DOI: 10.1002/ejic.201100777

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

Ling Huang,[a] Le Zeng,[a] Huimin Guo,[a] Wanhua Wu,[a] Wenting Wu,[a] Shaomin Ji,[a] and Jianzhang Zhao*[a]

Keywords: Photochemistry / Rhodamine / Platinum / Triplet–triplet annihilation / Upconversion / Chromophores

An *N^N* Pt^{II} bis(acetylide) complex was prepared with the rhodamine fluorophore [Pt–Rho, in which *N^N* is dbbpy = 4,4′-bis(*tert*-butyl-2,2′-bipyridine)]. Complex Pt–Rho shows intense absorption in the visible region (ε = 185800 $\text{M}^{-1}\,\text{cm}^{-1}$ at 556 nm) and a fluorescence emission of the ligand (λ_{em} = 580 nm, Φ_L = 41.1 %, τ_L = 2.50 ns). The long-lived rhodamine-localised intraligand triplet excited state (^{3}IL, τ_T = 83.0 µs) 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 comparison, the model complex (dbbpy)Pt^{II} bis(phenylacetylide) (Pt–Ph) shows weak absorption in the visible region (ε = 14700 $\text{M}^{-1}\,\text{cm}^{-1}$ at 424 nm) and a short-lived metal-to-ligand charge-transfer excited state (^{3}MLCT) (τ_T = 1.36 µs). Complex Pt–Rho was used as triplet sensitiser for upconversion based on triplet–triplet annihilation. An upconversion quantum yield of 11.2 % was observed. Our strategy to access the long-lived ^{3}IL 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 sensitisers 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 $S_0 \rightarrow S_1 \rightarrow T_1$ 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]

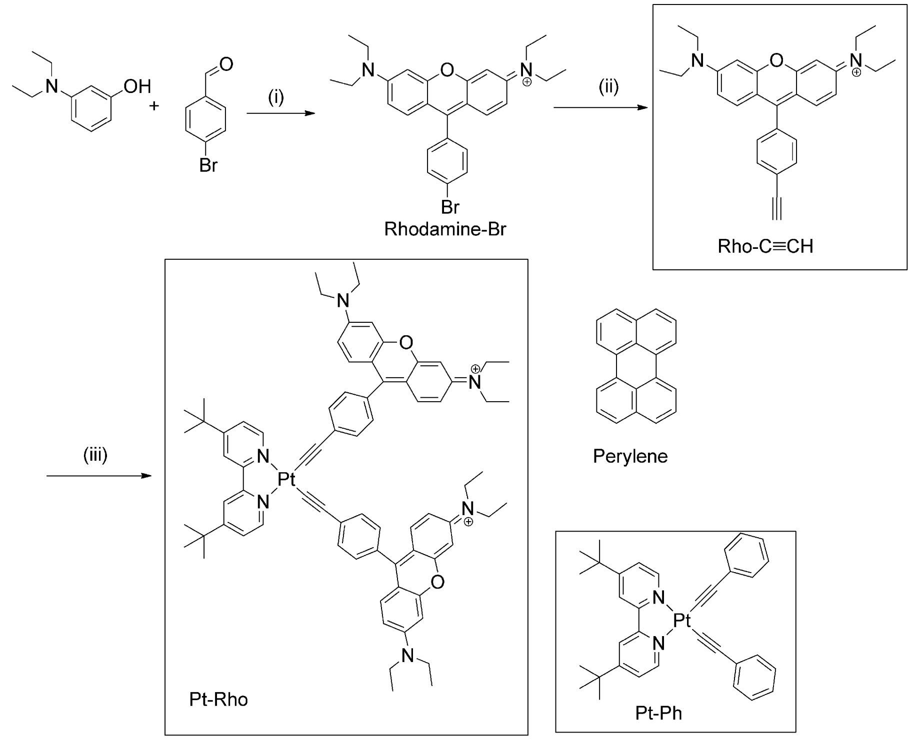
The typical Pt^{II} acetylide complexes, such as (dbbpy)Pt^{II} bis(phenylacetylide) (Pt–Ph; dbbpy = 4,4′-bis(*tert*-butyl)-2,2′-bipyridine; Scheme 1), however, show very poor absorption in the visible region (λ_{max} = 398 nm with ε = 9300 $\text{M}^{-1}\,\text{cm}^{-1}$), and the lifetime of the T_1 excited state is short (τ = 1.36 µs).[22] On the other hand, to establish an intraligand triplet excited state (^{3}IL) is fascinating, because the ^{3}IL state usually shows a prolonged lifetime compared with the ^{3}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^N* (or *N^N^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 ^{3}IL excited state (τ_T = 0.246 µs)[28] was found to be much shorter than that of the model complex Pt–Ph (τ_T = 1.36 µs).[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 ^{3}IL triplet excited state were observed.[10,14,15,29] These complexes, however, suffer from either short absorption

---

[a] State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology,
E-208 Western Campus, 2 Ling-Gong Road, Dalian 116024, China
Fax: +86-411-8498-6236
E-mail: zhaojzh@dlut.edu.cn
http://finechem.dlut.edu.cn/zhaojianzhang/guohm/index.htm

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100777.



Scheme 1. Synthesis of complex Pt–Rho. (i) CH_3COOH, *p*-TsOH, chloranil 45%; (ii) $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, ethynyltrimethylsilane, Ar, 70 °C, then CH_2Cl_2, methanol, K_2CO_3, r.t., 5 h, 40%; (iii) CH_2Cl_2, CuI, *i*Pr_2NH, 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 ^{3}IL 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 ^{3}IL 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 ^{3}IL excited state (Pt–Rho, Scheme 1). Our strategy was to use the aforementioned versatile *N^N* Pt^{II} bis(acetylide) scaffold to attach the acetylide rhodamine chromophore. Intense absorption in the visible region (λ_{abs} = 556 nm, ε = 185800 $\text{M}^{-1}\,\text{cm}^{-1}$ in CH_2Cl_2) and an exceptionally long-lived ^{3}IL excited state (τ_T = 83.0 µs) 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 ^{3}IL 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 sensitiser 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 sensitiser for TTA upconversion. The availability of triplet sensitisers 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 °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*-TsOH-catalysed condensation of 4-bromobenzaldehyde and 3-(diethylamino)phenol under mild conditions (70 °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 (–C≡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 (ε = 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≡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≡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≡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≡CH ligand.

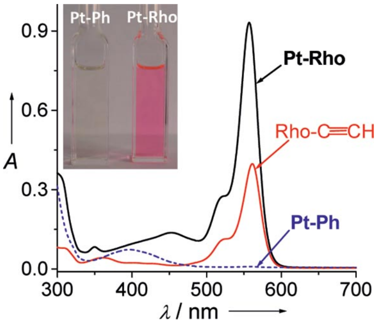


Figure 1. UV/Vis absorption spectra of the ligand Rho–C≡CH and the complexes Pt–Rho and Pt–Ph in CH_2Cl_2 (5.0×10^{-6} M; 25 °C).

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≡CH (see the Supporting Information); the emission of Pt–Rho is attributed to the fluorescence of Rho–C≡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 O_2 (Figure 2b). On the contrary, the emission of Pt–Ph was quenched by O_2 (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 triplet energy transfer from the ^{3}MLCT state to the rhodamine-localised ^{3}IL state. Indeed our time-dependent DFT (TDDFT) calculations showed that the energy level of the T_1 state of the rhodamine ligand Rho–C≡CH is 709 nm (see the Supporting Information), which is significantly lower than the T_1 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.

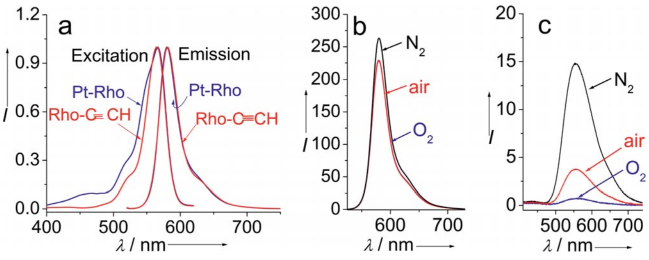


Figure 2. (a) Excitation and emission spectra of Pt–Rho and Rho–C≡CH. The O_2 dependency of the emission of (b) Pt–Rho and (c) Pt–Ph. The spectra were recorded in CH_2Cl_2 (5.0×10^{-6} M), 25 °C.

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 exited 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 T_1 excited state of Pt–Rho can be assigned as the rhodamine-localised ^{3}IL excited state. The lifetime of the triplet excited state was determined as τ_T = 83.0 µs. 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 ^{3}IL triplet excited state will be useful for applications such as photovoltaics and photocatalysis.

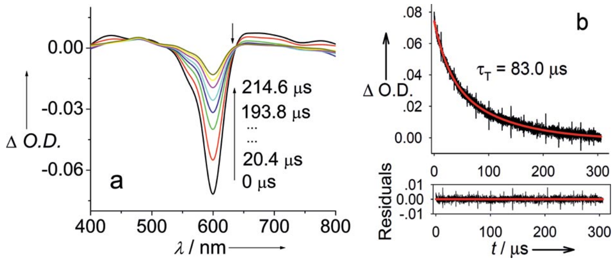


Figure 3. Nanosecond time-resolved transient difference absorption spectra of Pt–Rho: (a) transient absorption difference spectra and (b) decay trace at 560 nm. The spectra were recorded in deaerated toluene; 2.0×10^{-5} M, λ_{ex} = 532 nm, 25 °C.

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≡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 $^3\text{MLCT}\rightarrow{}^3\text{IL}$, with ^{3}IL as a dark state.

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

	λ_{abs}[b]	ε[c]	λ_{em}	Φ[d]	τ_T[e]	τ_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≡CH	561	7.96	581	67.1%[j]	–[k]	3.81 ns

[a] In CH_2Cl_2, 25 °C. [b] 5.0×10^{-6} M. [c] Molar extinction coefficient at the absorption maxima ε: $10^4\ M^{-1}cm^{-1}$. [d] $[Ru(dmb)_3][PF_6]_2$ as standard (Φ = 0.073 in CH_3CN). [e] Triplet-state lifetimes, measured by transient absorption 2.0×10^{-5} M in toluene. [f] Luminescence lifetime. [g] In CH_3CN. [h] Not determined. [i] Literature value.[22] [j] Rhodamine-B as standard (Φ = 0.65 in EtOH). [k] Not applicable.

Assignment of the ^{3}IL 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 T_1 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.

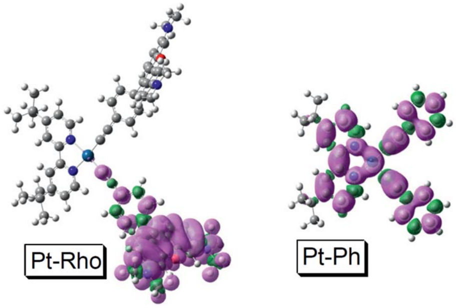


Figure 4. Isosurfaces of the spin density of Pt–Rho and Pt–Ph at the optimised triplet state. The calculations were performed at the B3LYP/6-31G/LANL2DZ level with Gaussian 09W.

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 ^{3}MLCT/^{3}LLCT feature of the T_1 state of Pt–Ph. The isosurface distributions clearly indicated that the T_1 state of Pt–Rho is a rhodamine-localised ^{3}IL excited state.[13–15,44]

The triplet excited states of Pt–Rho were also studied with TDDFT calculations. The T_1 state has an energy level of 1.69 eV (735 nm). The transition involved in the T_1 state is the HOMO-3→LUMO; both orbitals are localised on the rhodamine moiety (Figure 5). This means that the $T_1\rightarrow S_0$ transition is localised on the rhodamine moiety, that is, the T_1 excited state can be recognised as a ^{3}IL excited state. This result is in agreement with the spin-density analysis, the long-lived T_1 excited state observed with the time-resolved transient absorption, and the lack of ^{3}MLCT phosphorescence of Pt–Rho.

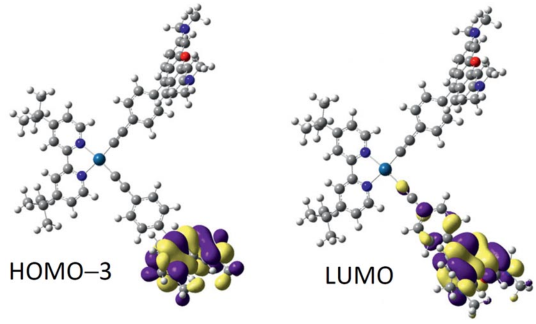


Figure 5. Frontier molecular orbitals involved in the T_1 excited state of Pt–Rho. The calculated S_0–T_1 energy gap is 1.69 eV (735 nm). The T_1 state is localised on the rhodamine moiety (for which the phenyl ring is tilted by 28° toward the Pt^{II} coordination plane), this is in line with the spin density analysis (see the main text). The T_1-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 ^{3}IL excited states have rarely been reported. For example, a PDI-containing Pt^{II} bis(acetylide) complex was reported with intense absorption at 573 nm (ε = 68000 $M^{-1}cm^{-1}$).[28] The lifetime of the PDI-localised ^{3}IL excited state, however, was short (τ = 0.246 µs)[28] compared with that of Pt–Ph (τ = 1.36 µs).[22] Recently, we prepared an NDI-containing Pt^{II} complex[15] for which the ^{3}IL triplet excited state lifetime was found to be τ = 22.3 µs. We have also reported the Pt^{II} bis(acetylide) complex containing NI, which showed a long-lived emissive ^{3}IL state (τ = 118 µs), but very weak absorption in the visible region.[10,29] The dipyrrin moiety has been coordinated to iridium and the emissive ^{3}IL excited state accessed; however, the T_1 state lifetime was found to be <15 µs.[44] The BODIPY chromophore has been connected to the bpy ligand of a cyclometalated Ir^{III} complex; in this case the lifetime of the T_1 excited state was 25 µs.[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 T_1 excited-state lifetime (τ = 83.0 µs at r.t. for Pt–Rho; Table 1).

Triplet–Triplet Annihilation Upconversion

As an application of the intense absorption and long-lived T_1 state of Pt–Rho, the complex was used as a triplet sensitiser 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 sensitiser and the acceptor (these should have matched T_1-state energy levels). Furthermore, 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 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 Φ_{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.

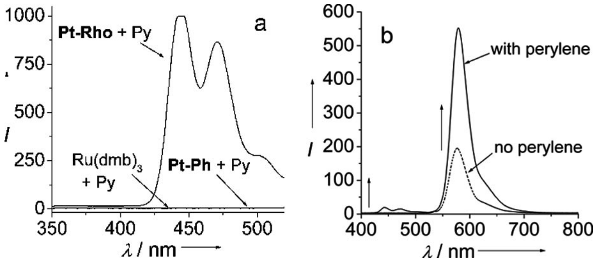
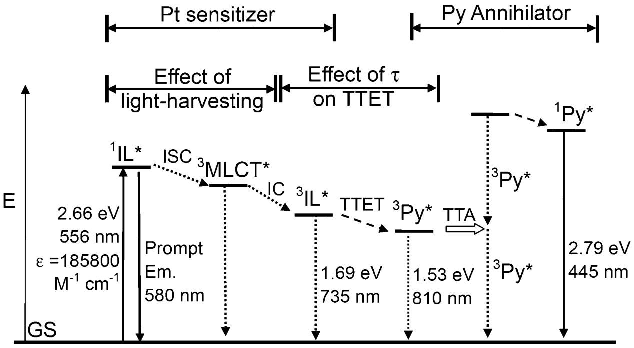


Figure 6. (a) Upconversion with Pt–Rho and Pt–Ph (1.0×10^{-5} M) as the triplet sensitisers. Perylene (Py; 3.0×10^{-5} M) was used as the triplet acceptor; λ_{ex} = 532 nm (5 mW laser). The residual luminescence of the sensitisers are not shown. (b) Enhancement of the emission of Pt–Rho in the presence of perylene; *c*(complex) = 1.0×10^{-5} M, *c*(perylene) = 3.0×10^{-5} 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 ^{3}IL excited state was finally populated. It should be pointed out that the emission from the ^{3}MLCT state was completely quenched in Pt–Rho, thus indicating a ^{3}IL excited state with a lower energy level than that of the ^{3}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 ^{3}IL 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}IL* = intraligand singlet excited state (rhodamine-localised), IC = internal conversion, ISC = intersystem crossing, ^{3}MLCT* = Pt^{II}-based metal-to-ligand charge-transfer triplet excited state, ^{3}IL* = intraligand triplet excited state (rhodamine-localised), ^{3}Py* = triplet excited state of perylene, ^{1}Py* = singlet excited state of Py. Note that direct ^{1}IL→^{3}IL is also possible. The ^{1}MLCT state is not presented in the scheme. The emission bands observed for the sensitisers alone is the ^{3}IL emissive excited state. The emission bands observed in the TTA experiment are attributed to the simultaneous ^{1}IL* emission (rhodamine fluorescence) and the ^{1}Py* emission (fluorescence).

Conclusion

Rhodamine was incorporated into a Pt^{II} acetylide complex (Pt–Rho), and intense UV/Vis absorption at 556 nm (ε = 185800 M^{-1} cm^{-1}) and an extensively prolonged triplet excited state lifetime (τ_T = 83.0 μs) were observed. The T_1 excited state of Pt–Rho was assigned as the rhodamine-localised ^{3}IL 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 ^{3}IL 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 intense 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 CH_2Cl_2 (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; CH_2Cl_2/methanol, 10:1, v/v) to give a purple solid; yield 2.15 g (45.0%). ^1H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz, $CDCl_3$): 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 ($[C_{27}H_{30}N_2OBr]^+$): calcd. 477.1541; found 477.1545.

Rhodamine-Ethynyl: A mixture of rhodamine-Br (956.0 mg, 2 mmol), PPh_3 (26.2 mg, 0.1 mmol) and $Pd(PPh_3)_2Cl_2$ (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; CH_2Cl_2/methanol, 10:1, v/v) to give a purple solid. The solid was dissolved in a solvent mixture (30 mL; CH_2Cl_2/methanol, 2:1, v/v); then K_2CO_3 (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; CH_2Cl_2/methanol, 10:1, v/v) to give a purple solid; yield 336.0 mg (40%). ^1H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz, $CDCl_3$): 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 ($[C_{29}H_{31}N_2O]^+$): calcd. 423.2436; found 423.2432.

Synthesis of Pt–Rho: Rhodamine–ethynyl (30.0 mg, 0.0709 mmol) and $Pt(dbbpy)Cl_2$ (24.7 mg, 0.0473 mmol) were dissolved in a solution of CH_2Cl_2 (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; CH_2Cl_2/methanol, 10:1, v/v), to give a purple solid; yield 20.0 mg (31.0%). ^1H NMR (400 MHz, $CDCl_3$): 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. ^{13}C NMR (100 MHz,$CDCl_3$): 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 ($[C_{76}H_{84}N_6O_2Pt]^{2+}/2$): 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 N_2 or Ar for 30 min before measuring. The upconversion quantum yields (Φ_{UC}) were determined with $[Ru(dmb)_3][PF_6]_2$ as the quantum-yield standard (Φ_F = 0.073 in deaerated CH_3CN) [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]

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

DFT calculations were used for the optimisation of the ground-state geometries, for both singlet states and triplet states. The energy levels of the T_1 states (energy gap between S_0 and T_1) 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.

Acknowledgments

We thank the National Natural Science Foundation of China (NSFC) (20972024 and 21073028), the Fundamental Research Funds for the Central Universities (DUT10ZD212 and DUT11LK19), The Royal Society (U.K.)–NSFC (China) China–U.K. Cost-Share Program (21011130154), the State Key Laboratory of Fine Chemicals (KF0802) and the Ministry of Education of China (SRFDP-200801410004 and NCET-08-0077) for financial support.

---

[1] a) J. A. G. Williams, *Top. Curr. Chem.* **2007**, *281*, 205–268; b) V. Balzani, G. Bergamini, P. Ceroni and E. Marchi, *New J. Chem.* **2011**, DOI: 10.1039/c1nj20142e.
[2] J. McGarrah, Y. Kim, M. Hissler, R. Eisenberg, *Inorg. Chem.* **2001**, *40*, 4510–4511.
[3] Q. Wang, W. Y. Wong, *Polym. Chem.* **2011**, *2*, 432–440.
[4] X. Wang, S. Goeb, Z. Ji, N. A. Pogulaichenko, F. N. Castellano, *Inorg. Chem.* **2011**, *50*, 705–707.
[5] G. Zhou, W. Wong, *Chem. Soc. Rev.* **2011**, *40*, 2541–2566.
[6] D. M. Khramov, A. J. Boydston, C. W. Bielawski, *Angew. Chem.* **2006**, *118*, 6332–6335; *Angew. Chem. Int. Ed.* **2006**, *45*, 6186–6189.
[7] Q. Zhao, F. Li, C. Huang, *Chem. Soc. Rev.* **2010**, *39*, 3007–3030.
[8] S. Ji, W. Wu, W. Wu, P. Song, K. Han, Z. Wang, S. Liu, H. Guo, J. Zhao, *J. Mater. Chem.* **2010**, *20*, 1953–1963.
[9] W. Wu, W. Wu, S. Ji, H. Guo, P. Song, K. Han, L. Chi, J. Shao, J. Zhao, *J. Mater. Chem.* **2010**, *20*, 9775–9786.
[10] H. Guo, S. J, W. Wu, W. Wu, J. Shao, J. Zhao, *Analyst* **2010**, *135*, 2832–2840.

[11] W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *Eur. J. Inorg. Chem.* **2010**, 4470–4482.

[12] a) S. Ji, W. Wu, W. Wu, H. Guo, J. Zhao, *Angew. Chem.* **2011**, *123*, 1664–1667; *Angew. Chem. Int. Ed.* **2011**, *50*, 1626–1629; b) S. Ji, H. Guo, W. Wu, W. Wu, J. Zhao, *Angew. Chem. Int. Ed.* **2011**, *50*, 8283–8286.

[13] W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *Dalton Trans.* **2011**, *40*, 5953–5963.

[14] H. Sun, H. Guo, W. Wu, X. Liu, J. Zhao, *Dalton Trans.* **2011**, *40*, 7834–7841.

[15] Y. Liu, W. Wu, J. Zhao, X. Zhang, H. Guo, *Dalton Trans.* **2011**, DOI: 10.1039/c1dt10679a.

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

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

[18] a) A. I. Baba, J. R. Shaw, J. A. Simon, R. P. Thummel, R. H. Schmehl, *Coord. Chem. Rev.* **1998**, *171*, 43–59; b) B. Maubert, N. D. McClenaghan, M. T. Indelli, S. Campagna, *J. Phys. Chem. A* **2003**, *107*, 447–455.

[19] D. B. Papkovsky, T. C. O'Riordan, *J. Fluoresc.* **2005**, *15*, 569–584.

[20] a) F. N. Castellano, I. E. Pomestchenko, E. Shikhova, F. Hua, M. L. Muro, N. Rajapakse, *Coord. Chem. Rev.* **2006**, *250*, 1819–1828; b) T. J. Wadas, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2003**, *42*, 3772–3778.

[21] L. Falmigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Top. Curr. Chem.* **2007**, *281*, 143–203.

[22] a) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2000**, *39*, 447–457; b) C. E. Whittle, J. A. Weinstein, M. W. George, K. S. Schanze, *Inorg. Chem.* **2001**, *40*, 4053–4062; c) E. O. Danilov, I. E. Pomestchenko, S. Kinayyigit, P. L. Gentili, *J. Phys. Chem. A* **2005**, *109*, 2465–2471; d) F. Hua, S. Kinayyigit, A. A. Rachford, E. A. Shikhova, S. Goeb, J. R. Cable, C. J. Adams, K. Kirschbaum, A. A. Pinkerton, F. N. Castellano, *Inorg. Chem.* **2007**, *46*, 8771–8783; e) A. A. Rachford, S. Goeb, R. Ziessel, F. N. Castellano, *Inorg. Chem.* **2008**, *47*, 4348–4355.

[23] J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055–3066.

[24] D. V. Kozlov, D. S. Tyson, C. Goze, R. Ziessel, F. N. Castellano, *Inorg. Chem.* **2004**, *43*, 6083–6092.

[25] A. Harriman, A. Khatyr, R. Ziessel, *Dalton Trans.* **2003**, 2061–2068.

[26] Q. Yang, L. Wu, Z. Wu, L. Zhang, C. H. Tung, *Inorg. Chem.* **2002**, *41*, 5653–5655.

[27] F. Nastasi, F. Puntoriero, S. Campagna, J. H. Olivier, R. Ziessel, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7392–7402.

[28] A. A. Rachford, S. Goeb, F. N. Castellano, *J. Am. Chem. Soc.* **2008**, *130*, 2766–2767.

[29] H. Guo, M. L. M. Small, S. Ji, J. Zhao, F. N. Castellano, *Inorg. Chem.* **2010**, *49*, 6802–6804.

[30] W. Lin, L. Yuan, Z. Cao, Y. Feng, J. Song, *Angew. Chem.* **2010**, *122*, 385–389; *Angew. Chem. Int. Ed.* **2010**, *49*, 375–379.

[31] V. N. Belov, C. A. Wurm, V. P. Boyarskiy, S. Jakobs, S. W. Hell, *Angew. Chem.* **2010**, *122*, 3598–3602; *Angew. Chem. Int. Ed.* **2010**, *49*, 3520–3523.

[32] G. He, D. Guo, C. He, X. Zhang, X. Zhao, C. Duan, *Angew. Chem.* **2009**, *121*, 6248–6251; *Angew. Chem. Int. Ed.* **2009**, *48*, 6132–6135.

[33] X. Zhang, Y. Xiao, X. Qian, *Angew. Chem.* **2008**, *120*, 8145–8149; *Angew. Chem. Int. Ed.* **2008**, *47*, 8025–8029.

[34] Y. Koide, Y. Urano, K. Hanaoka, T. Terai, T. Nagano, *J. Am. Chem. Soc.* **2011**, *133*, 5680–5682.

[35] K. Krishnamoorthy, T. P. Begley, *J. Am. Chem. Soc.* **2010**, *132*, 11608–11612.

[36] B. Tang, Y. Xing, P. Li, N. Zhang, F. Yu, G. Yang, *J. Am. Chem. Soc.* **2007**, *129*, 11666–11667.

[37] S. Kenmoku, Y. Urano, H. Kojima, T. Nagano, *J. Am. Chem. Soc.* **2007**, *129*, 7313–7318.

[38] Y. K. Yang, K. J. Yook, J. S. Tae, *J. Am. Chem. Soc.* **2005**, *127*, 16760–16761.

[39] M. J. Uddin, L. J. Marnett, *Org. Lett.* **2008**, *10*, 4799–4801.

[40] G. Jiao, J. C. Castro, L. H. Thoresen, K. Burgess, *Org. Lett.* **2003**, *5*, 3675–3677.

[41] D. N. Kozhevnikov, V. N. Kozhevnikov, M. Z. Shafikov, A. M. Prokhorov, D. W. Bruce, J. A. G. Williams, *Inorg. Chem.* **2011**, *50*, 3804–3815.

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

[43] M. Galletta, S. Campagna, M. Quesada, G. Ulrich, R. Ziessel, *Chem. Commun.* **2005**, 4222–4224.

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

[45] a) T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, *254*, 2560–2573; b) R. R. Islangulov, J. Lott, C. Weder, F. N. Castellano, *J. Am. Chem. Soc.* **2007**, *129*, 12652–12653.

[46] Y. Y. Cheng, B. Fückel, T. Khoury, R. G. C. R. Clady, M. J. Y. Tayebjee, N. J. Ekins-Daukes, M. J. Crossley, T. W. Schmidt, *J. Phys. Chem. Lett.* **2010**, *1*, 1795–1799.

[47] a) A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino, F. Meinardi, *Phys. Rev. B* **2008**, *78*, 195112-1–195112-5; b) P. E. Keivanidis, S. Baluschev, T. Miteva, G. Nelles, U. Scherf, A. Yasuda, G. Wegner, *Adv. Mater.* **2003**, *15*, 2095–2098; c) J. Sun, W. Wu, H. Guo, J. Zhao, *Eur. J. Inorg. Chem.* **2011**, 3165–3173.

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

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

[50] P. Du, R. Eisenberg, *Chem. Sci.* **2010**, *1*, 502–506.

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

Received: July 26, 2011