the Re(1) complexes with the coumarin- or naphthalene-containing ligands, the phosphorescence quantum yields are much lower, but the phosphorescence lifetimes are much longer than that of **Re-0**. For example, phosphorescence lifetimes up to 70.4 μ s and 80.1 μ s were observed for **Re-1** and **Re-2**, respectively. The phosphorescence lifetimes of **Re-1** and **Re-2** are much longer than the normal phosphorescent Re(1) complexes.^{1,4,8,9,29} **Re-1** shows very long-lived phosphorescence at 77 K (63.1 ms, Table 1), which is an indication of a ³IL state. Previously a Re(1) tricarbonyl complex with an exceptionally long-lived triplet excited state was reported ($\tau = 651 \ \mu$ s).²⁸ The long lifetime of that complex is due to the intramolecular "ping-pong" energy transfer, or ³MLCT/³IL excited state equilibrium. For **Re-1**, however, it is due to the low-lying ³IL excited state.

Re-1 and **Re-2** show much lower phosphorescence quantum yields than **Re-0** (Table 1). However, the low phosphorescence quantum yields do not necessarily mean the triplet excited state was inefficiently populated, or the non-radiative decay of the triplet excited state is significant.¹³ Rather, it is possible that the triplet excited state of the complexes was efficiently populated. We will demonstrate the efficient production of the triplet excited states by the TTA upconversion experiments (see later section).^{16c}

77 K emission spectra

In order to study the emissive triplet excited states of the complexes, the emission spectra at 77 K were studied (Fig. 3). The emission of **Re-0** is blue-shifted compared to that at RT by 1756 cm⁻¹ (thermally induced Stokes shifts, ΔE_S). The emission band of **Re-0** are broad at both RT and 77 K. Thus the emissive triplet excited state of **Re-0** is mainly metal-to-ligand-chargetransfer (³MLCT) in character.⁷ For **Re-2**, a similar large ΔE_S was observed (2816 cm⁻¹). The emission at 77 K is blue-shifted compared to that at RT. Furthermore, the emission band at 77 K is more structured compared to that at RT.

A different emission profile was observed for **Re-1** at 77 K (Fig. 3b). The emission at 77 K shows no substantial blue-shift compared to RT. Both the emission at RT and 77 K are highly structured, which is different from the normal phosphorescent Re(1) complexes that show the MLCT emission.⁷ Based on these results, the emissive triplet excited state of **Re-1** can be assigned mainly as intraligand (³IL state).³⁰ Previously a ligand-localized triplet excited state was observed for an anthracene-containing



Fig. 3 Photoluminescence spectra of the complexes at RT and 77 K. (a) **Re-0** ($\lambda_{ex} = 440$ nm), (b) **Re-1** ($\lambda_{ex} = 470$ nm), (c) **Re-2** ($\lambda_{ex} = 430$ nm). $c = 1.0 \times 10^{-5}$ M in C₂H₅OH–CH₃OH (4 : 1, v/v).

Re(1) complex.^{3*a*} Both the fluorescence of the anthracene and the ³MLCT emission of the Re(1) coordination center were quenched. Intramolecular Föster energy transfer from the anthracene to Re(1) coordination center is responsible for the quenching of the anthracene fluorescence, whereas the Dexter triplet excited state energy transfer from the Re(1) coordination center to anthracene is responsible for the quenching of the ³MLCT emission.^{3*a*}

Nanosecond time-resolved transient difference absorption spectroscopy

In order to study the triplet excited states, the nanosecond timeresolved transient difference absorption spectra of the complexes were studied (Fig. 4). Upon pulsed laser excitation at 355 nm, significant bleaching at 470 nm was observed for **Re-1** (Fig. 4a), which is assigned to the depletion of the ground state of the ligand. At the same time, positive transient absorption bands in the range 300 nm–400 nm and 500 nm–750 nm were observed.

The lifetime of the transient was determined as $86.0 \ \mu$ s. This long-lived transient species is assigned to a triplet excited state of **Re-1** because the lifetime is significantly reduced in an



Fig. 4 Nanosecond time-resolved transient absorption difference spectra of (a) Re-1 and (c) Re-2 after pulsed excitation ($\lambda_{ex} = 355$ nm). Decay traces of (b) Re-1 at 470 nm and (d) Re-2 at 580 nm. In deaerated toluene, $c = 1.0 \times 10^{-5}$ M. 20 °C.

aerated solution to 0.43 µs. The time-resolved transient absorption of **Re-2** was also studied (Fig. 4c). A significant positive absorption band in the range 500 nm–700 nm was observed, which is different from **Re-1**. The lifetime of the transient of **Re-2** was determined as 64.0 µs. These long-lived transients of **Re-1** and **Re-2** are drastically different from that of **Re-0** ($\tau_T = 2.2 \mu_s$, ESI†). Thus the aryl groups on the imidazole moiety impart substantial influence on the triplet excited states of **Re-1** and **Re-2**. We propose the long-lived T₁ excited state of **Re-1** is due to the ligand-localized ³IL excited state. Previously an anthracene-containing Re(1) complex showed a long-lived triplet excited state (42 µs), which is localized on the anthracene, due to the energy transfer from the Re(1) coordination center to the anthracene ligand.^{6c} However, that complex shows the typical weak absorption in the visible range.^{6c}

DFT calculations on the complexes: spin density surfaces and electronic transitions

In order to study the triplet state of the complexes from a theoretical perspective, the spin density surfaces of the complexes were calculated (Fig. 5). For the model complex **Re-0**, the spin density is distributed on the Re(1) atom, the CO ligand and the phen unit of the imidazole moiety, which is in agreement with the MLCT feature of the triplet excited state of **Re-0**. For **Re-1**, however, the spin density is distributed on the coumarin ligand, and the Re(1) made no contribution to the spin density, thus the T₁ excited state of **Re-1** can be assigned as ³IL state, which is in full agreement with the transient absorption spectroscopy studies (Fig. 4).³¹ **Re-2** gives a similar spin density to that of **Re-0**.

The electronic transitions of the complexes were calculated on DFT and TDDFT calculations (ESI[†]). The Re(1) coordination center of **Re-1** takes a octahydro geometry. The C–Re–C angle is 92.1°, which is close to the single crystal structures of the Re(1) carbonyl complexes.



Fig. 5 Spin density of the complexes **Re-0**, **Re-1** and **Re-2**. Calculated based on the optimized triplet state by DFT at the B3LYP/6-31G/LanL2DZ level using Gaussian 09W.

The electronic transitions of the **Re-1** was calculated based on the optimized ground state geometry, *i.e.* the UV-vis absorption spectra. The absorption of **Re-1** in the visible range is due to the transitions of $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_4$, the related transitions are characterized as intraligand $H \rightarrow L$, and $H \rightarrow L + 1$. These calculation results are in good agreement with the experimental results (ESI[†]).

The triplet excited states of **Re-1** were studied with the TDDFT method (approximated with the optimized ground state geometry). The energy level of the T_1 excited state was calculated as 597 nm (ESI[†]), which is close to the experimental results of the RT phosphorescence at 605 nm (Fig. 2). The major electronic transition of the T_1 state is $H \rightarrow L + 1$, which is localized on the coumarin ligand. Thus the T_1 state can be identified as the coumarin-imidazole localized ³IL excited state,^{20,30,32} which is in full agreement with the result observed with the time-resolved transient absorption spectra (Fig. 4a).

Similar DFT/TDDFT calculations were carried out for **Re-0** and **Re-2** (ESI[†]). Generally the calculations support the experimental observations.

Triplet-triplet annihilation upconversion

TTA upconversion has attracted much attention, due to its potential applications in photovoltaics and photocatalysis.^{15–18,33–36} Transition metal complexes, such as Pt(II)/Pd(II) porphyrin complexes, or the complexes with visible light-harvesting cyclometalated Ir(III), Pt(II) and Ru(II) complexes have been used as the triplet photosensitizers.¹⁶ However, much room is left to explore other transition metal complexes as triplet photosensitizers for TTA upconversion. For example, to the best of our knowledge, no Re(I) tricarbonyl complexes have been used as triplet photosensitizers for TTA upconversion.¹⁶ Herein the Re(I) complexes were used as triplet photosensitizers for TTA upconversion and significant TTA upconversion was observed.

Firstly the emission of complexes upon 473 nm laser excitation were studied (Fig. 6a). **Re-0** and **Re-2** gave similar emission, whereas **Re-1** shows red-shifted emission. A bench mark Ru(II) complex, $Ru(dmb)_3^{2+}$ (dmb = 4,4'-dimethyl-2,2'-



Fig. 6 Emission and upconversion with the Re(1) complexes as triplet photosensitizers. Excited with 473 nm (5 mW) laser. (a) Emission of the photosensitizers alone. (b) The upconverted DPA fluorescence and the residual phosphorescence photosensitizers [Ru(dmb)₃]²⁺, **Re-1**, **Re-2** or **Re-0** respectively. c[DPA] = 1.5 × 10⁻⁵ M; c[sensitizers] = 5.0 × 10⁻⁶ M. In de-aerated toluene. The asterisks in (a) and (b) indicate the scattered 473 nm excitation laser. 20 °C.

bipyridine) was also studied for comparison (Fig. 6a).³⁷ We noted the weak phosphorescence of **Re-1** ($\Phi_{\rm P} = 0.03\%$. Table 2). However, as we proved previously,^{16c} the weak phosphorescence do not necessarily mean an inefficient producing of the triplet state of the complexes upon photoexcitation.

Next, the emission in the presence of 9,10-diphenylanthracene (DPA, triplet acceptor) were studied (Fig. 6b). In the presence of DPA, intense blue emission in the range 400 nm–550 nm were observed with **Re-1** as the triplet photosensitizer. Irradiation of DPA or the sensitizer alone did not produce this blue emission band, thus the TTA upconversion was confirmed. For **Re-2**, much weaker upconverted emission was observed, due to its weak absorption in the visible range. For **Re-0** and **Ru-1**-([Ru(dmb)₃]²⁺), no upconversions were observed under the same experimental conditions. The upconversion quantum yields ($\Phi_{\rm UC}$) for **Re-0**, **Re-1**, **Re-2** as triplet photosensitizers were determined as 0.0%, 17.0% and 16.9%, respectively.

It should be pointed out that the upconverted fluorescence emission peak area with **Re-1** is much larger than the quenched phosphorescence band of **Re-1**. This result is in contrast to the $Pt(\pi)/Pd(\pi)$ porphyrin complex sensitizers, which give intense phosphorescence.^{14–17} Our finding with **Re-1** as the triplet photosensitizer confirms our previous postulation that the weakly phosphorescent transition metal complex, *i.e.* the dark triplet excited states, can be used for TTA upconversion.^{16c}

 Table 2
 Upconversion related photophysical properties of the Re(I) complexes

	$\tau/\mu s^a$	${{{{{\pmb \Phi}}_{ m{P}}}}^{b}}$	$K_{\rm sv}/(10^5 {\rm M}^{-1})^c$	$\Phi_{ m UC}{}^{d}$
$[\operatorname{Ru}(\operatorname{dmb})_3]^{2+}$	0.84	7.3%	0.017	_
Re-0	0.12	23.4%	0.048	_
Re-1	70.4	0.03%	2.67	17.0%
Re-2	80.1	3.3%	2.76	16.9%
^{<i>a</i>} Phosphorescenc	e lifetim	e. ^b Phosph	orescence quant quantum vields	tum yield.
coumarin-6 as the	e standard ($\Phi_{\rm F} = 78\%$ in	EtOH).	una with

We found that non-coherent excitation light with lower power density, such as the deem light of the excitation beam of a spectrofluorometer, is sufficient to impart the TTA upconversion with **Re-1** as the triplet photosensitizer (Fig. 7). Upon excitation with the spectrofluorometer, significant TTA upconversion was observed. Lower upconversion quantum yield (10.3%) than that with the laser excitation was observed. This finding is useful for the application of the upconversion in photocatalysis or photovoltaics, for which the terrestrial solar radiance can be used as the excitation source (100 mW cm⁻², AM 1.5 G).

In order to unambiguously prove that the blue emission observed in Fig. 6 and 7 are due to the TTA upconversion, the luminescence lifetimes of the upconverted fluorescence emission of DPA was measured (Fig. 8).¹⁸ For the upconversion with **Re-1** as the triplet photosensitizer, a luminescence lifetime of 225.0 µs was observed. The prompt fluorescence lifetime of DPA was determined as 5.5 ns. Therefore, the long-lived blue emission in Fig. 6b is the typical delayed fluorescence of TTA upconversion. Thus the TTA upconversion with **Re-1** as the triplet photosensitizer was unambiguously confirmed. Similar long-lived delayed fluorescence was observed with **Re-2** as the triplet photosensitizer ($\tau_{\text{DF}} = 210.4 \, \mu\text{s}$, ESI[†]).

The upconversion is significant to unaided eyes (Fig. 9). For example, in the presence of DPA, intense blue emission was observed with **Re-1** as the triplet photosensitizer. For **Re-2**, much weaker blue emission was observed. For other triplet photosensitizers, such as **Re-0** and **Ru-1**($[Ru(dmb)_3]^{2+}$), no upconversion was observed under the same experimental conditions. The different TTA upconversion efficiency of the triplet photosensitizers can be rationalized by the efficiency of the TTET process. TTET efficiency was studied by the quenching of the luminescence or the triplet state lifetime of the photosensitizers by the triplet acceptor DPA (Fig. 10).

The TTET efficiency of **Re-1** and **Re-2** are similar, due to the similar T_1 state lifetime of the complexes. **Re-0** and **Ru-1** ([Ru(dmb)₃]²⁺) gave much weaker quenching, due to their short-lived T_1 excited states. The quenching study also confirms that the light harvesting effect of the triplet photosensitizers is crucial for the TTA upconversion. For example, **Re-2** shows weak absorption in the visible range, thus its TTA upconversion is much lower than that of **Re-1**, despite the T_1 state lifetime, or the TTET efficiency, is close to that of **Re-1**.

Upconversion with **Re-1** as the triplet photosensitizer can be summarized in Scheme 2. Upon excitation, the singlet excited state of **Re-1** was produced. In turn the ³IL triplet excited state was populated due to the heavy atom effect of Re. The TTET



Fig. 7 Upconversion with excitation by the light of a Shimadzu RF5301 spectrofluorometer. Light power density: 0.5 mW cm⁻². The asterisk indicates the scattered 473 nm excitation light of the spectro-fluorometer. $c[\text{Re-1}] = 5.0 \times 10^{-6}$ M; $c[\text{DPA}] = 1.5 \times 10^{-5}$ M. In de-aerated toluene. 20 °C.



Fig. 8 (a) Delayed fluorescence observed in the TTA upconversion with **Re-1** as the triplet photosensitizer and DPA as the triplet acceptor. Excited at 473 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and the decay of the emission was monitored at 410 nm. Under this circumstance the **Re-1**, not DPA, is selectively excited and the emission is due to the upconverted emission of DPA. (b) The prompt fluorescence decay of DPA determined in a different experiment (excited with a picosecond 405 nm laser, the decay of the emission was monitored at 410 nm). In de-aerated toluene. c[Sensitizers] = 5.0×10^{-6} M; c[DPA] = 1.5×10^{-5} M; 20 °C.

between the triplet photosensitizer and triplet acceptor will produce the triplet excited state of the acceptor (DPA). TTA of DPA at the triplet excited state will give the singlet excited state of DPA. Radiative decay from the singlet excited state of DPA will give the delayed fluorescence, *i.e.* the upconverted fluorescence emission. It is clear that both the light-harvesting ability and the lifetime of the triplet excited state of a photosensitizer are crucial for the improvement of the biomolecular TTET process, a key step of TTA upconversion. Therefore, the Re(1) complexes that show strong absorption of visible light and longlived triplet state are ideal triplet photosensitizers for TTA upconversions.

Conclusions

In conclusion, rhenium(1) tricarbonyl polypyridine complexes with strong absorption of visible light ($\varepsilon = 60\ 800\ M^{-1}\ cm^{-1}$ at 473 nm) and long-lived triplet excited state (86.0 µs) were



Fig. 9 (a) Photographs of the emission of sensitizers alone and (b) the upconversion. (c) CIE diagram of the emission of sensitizers alone and (d) in the presence of DPA (upconversion). $\lambda_{ex} = 473$ nm (laser power: 5 mW). In de-aerated toluene, c[sensitizer] = 5.0×10^{-6} M, c[DPA] = 1.5×10^{-5} M, 20 °C.



Fig. 10 Stern–Volmer plots for phosphorescence or lifetime quenching. Quenching of the lifetime of the triplet photosensitizers with increasing the concentration of DPA. c[photosensitizers] = 1.0 × 10⁻⁵ M, in de-aerated toluene. 20 °C.

prepared. These properties are in stark contrast to the weak visible light absorption and short-lived triplet excited states of the conventional rhenium(I) tricarbonyl polypyridine complexes. The light-harvesting antenna in the Re(I) complex is the coumarin-integrated imidazole ligands. Intra-ligand triplet excited state (³IL) is proposed to be responsible for the exceptionally long-lived T₁ state, proved by nanosecond time-resolved transient absorption spectroscopy, spin density analysis and emission spectra at 77 K. It is for the first time that Re(I) complexes were used as triplet photosensitizers for triplet–triplet annihilation based upconversion, and an upconversion quantum yield up to 17.0% was observed. Our results may pave the way for preparation of the Re(I) tricarbonyl polypyridine complexes that show strong absorption of visible light and long-lived triplet excited states and for explorations of the application of these



Scheme 2 Jablonski diagram of TTA upconversion with **Re-1** as the triplet photosensitizer. GS stands for ground state. E is energy. GS is ground state (S_0). ¹IL* is intraligand singlet excited state. ³IL* is intraligand triplet excited state. TTET is triplet-triplet energy transfer. ³DPA* is the triplet excited state of DPA. TTA is triplet–triplet annihilation. ¹DPA* is the singlet excited state of DPA. The emission bands observed for the sensitizers is the ³MLCT/³IL emission. The emission bands observed in the TTA upconversion experiment is the delayed emission of DPA.

complexes in photocatalysis, photovoltaics, luminescent molecular probes and upconversion.

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