

Room-Temperature Long-Lived ^3IL Excited State of Rhodamine in an $N^{\wedge}N$ Pt^{II} Bis(acetylide) Complex with Intense Visible-Light Absorption

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An $N^{\wedge}N$ Pt^{II} bis(acetylide) complex was prepared with the rhodamine fluorophore [Pt–Rho, in which $N^{\wedge}N$ is dbbpy = 4,4'-bis(*tert*-butyl-2,2'-bipyridine)]. Complex Pt–Rho shows intense absorption in the visible region ($\epsilon = 185800 \text{ M}^{-1} \text{ cm}^{-1}$ at 556 nm) and a fluorescence emission of the ligand ($\lambda_{\text{em}} = 580 \text{ nm}$, $\Phi_{\text{L}} = 41.1\%$, $\tau_{\text{L}} = 2.50 \text{ ns}$). The long-lived rhodamine-localised intraligand triplet excited state (^3IL , $\tau_{\text{T}} = 83.0 \mu\text{s}$) was proposed to be populated upon excitation of the rhodamine ligand, proved by nanosecond time-resolved transient absorption and spin density analysis; the triplet excited state was studied by time-dependent DFT calculations. In com-

parison, the model complex (dbbpy) Pt^{II} bis(phenylacetylide) (Pt–Ph) shows weak absorption in the visible region ($\epsilon = 14700 \text{ M}^{-1} \text{ cm}^{-1}$ at 424 nm) and a short-lived metal-to-ligand charge-transfer excited state ($^3\text{MLCT}$) ($\tau_{\text{T}} = 1.36 \mu\text{s}$). Complex Pt–Rho was used as triplet sensitizer for upconversion based on triplet–triplet annihilation. An upconversion quantum yield of 11.2% was observed. Our strategy to access the long-lived ^3IL excited state of the organic chromophore by metallation with Pt^{II} will be useful for the preparation of transition metal complexes that show intense absorption of visible light and long-lived triplet excited states.

Introduction

The population of long-lived triplet excited states upon visible-light excitation is significant due to their potential applications in areas such as photovoltaics,^[1] photoinduced charge separation,^[2,3] photocatalysis,^[4] optical limiting^[5,6] and molecular probes.^[7] For example, it has been demonstrated that a long-lived triplet excited state can improve the oxygen-sensing properties of Ru^{II} and Pt^{II} complexes.^[8–11] Recently, we proved that upconversion based on triplet–triplet annihilation (TTA) can be significantly enhanced by sensitizers with long-lived triplet excited states.^[12–15]

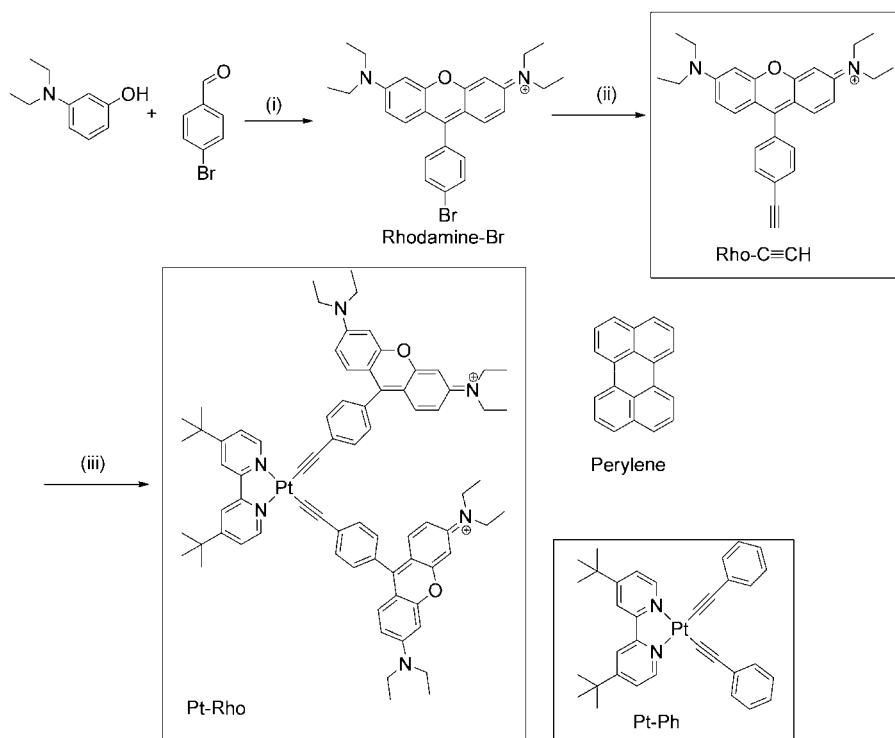
The heavy-atom effect or, more generally, spin-orbital coupling is required for population of the triplet excited state of a chromophore, through the $\text{S}_0 \rightarrow \text{S}_1 \rightarrow \text{T}_1$ process. Transition-metal complexes are representative chromophores for which the triplet excited state can be populated upon photoexcitation, such as in Ru^{II} -diimine complexes,^[16–18] Pt^{II} / Pd^{II} -porphyrin complexes^[19] and more recently the Pt^{II} / Ir^{III} complexes.^[1,20–23] Concerning this aspect, the (diimine) Pt^{II} bis(acetylide) complexes are particularly interesting due to their readily tuneable photophysical

properties; tunability can be achieved simply by changing the acetylide ligands attached to the Pt^{II} centre, which is feasible from a synthetic perspective.^[18,22]

The typical Pt^{II} acetylide complexes, such as (dbbpy) Pt^{II} bis(phenylacetylide) (Pt–Ph; dbbpy = 4,4'-bis(*tert*-butyl)-2,2'-bipyridine; Scheme 1), however, show very poor absorption in the visible region ($\lambda_{\text{max}} = 398 \text{ nm}$ with $\epsilon = 9300 \text{ M}^{-1} \text{ cm}^{-1}$), and the lifetime of the T_1 excited state is short ($\tau = 1.36 \mu\text{s}$).^[22] On the other hand, to establish an intraligand triplet excited state (^3IL) is fascinating, because the ^3IL state usually shows a prolonged lifetime compared with the $^3\text{MLCT}$ state (metal-to-ligand charge transfer).^[16,17,24,25] We noticed that some attempts have been made to prepare light-harvesting molecular arrays by attaching organic chromophores, such as benzyl, naphthyl, pyrenyl, perylene or boron-dipyrromethene (BODIPY) moieties, to $N^{\wedge}N$ (or $N^{\wedge}N^{\wedge}N$) Pt^{II} acetylide scaffolds.^[20,22,26,27] The UV/Vis absorption of these dyads is still limited to the UV/blue region; however, in some cases the photophysics of the respective components was found to collapse. For example, perylenediimide (PDI) was attached to Pt^{II} through the acetylide bond (Pt–PDI);^[28] the lifetime of its non-emissive ^3IL excited state ($\tau_{\text{T}} = 0.246 \mu\text{s}$)^[28] was found to be much shorter than that of the model complex Pt–Ph ($\tau_{\text{T}} = 1.36 \mu\text{s}$).^[22]

Previously, we have attached naphthalimide (NI), coumarin and naphthalenediimide (NDI) moieties to the Pt^{II} centre in Pt^{II} bis(acetylide) complexes, and in some cases long-lived ^3IL triplet excited state were observed.^[10,14,15,29] These complexes, however, suffer from either short absorption

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Scheme 1. Synthesis of complex Pt-Rho. (i) CH_3COOH , $p\text{-TsOH}$, chloranil 45%; (ii) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , NEt_3 , ethynyltrimethylsilane, Ar, $70\text{ }^\circ\text{C}$, then CH_2Cl_2 , methanol, K_2CO_3 , r.t., 5 h, 40%; (iii) CH_2Cl_2 , CuI , $i\text{Pr}_2\text{NH}$, r.t., 28 h. The model complex Pt-Ph and the triplet acceptor perylene are shown for comparison.

wavelengths or short T_1 lifetimes.^[15] Considering the large numbers of organic chromophores, much room is left for exploring different organic chromophores to prepare Pt^{II} bis(acetylide) complexes that show intense absorption in the visible region and to access the long-lived ^3IL triplet excited state.

Rhodamine is a versatile fluorophore that has been used extensively for fluorescent molecular probes and fluorescent bioimaging due to its intense visible-light absorption and the high fluorescence quantum yields.^[30–38] To the best of our knowledge, the studies of its triplet excited state and its application as a light-harvesting moiety in transition-metal complexes have never been reported. In our continuous attempts to access the long-lived ^3IL excited state of organic chromophores in transition-metal complexes,^[8–10,13–15,29] we herein report on the incorporation of the rhodamine chromophore into a transition-metal complex to access the rhodamine-localised long-lived ^3IL excited state (Pt-Rho, Scheme 1). Our strategy was to use the aforementioned versatile $N^N\text{Pt}^{\text{II}}$ bis(acetylide) scaffold to attach the acetylide rhodamine chromophore. Intense absorption in the visible region ($\lambda_{\text{abs}} = 556\text{ nm}$, $\epsilon = 185800\text{ M}^{-1}\text{ cm}^{-1}$ in CH_2Cl_2) and an exceptionally long-lived ^3IL excited state ($\tau_{\text{T}} = 83.0\text{ }\mu\text{s}$) were observed for the Pt-Rho complex. The fluorescence due to the rhodamine-acetylide ligand was observed for Pt-Rho (Scheme 1), which is not phosphorescent at either room temperature or 77 K . We proved, however, that the rhodamine-localised ^3IL excited state was populated upon photoexcitation with nanosecond time-resolved transient

difference absorption spectroscopy, analysis of the spin density of the complex and the electronic component of the triplet excited state (T_1) of Pt-Rho. The complex was used as a triplet sensitizer for TTA-based upconversion; an upconversion quantum yield (Φ_{UC}) of 11.2% was observed. We have proposed a new concept of using transition-metal complexes with a non-emissive triplet excited state as triplet sensitizer for TTA upconversion. The availability of triplet sensitizers will increase with this new concept.

Results and Discussion

Design of a Rhodamine-Containing Pt^{II} Complex

We employed a new strategy for the preparation of the chromophoric rhodamine. In the conventional preparation of rhodamine, harsh conditions, such as high temperature ($150\text{ }^\circ\text{C}$) and strong acid H_2SO_4 , are required, regioisomers are obtained and purification is difficult.^[39,40] In our strategy, we used the $p\text{-TsOH}$ -catalysed condensation of 4-bromobenzaldehyde and 3-(diethylamino)phenol under mild conditions ($70\text{ }^\circ\text{C}$). Importantly, chloranil was used as an oxidant in the final step of the preparation. The product was readily purified and the yield satisfactory (see the Experimental Section). The acetylide moiety ($-\text{C}\equiv\text{C}-$) was introduced onto the rhodamine moiety by using the Sonogashira cross-coupling reaction. Complex Pt-Rho was obtained in a satisfying yield (31%; Scheme 1).

Intense absorption at 556 nm ($\epsilon = 185800 \text{ M}^{-1} \text{ cm}^{-1}$) was observed for Pt-Rho, which is due to the π - π^* transition of the rhodamine core (Figure 1). Ligand Rho-C \equiv CH shows weaker absorption in the 500–600 nm region. For the model complex Pt-Ph, however, the absorption was observed at a blueshifted wavelength (400 nm). The absorption of Pt-Rho at 556 nm was not redshifted compared to that of the free ligand Rho-C \equiv CH, which is in contrast to the normal Pt^{II} bis(acetylide) complexes.^[28] This is also different from our previous Pt^{II} bis(acetylide) complexes with NI and NDI chromophores.^[10,15,29] We therefore propose that the π -conjugated core of Rho-C \equiv CH is not directly coupled to the Pt^{II} centre. Thus, interaction of the excited states is possible between the Pt^{II} coordination centre and the Rho-C \equiv CH ligand.

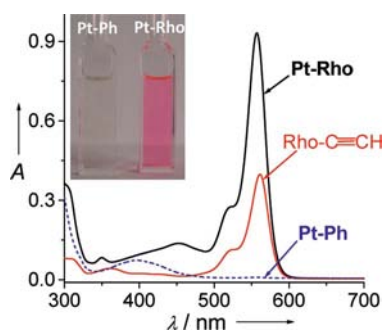


Figure 1. UV/Vis absorption spectra of the ligand Rho-C \equiv CH and the complexes Pt-Rho and Pt-Ph in CH₂Cl₂ ($5.0 \times 10^{-6} \text{ M}$; 25 °C).

Steady-State Spectroscopic Properties

Intense emission at 580 nm was observed for Pt-Rho (Figure 2) in comparison with the emission of the acetylide ligand Rho-C \equiv CH (see the Supporting Information); the emission of Pt-Rho is attributed to the fluorescence of Rho-C \equiv CH.^[41–43] This is supported by the observation of the small Stokes shift (24 nm) and the fact that the emission of Pt-Rho could not be quenched by O₂ (Figure 2b). On the contrary, the emission of Pt-Ph was quenched by O₂ (Figure 2c), and a large Stokes shift was observed (131 nm). No phosphorescence was observed for Pt-Rho (Figure 2b). Furthermore, the intrinsic phosphorescence of the Pt^{II} bis-(phenylacetylide) coordination moiety (Pt-Ph) at 555 nm was completely quenched in Pt-Rho.^[42] This is due to the

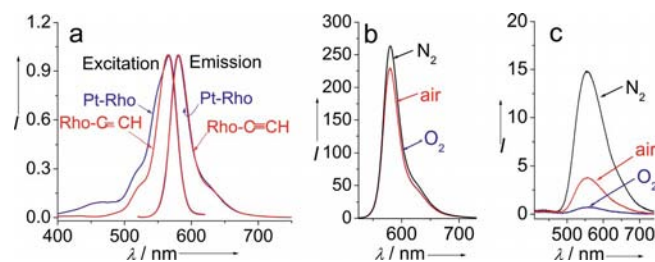


Figure 2. (a) Excitation and emission spectra of Pt-Rho and Rho-C \equiv CH. The O₂ dependency of the emission of (b) Pt-Rho and (c) Pt-Ph. The spectra were recorded in CH₂Cl₂ ($5.0 \times 10^{-6} \text{ M}$), 25 °C.

triplet energy transfer from the ³MLCT state to the rhodamine-localised ³IL state. Indeed our time-dependent DFT (TDDFT) calculations showed that the energy level of the T₁ state of the rhodamine ligand Rho-C \equiv CH is 709 nm (see the Supporting Information), which is significantly lower than the T₁ excited state of Pt-Ph (ca. 580 nm) approximated by the emission of Pt-Ph in EtOH/MeOH (4:1, v/v) at 77 K (see the Supporting Information). The emission profiles of Pt-Rho at 77 K and room temperature were compared (see the Supporting Information); the emission of Pt-Rho at 77 K is more structured compared with that at room temperature.

Nanosecond Time-Resolved Transient Difference Absorption

The lack of phosphorescence of Pt-Rho does not necessarily mean that the triplet excited state was not populated upon photoexcitation. To investigate the triplet excited state of Pt-Rho, nanosecond time-resolved transient difference spectra of Pt-Rho were studied (Figure 3). Upon pulsed laser excitation at 532 nm, significant bleaching at 600 nm was observed (Figure 3a). This is due to depletion of the ground state of the rhodamine-acetylide ligand. Transient absorption at 620–800 nm was observed. Thus, the T₁ excited state of Pt-Rho can be assigned as the rhodamine-localised ³IL excited state. The lifetime of the triplet excited state was determined as $\tau_T = 83.0 \mu\text{s}$. To the best of our knowledge, this is the first time that the triplet excited state of rhodamine was studied in transition-metal complexes. The intense UV/Vis absorption of Pt-Rho and its long-lived ³IL triplet excited state will be useful for applications such as photovoltaics and photocatalysis.

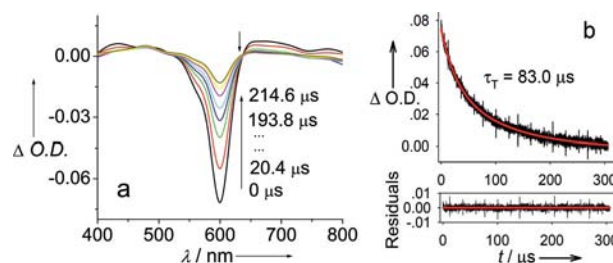


Figure 3. Nanosecond time-resolved transient difference absorption spectra of Pt-Rho: (a) transient absorption difference spectra and (b) decay trace at 560 nm. The spectra were recorded in deaerated toluene; $2.0 \times 10^{-5} \text{ M}$, $\lambda_{\text{ex}} = 532 \text{ nm}$, 25 °C.

The transient absorption feature of Pt-Rho is drastically different from that of the model complex Pt-Ph.^[22c–22e] For example, the model complex does not show any bleaching at 600 nm, instead Pt-Ph is bleached at 380 nm.^[22c]

The photophysical properties of Pt-Rho, the acetylide ligand and the model complex Pt-Ph are summarised in Table 1. The fluorescence quantum yield of the free ligand Rho-C \equiv CH is decreased in the complex Pt-Rho, as well as the fluorescence lifetime (τ) (Table 1). The quench of the phosphorescence of the Pt^{II} coordination moiety in Pt-Rho can be rationalised by the internal conversion of ³MLCT→³IL, with ³IL as a dark state.

Table 1. Photophysical parameters of the Pt^{II} complexes and the ligand.^[a]

	$\lambda_{\text{abs}}^{[b]}$	$\epsilon^{[c]}$	λ_{em}	$\Phi^{[d]}$	$\tau_{\text{T}}^{[e]}$	$\tau_{\text{L}}^{[f]}$
Pt-Rho	556	18.58	580	41.1 %	83.0 μs	2.50 ns
Pt-Ph ^[g]	424	1.47	555	31.3 %	— ^[h]	1.36 μs ^[i]
Rho-C \equiv CH	561	7.96	581	67.1 % ^[j]	— ^[k]	3.81 ns

[a] In CH₂Cl₂, 25 °C. [b] 5.0×10^{-6} M. [c] Molar extinction coefficient at the absorption maxima ϵ : $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. [d] [Ru(dmb)₃](PF₆)₂ as standard ($\Phi = 0.073$ in CH₃CN). [e] Triplet-state lifetimes, measured by transient absorption 2.0×10^{-5} M in toluene. [f] Luminescence lifetime. [g] In CH₃CN. [h] Not determined. [i] Literature value.^[22] [j] Rhodamine-B as standard ($\Phi = 0.65$ in EtOH). [k] Not applicable.

Assignment of the ³IL Excited State by DFT Calculations

To study the low-lying triplet excited state of Pt-Rho, the spin densities of Pt-Rho and Pt-Ph were compared (Figure 4). The optimised T₁ geometry showed that the two phenyl groups on the rhodamine moiety differ in orientation with respect to the Pt^{II} coordination plane; one is almost coplanar with the Pt^{II} coordination plane (dihedral angle of 0.2°), whereas the other is tilted about 28° towards the Pt^{II} coordination plane. On the other hand, the two phenyl rings have a similar orientation toward the xanthene moiety of the rhodamine (the dihedral angles are 56° and 59°). For Pt-Ph, however, the two phenyl rings of the acetylide moiety are coplanar with the Pt^{II} coordination plane.

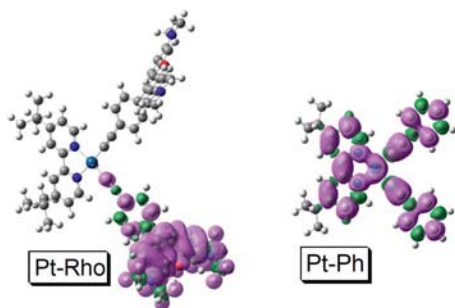


Figure 4. Isosurfaces of the spin density of Pt-Rho and Pt-Ph at the optimised triplet state. The calculations were performed at the B3LYP/6-31G/LANL2DZ level with Gaussian 09W.

For Pt-Rho, the spin density of the triplet state is localised on the rhodamine (the chromophore for which the phenyl ring is tilted by 28° toward the Pt^{II} coordination plane; Figure 4). For Pt-Ph, however, the spin density of the triplet state is distributed over the phenylacetylide moiety, the Pt^{II} centre and the dbbpy ligand (Figure 4), which are in line with the known ³MLCT/³LLCT feature of the T₁ state of Pt-Ph. The isosurface distributions clearly indicated that the T₁ state of Pt-Rho is a rhodamine-localised ³IL excited state.^[13–15,44]

The triplet excited states of Pt-Rho were also studied with TDDFT calculations. The T₁ state has an energy level of 1.69 eV (735 nm). The transition involved in the T₁ state is the HOMO-3→LUMO; both orbitals are localised on the rhodamine moiety (Figure 5). This means that the T₁→S₀ transition is localised on the rhodamine moiety, that is, the T₁ excited state can be recognised as a ³IL excited state.

This result is in agreement with the spin-density analysis, the long-lived T₁ excited state observed with the time-resolved transient absorption, and the lack of ³MLCT phosphorescence of Pt-Rho.

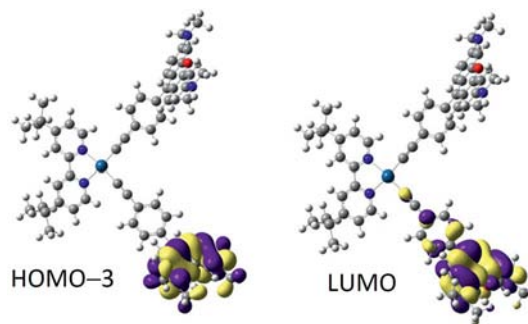


Figure 5. Frontier molecular orbitals involved in the T₁ excited state of Pt-Rho. The calculated S₀–T₁ energy gap is 1.69 eV (735 nm). The T₁ state is localised on the rhodamine moiety (for which the phenyl ring is tilted by 28° toward the Pt^{II} coordination plane), this is in line with the spin density analysis (see the main text). The T₁-state geometry was optimised with the TDDFT method, toluene was used as the solvent in the calculation (CPCM model). The calculation was carried out at the B3LYP/6-31G(d)/LanL2DZ level with Gaussian 09W.

To the best of our knowledge, *N,N* Pt^{II} bis(acetylide) complexes with intense absorption and long-lived ³IL excited states have rarely been reported. For example, a PDI-containing Pt^{II} bis(acetylide) complex was reported with intense absorption at 573 nm ($\epsilon = 68000 \text{ M}^{-1} \text{ cm}^{-1}$).^[28] The lifetime of the PDI-localised ³IL excited state, however, was short ($\tau = 0.246 \mu\text{s}$)^[28] compared with that of Pt-Ph ($\tau = 1.36 \mu\text{s}$).^[22] Recently, we prepared an NDI-containing Pt^{II} complex^[15] for which the ³IL triplet excited state lifetime was found to be $\tau = 22.3 \mu\text{s}$. We have also reported the Pt^{II} bis(acetylide) complex containing NI, which showed a long-lived emissive ³IL state ($\tau = 118 \mu\text{s}$), but very weak absorption in the visible region.^[10,29] The dipyrin moiety has been coordinated to iridium and the emissive ³IL excited state accessed; however, the T₁ state lifetime was found to be $<15 \mu\text{s}$.^[44] The BODIPY chromophore has been connected to the bpy ligand of a cyclometalated Ir^{III} complex; in this case the lifetime of the T₁ excited state was $25 \mu\text{s}$.^[42] All these examples demonstrate the elusive photophysics of the Pt^{II}-chromophoric dyads, and Pt-Rho represents the first example that shows intense absorption in the region beyond 500 nm and, at the same time, shows a significantly prolonged T₁ excited-state lifetime ($\tau = 83.0 \mu\text{s}$ at r.t. for Pt-Rho; Table 1).

Triplet–Triplet Annihilation Upconversion

As an application of the intense absorption and long-lived T₁ state of Pt-Rho, the complex was used as a triplet sensitizer for TTA upconversion.^[45–47] TTA upconversion is a particularly interesting upconversion scheme in that the excitation/emission wavelength can be readily tuned by independent selection of the triplet sensitizer and the acceptor (these should have matched T₁-state energy levels). Further-

more, the excitation-power density for TTA upconversion can be very low, in the same order of terrestrial sunlight (0.1 W cm^{-2} ; AM1.5G).^[48,49]

Currently, the major challenge for the development of TTA upconversion is the poor availability of triplet sensitisers; these are limited to the Pt^{II}/Pd^{II}-porphyrin complexes for which the T_1 energy level is difficult to tune.^[45] This challenge can be addressed by using Pt^{II} bis(acetylide) complexes for which the photophysical properties, including the energy level of the T_1 excited state, can be readily tuned by using different arylacetylides. Previously, an *N*[^]*N**N* Pt^{II} acetylide complex was used as a triplet sensitiser, but with weak absorption in visible region and a short T_1 lifetime (4.8 μs), the upconversion quantum yield was less than 1.5%.^[50] Recently, we used coumarin- or NDI-containing *N*[^]*N* Pt^{II} bis(acetylide) complexes as the triplet sensitisers for TTA upconversion and achieved quantum yields up to 9.5%.^[13–15]

In the presence of perylene as the triplet acceptor ($T_1 = 1.53 \text{ eV}$; 810 nm), upconverted blue emission was observed with Pt–Rho upon excitation at 532 nm (Figure 6). Irradiation of perylene with a 532 nm laser did not produce any emission, thus verifying the upconversion feature of the blue emission for the mixed solution of Pt–Rho and perylene. The upconversion quantum yield was determined as $\Phi_{\text{UC}} = 11.2\%$. Considering the intense absorption of Pt–Rho, this upconversion quantum yield is underestimated, because the emission of the perylene will be reabsorbed by Pt–Rho (the emission of Pt–Rho was enhanced in the presence of perylene; Figure 6b). Thus, an upconversion quantum yield higher than 11.2% is expected for Pt–Rho. The significant TTA upconversion for Pt–Rho is due to its intense absorption of the excited light and the long-lived T_1 excited state. No upconversion was observed for Pt–Ph under the same experimental conditions.

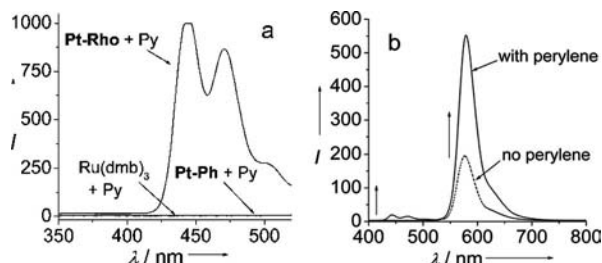
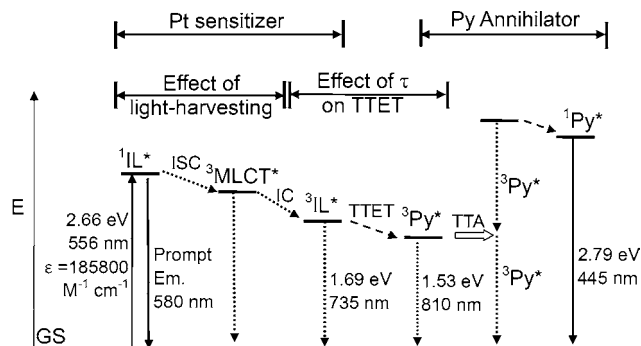


Figure 6. (a) Upconversion with Pt–Rho and Pt–Ph ($1.0 \times 10^{-5} \text{ M}$) as the triplet sensitisers. Perylene (Py; $3.0 \times 10^{-5} \text{ M}$) was used as the triplet acceptor; $\lambda_{\text{ex}} = 532 \text{ nm}$ (5 mW laser). The residual luminescence of the sensitisers are not shown. (b) Enhancement of the emission of Pt–Rho in the presence of perylene; $c(\text{complex}) = 1.0 \times 10^{-5} \text{ M}$, $c(\text{perylene}) = 3.0 \times 10^{-5} \text{ M}$. The measurements were recorded in deaerated CH_2Cl_2 , 25 °C.

The photophysics of Pt–Rho and the TTA upconversion with Pt–Rho as the triplet sensitiser are summarised in Scheme 2. Excitation of either the rhodamine ligand or the MLCT state lead to the prompt fluorescence emission of the rhodamine ligand. Our studies, however, show that the long-lived non-emissive ^3IL excited state was finally populated. It should be pointed out that the emission from the

$^3\text{MLCT}$ state was completely quenched in Pt–Rho, thus indicating a ^3IL excited state with a lower energy level than that of the $^3\text{MLCT}$ state. The upconversion with Pt–Rho as the triplet sensitiser proved the new concept that the TTA upconversion can be sensitised with a non-emissive triplet excited state, that is, the non-emissive ^3IL excited state was involved in the triplet–triplet energy transfer (TTET) between the sensitiser and the acceptor perylene (Scheme 2), and eventually leads to the upconverted emission of perylene. This new concept of TTA upconversion with a non-phosphorescent triplet excited state in transition-metal complexes will greatly increase the availability of triplet sensitisers for TTA upconversion, which are limited to the phosphorescent Pt^{II}, Pd^{II} or Ir^{III} complexes.



Scheme 2. Qualitative Jablonski diagram illustrating the sensitised TTA upconversion process between Pt–Rho and perylene (Py). The effect of the light-harvesting ability and the luminescence lifetime of the Pt^{II} sensitiser on the efficiency of TTA upconversion is also shown. E = energy, GS = ground state (S_0), $^1\text{IL}^*$ = intraligand singlet excited state (rhodamine-localised), IC = internal conversion, ISC = intersystem crossing, $^3\text{MLCT}^*$ = Pt^{II}-based metal-to-ligand charge-transfer triplet excited state, $^3\text{IL}^*$ = intraligand triplet excited state (rhodamine-localised), $^3\text{Py}^*$ = triplet excited state of perylene, $^1\text{Py}^*$ = singlet excited state of Py. Note that direct $^1\text{IL} \rightarrow ^3\text{IL}$ is also possible. The $^1\text{MLCT}$ state is not presented in the scheme. The emission bands observed for the sensitisers alone is the ^3IL emissive excited state. The emission bands observed in the TTA experiment are attributed to the simultaneous $^1\text{IL}^*$ emission (rhodamine fluorescence) and the $^1\text{Py}^*$ emission (fluorescence).

Conclusion

Rhodamine was incorporated into a Pt^{II} acetylide complex (Pt–Rho), and intense UV/Vis absorption at 556 nm ($\epsilon = 185800 \text{ M}^{-1} \text{ cm}^{-1}$) and an extensively prolonged triplet excited state lifetime ($\tau_T = 83.0 \mu\text{s}$) were observed. The T_1 excited state of Pt–Rho was assigned as the rhodamine-localised ^3IL state by using steady and nanosecond time-resolved spectroscopy, as well as DFT calculations. Pt–Rho was used as the sensitiser for TTA upconversion. We proved that the non-emissive ^3IL excited state can be used for TTA upconversion, and an upconversion quantum yield of 11.2% was observed. Using transition metal complexes with non-emissive triplet excited states as the triplet sensitisers for TTA upconversion will greatly increase the availability of triplet sensitisers. Our strategy paved the way for the preparation of transition-metal complexes that show in-

tense visible-light absorption and long-lived triplet excited states, and for their applications in areas such as photovoltaics, photocatalysis and upconversions.

Experimental Section

Rhodamine-Br: A mixture of 4-bromobenzaldehyde (1.85 g, 10 mmol), 3-(diethylamino)phenol (3.4 g, 20 mmol), *p*-TsOH (0.258 g, 1.5 mmol) and acetic acid (100 mL) was heated to 70 °C and stirred for 7 h. The reaction mixture was cooled to r.t., and the pH was adjusted to above 7 with a 10% NaOH solution. The precipitate was filtered and washed with water (100 mL). The solid was dissolved in CH₂Cl₂ (100 mL), to which chloranil (1.23 g, 5 mmol) was added. The mixture was stirred for 2 h. After removal of the solvent, the residue was purified by column chromatography (silica gel; CH₂Cl₂/methanol, 10:1, v/v) to give a purple solid; yield 2.15 g (45.0%). ¹H NMR (400 MHz, CDCl₃): δ = 7.79–7.77 (d, *J* = 8.0 Hz, 2 H), 7.34–7.28 (m, 4 H), 7.00–6.98 (m, 2 H), 6.85 (s, 2 H), 3.72–3.66 (t, *J* = 7.2 Hz, 8 H), 1.37–1.33 (m, 12 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 12.8, 46.4, 96.8, 113.3, 114.5, 125.2, 130.9, 131.2, 131.9, 132.5, 155.8, 158.1 ppm. ESI-HRMS ([C₂₇H₃₀N₂OBr]⁺): calcd. 477.1541; found 477.1545.

Rhodamine-Ethynyl: A mixture of rhodamine-Br (956.0 mg, 2 mmol), PPh₃ (26.2 mg, 0.1 mmol) and Pd(PPh₃)₂Cl₂ (70.2 mg, 0.1 mmol) was dissolved in a solvent mixture of triethylamine (10 mL) and THF (10 mL) under Ar. Ethynyltrimethylsilane (1.0 mL) and CuI (19.1 mg, 0.1 mmol) were sequentially added to the above solution. The mixture was stirred at 70 °C for 7 h. After removal of triethylamine and THF in vacuo, the residue was purified by column chromatography (silica gel; CH₂Cl₂/methanol, 10:1, v/v) to give a purple solid. The solid was dissolved in a solvent mixture (30 mL; CH₂Cl₂/methanol, 2:1, v/v); then K₂CO₃ (840.0 mg, 6 mmol) was added, and the mixture was stirred at r.t. for 5 h. The precipitate was removed by filtration, and the organic phase was washed with water (30 mL), and the residue was purified by column chromatography (silica gel; CH₂Cl₂/methanol, 10:1, v/v) to give a purple solid; yield 336.0 mg (40%). ¹H NMR (400 MHz, CDCl₃): δ = 7.78–7.72 (m, 2 H), 7.38–7.30 (m, 4 H), 6.98–6.93 (m, 2 H), 6.89–6.88 (d, *J* = 4.0 Hz, 2 H), 3.70–3.65 (m, 8 H), 3.27 (s, 1 H), 1.36–1.32 (t, *J* = 8.0 Hz, 12 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 12.6, 46.5, 96.9, 113.3, 114.5, 125.0, 129.7, 131.2, 131.9, 132.5, 132.8, 155.7, 158.1 ppm. ESI-HRMS ([C₂₉H₃₁N₂O]⁺): calcd. 423.2436; found 423.2432.

Synthesis of Pt-Rho: Rhodamine-ethynyl (30.0 mg, 0.0709 mmol) and Pt(dbbpy)Cl₂ (24.7 mg, 0.0473 mmol) were dissolved in a solution of CH₂Cl₂ (10 mL) under Ar. Diisopropylamine (2 mL) and CuI (5.0 mg, 0.0024 mmol) were sequentially added to the above solution. The mixture was stirred at 25 °C for 28 h. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel; CH₂Cl₂/methanol, 10:1, v/v), to give a purple solid; yield 20.0 mg (31.0%). ¹H NMR (400 MHz, CDCl₃): δ = 9.69 (s, 2 H), 8.11 (s, 2 H), 7.78–7.76 (d, *J* = 8.0 Hz, 4 H), 7.72 (s, *J* = 2 Hz), 7.52–7.49 (d, *J* = 12.0 Hz, 4 H), 7.31–7.29 (d, *J* = 8.0 Hz, 4 H), 6.99–6.96 (d, *J* = 12.0 Hz, 4 H), 6.80 (s, 4 H), 3.67–3.66 (s, 16 H), 1.35 (s, 24 H), 1.25 (s, 18 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 8.9, 12.7, 29.5, 46.1, 70.8, 96.6, 105.8, 110.8, 113.4, 114.4, 119.6, 128.8, 129.5, 129.8, 130.1, 132.2, 132.6, 132.7, 155.4, 157.9 ppm. ESI-HRMS ([C₇₆H₈₄N₆O₂Pt]^{2+/2}): calcd. 653.8152; found 653.8148.

Physical Measurements: UV/Vis absorption spectra were taken with an HP8453 UV/Vis spectrophotometer. Fluorescence spectra were

recorded with a Shimadzu RF 5301PC spectrofluorometer, or a Sanco 970 CRT spectrofluorometer. Fluorescence/phosphorescence lifetimes were measured with an OB920 fluorescence/phosphorescence lifetime spectrometer (Edinburgh, U.K.). The nanosecond time-resolved transient-difference absorption spectra were detected by using Edinburgh LP920 instruments (Edinburgh Instruments, U.K.). The signal was buffered with a Tektronix TDS 3012B oscilloscope and analysed by the LP900 software. All samples in flash-photolysis experiments were deaerated with argon for ca. 15 min before measurement, and the gas flow was maintained during the measurement. A diode-pumped solid-state (DPSS) laser was used for the upconversions (532 nm). The samples were purged with N₂ or Ar for 30 min before measuring. The upconversion quantum yields (Φ_{UC}) were determined with [Ru(dmb)₃][PF₆]₂ as the quantum-yield standard ($\Phi_F = 0.073$ in deaerated CH₃CN) [Equation (1)],^[45] in which Φ_{UC} , A_{unk} , I_{unk} and η_{unk} represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the samples and solvents, respectively.^[45]

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

DFT calculations were used for the optimisation of the ground-state geometries, for both singlet states and triplet states. The energy levels of the T₁ states (energy gap between S₀ and T₁) were calculated with time-dependent DFT (TDDFT) on the basis of optimised triplet-state geometries. All calculations were carried out with Gaussian 09W.^[51]

Supporting Information (see footnote on the first page of this article): Additional characterisation and photophysical data.

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