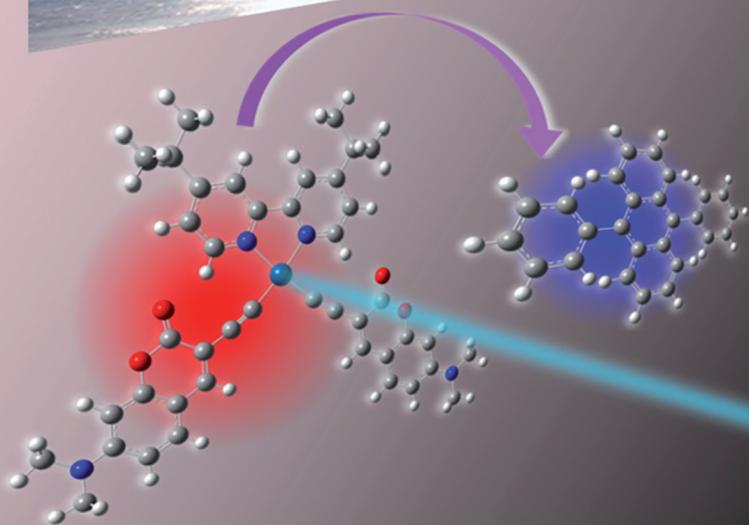
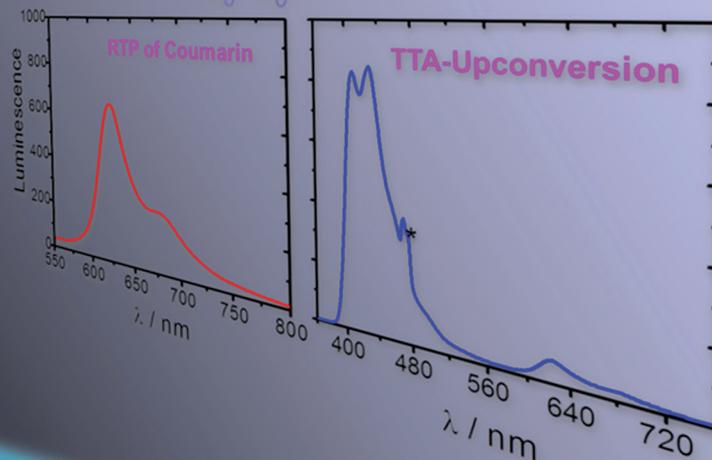
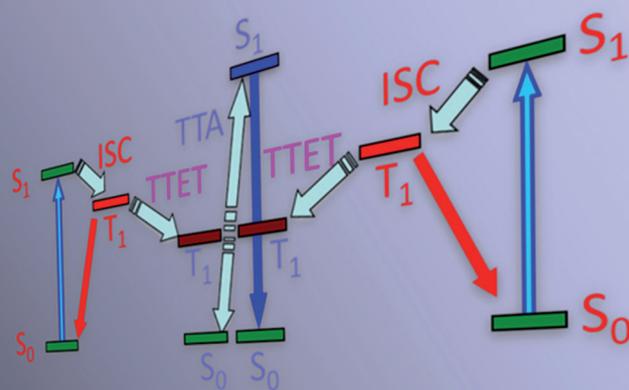
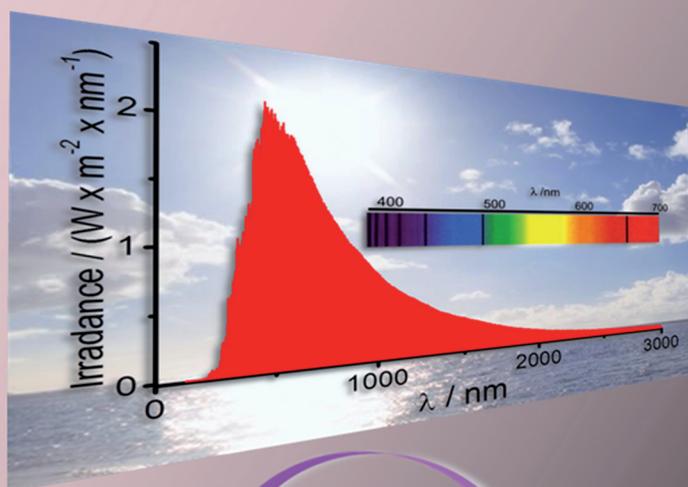


# Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Volume 40 | Number 31 | 21 August 2011 | Pages 7793–8036



ISSN 1477-9226

RSC Publishing

**COVER ARTICLE**

Guo, Zhao *et al.*

Coumarin phosphorescence observed with  $\text{N}^{\wedge}\text{N}$  Pt(II) bisacetylide complex and its applications for luminescent oxygen sensing and triplet-triplet-annihilation based upconversion

# Coumarin phosphorescence observed with $N^N$ Pt(II) bisacetylide complex and its applications for luminescent oxygen sensing and triplet–triplet-annihilation based upconversion†

Haiyang Sun, Huimin Guo,\* Wenting Wu, Xin Liu and Jianzhang Zhao\*

Received 23rd March 2011, Accepted 26th April 2011

DOI: 10.1039/c1dt10490j

A *dbbpy* platinum(II) bis(coumarin acetylide) complex (**Pt-1**, *dbbpy* = 4,4'-di-*tert*-butyl-2,2'-bipyridine) was prepared. **Pt-1** shows intense absorption in the visible region ( $\lambda_{\text{abs}} = 412$  nm,  $\epsilon = 3.23 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) compared to the model complex *dbbpy* Pt(II) bis(phenylacetylide) (**Pt-2**,  $\lambda_{\text{abs}} = 424$  nm,  $\epsilon = 8.8 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>). Room temperature phosphorescence was observed for **Pt-1** (<sup>3</sup>IL,  $\tau_{\text{p}} = 2.52$   $\mu$ s,  $\lambda_{\text{em}} = 624$  nm,  $\Phi_{\text{p}} = 2.6\%$ ) and the emissive triplet excited state was assigned as mainly intraligand triplet excited state (<sup>3</sup>IL), proved by 77 K steady state emission, nanosecond time-resolved transient absorption spectroscopy and DFT calculations. Complex **Pt-1** was used for phosphorescent oxygen sensing and the sensitivity (Stern–Volmer quenching constant  $K_{\text{SV}} = 0.012$  Torr<sup>-1</sup>) is 12-fold of the model complex **Pt-2** ( $K_{\text{SV}} = 0.001$  Torr<sup>-1</sup>). **Pt-1** was also used as triplet sensitizer for triplet–triplet-annihilation based upconversion, upconversion quantum yield  $\Phi_{\text{UC}}$  up to 14.1% was observed, vs. 8.9% for the model complex **Pt-2**.

## Introduction

Diimine ( $N^N$ ) Pt(II) bisacetylide complexes are of particular interesting due to their applications in electroluminescence, photovoltaics, photocatalysis and molecular probes, *etc.*<sup>1–4</sup> The photon emission of Pt(II) bis(acetylide) complexes are attributed to triplet excited state with a <sup>3</sup>MLCT/<sup>3</sup>LLCT mixed feature (metal-to-ligand charge transfer and ligand-to-ligand-charge transfer).<sup>1</sup> The photophysics of the complexes, such as absorption/phosphorescence wavelength and phosphorescence quantum yields, are largely dependent on the acetylide ligands, thus the photophysical properties of these complexes can be readily tuned by variation of the acetylide ligands, which is feasible from a synthetic perspective.<sup>1,2,5–8</sup>

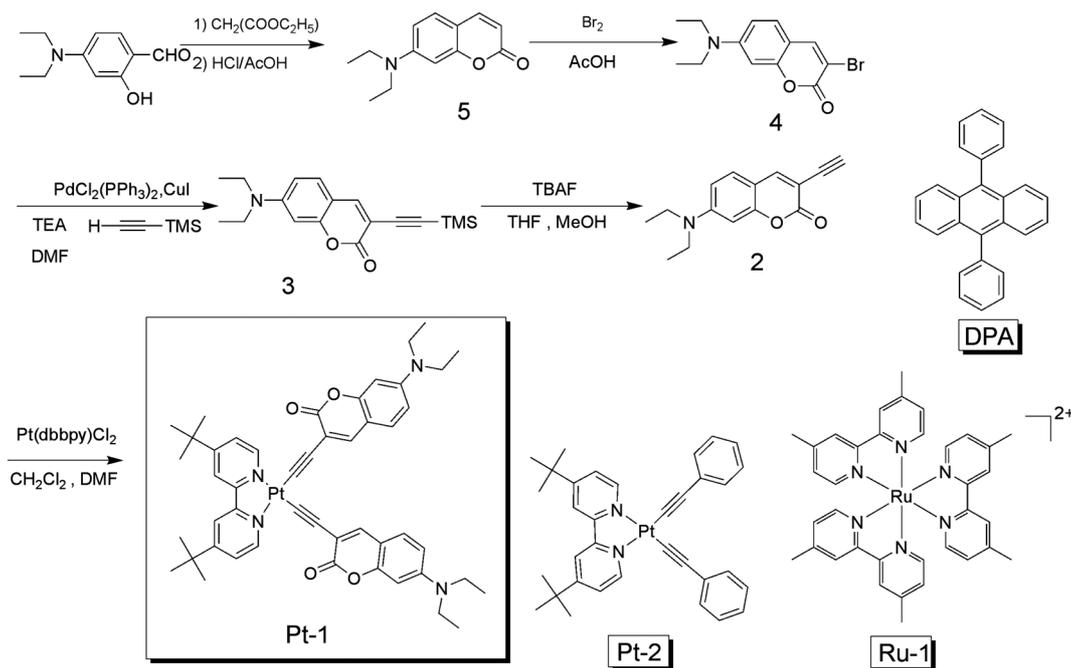
However, much room is left for the current development of the  $N^N$  Pt(II) bis(acetylide) complexes to optimize their photophysical properties, such as (1) the UV-vis absorption and emission properties. For example, the absorption of the typical diimine Pt(II) bisacetylide complex is usually weak in visible region (the  $\epsilon$  is less than 5000 M<sup>-1</sup> cm<sup>-1</sup>),<sup>6</sup> and the phosphorescence lifetime ( $\tau_{\text{p}}$ ), or more generally, the triplet excited state lifetime ( $\tau_{\text{T}}$ ), is usually short (*ca.* 1.0  $\mu$ s). Complexes with intense absorption as

well as long-lived triplet excited state are rarely reported.<sup>9</sup> (2) The structural diversity of the acetylide ligands is limited to the typical aromatic moieties, such as substituted phenyl, naphthyl, pyrenyl, *etc.*, and very few organic fluorophores have been attached to the Pt(II) center to investigate the phosphorescence of the acetylide ligand, *i.e.* emission of the intraligand triplet excited state (<sup>3</sup>IL).<sup>1</sup> The <sup>3</sup>IL excited state is particularly interesting, because longer lifetimes or red-shifted emission were usually observed with the <sup>3</sup>IL excited state, vs. the normal <sup>3</sup>MLCT excited state. We have shown that the <sup>3</sup>IL excited state is important for applications such as oxygen sensing and upconversion.<sup>10–15</sup> Previously we prepared an  $N^N$  Pt(II) bis(acetylide) complex containing the naphthalimide (NI) subunit,<sup>14,15</sup> which shows intense long-lived room temperature NI localized <sup>3</sup>IL phosphorescence ( $\tau_{\text{p}} = 118$   $\mu$ s,  $\Phi_{\text{p}} = 17.5\%$ ). To the best of our knowledge, however, only the ethynylated pyrene and NI that show intense absorption were attached to Pt(II) to investigate the emissive <sup>3</sup>IL excited states.<sup>1,2,14–20</sup>

In order to tackle the above limitations, herein we designed a  $N^N$  Pt(II) bis(acetylide) complex containing coumarin (**Pt-1**, Scheme 1). Enhanced absorption in the visible range, as well as prolonged phosphorescence lifetime, were observed for **Pt-1** compared to the model complex **Pt-2** (Scheme 1). With steady state and time-resolved spectroscopy and DFT calculations, we proved that the intraligand triplet excited state (<sup>3</sup>IL) is the main component of the triplet excited state of **Pt-1**. **Pt-1** was used as energy donor in two triplet–triplet-energy transfer processes, *i.e.* luminescent oxygen sensing and triplet–triplet-annihilation (TTA) based upconversion.

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, P. R. China. E-mail: zhaojzh@dlut.edu.cn, guohm@dlut.edu.cn; Fax: + 86 (0)411 8498 6236; Tel: + 86 (0)411 8498 6236

† Electronic supplementary information (ESI) available: structural characterization spectra, determination of the upconversion quantum yields and NBO analysis. See DOI: 10.1039/c1dt10490j



**Scheme 1** Molecular structures of **Pt-1** and the model complex **Pt-2**. The coumarin acetylide (**L-1**) and the triplet acceptor 9,10-diphenylanthracene (DPA) used in TTA upconversion are also shown. The model complex used as a triplet sensitizer in the upconversion, **Ru-1**, is also shown.

## Experimental

### Materials and reagents

4,4'-Di-*tert*-butyl-2,2'-bipyridine (*dbbpy*) is a product of Aldrich. Other chemicals are analytical pure and were used as received without further purification. Solvents were dried or distilled before used for synthesis or spectroscopic studies.

### Apparatus

NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded with Q-TOF Micro spectrometer and MALDI micro MX. UV-vis absorption spectra were recorded on a HP8453 UV-visible spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 or a Sanco 970 CRT spectrofluorometer.

Fluorescence or phosphorescence lifetimes were measured on Horiba Jobin Yvon Fluoro Max-4 (TCSPC). Nanosecond time-resolved transient absorption spectroscopy was obtained with LP-920 pump-probe spectrometer (Edinburgh Instruments). The emission at 77 K was measured with a Oxford Optistat DN<sup>TM</sup> cryostat (with liquid nitrogen filling) and FS920 fluorospectrometer (Edinburgh Instruments). Flow cell coupled to a fluorospectrometer was used in the luminescent O<sub>2</sub> sensing.

### Synthesis of compound 5

4-Diethylaminosalicylaldehyde (1.93 g, 10 mmol), diethylmalonate (3.2 g, 20 mmol) and piperidine (1 mL) were combined in absolute ethanol (30 mL) and stirred for 6 h under reflux conditions. Ethanol was evaporated under reduced pressure, then concentrated HCl (20 mL) and glacial acetic acid (20 mL) were added to hydrolyze the reaction with stirring for another 6 h. The

solution was cooled to room temperature and poured into ice water (100 mL). NaOH solution (40%) was added dropwise to adjust pH of the solution to 5.0, and a pale precipitate formed immediately. After stirring for 30 min, the mixture was filtered, washed with water, dried, then the residue was purified with column chromatography (silica gel, dichloromethane) to give 1.05 g product **5** (yield: 48%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, 1H, *J* = 8.0 Hz, ArH), 7.23 (d, 1H, *J* = 8.0 Hz, Ar-CH), 6.57 (d, 1H, *J* = 12.0 Hz, ArH), 6.48 (s, 1H, ArH), 6.04 (d, 1H, *J* = 12.0 Hz, Ar-CH), 3.42 (m, 4H, CH<sub>2</sub>), 1.20 (t, 6H, CH<sub>3</sub>).

### Synthesis of compound 4

Br<sub>2</sub> (0.23 mL, 4.5 mmol) was added dropwise to a solution of 7-diethylaminocoumarin (1.0 g, 4.5 mmol) in acetic acid (23 mL), and the mixture was stirred at rt for 2–3 h. Resulting white solid was filtered and washed with acetic acid, and dried. The solid was recrystallized in acetonitrile (white solid, 1.1 g, 80% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 8.37 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 3.48 (q, *J* = 7.2 Hz, 4H), 1.21 (t, 6H, CH<sub>3</sub>).

### Synthesis of compound 3

PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (24.0 mg, 0.03 mmol, 5.0 mol%), CuI (6.5 mg, 0.03 mmol, 5.0 mol%), TEA (190 μL, 1.4 mmol), and (trimethylsilyl)acetylene (192 μL, 2.0 mmol) were added to a solution of **4** (200.0 mg, 0.67 mmol) in anhydrous DMF (7 mL) under Ar. The mixture was stirred at 60 °C for 6 h. The resulting solution was cooled to rt, diluted with water, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the compound was purified by column chromatography (silica gel, petroleum ether–EA 4 : 1,

v/v) to afford product **3**. (Yellow solid, 190 mg, 90% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.93 (s, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 6.78 (dd, *J* = 8.9 Hz, *J* = 2.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 3.58 (q, *J* = 7.0 Hz, 4H), 1.26 (t, *J* = 7.0 Hz, 6H), 0.24 (s, 9H).

### Synthesis of compound **2**

A 1.0 M solution of tetrabutylammoniumfluoride (TBAF) in THF (0.78 mL, 0.78 mmol) was added to a solution of **3** (163 mg, 0.52 mmol) in 10 mL of THF and MeOH (4/1, v/v). The mixture was stirred at rt for 8 h. The solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel with PE-EA (7 : 2, v/v) as the eluent, affording the product **2**. (Yellow solid, 76 mg, 60% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.77 (s, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 6.59 (dd, *J* = 8.9 Hz, *J* = 2.4 Hz, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 3.43 (q, *J* = 7.0 Hz, 4H), 3.26 (s, 1H), 1.22 (s, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.16, 156.45, 151.39, 146.96, 129.06, 109.27, 108.01, 103.41, 97.29, 81.14, 78.57, 77.22, 44.95, 12.43. TOF-MS: C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>, calculated *m/z* = 241.1103, found *m/z* = 241.1112.

### Synthesis of Pt-1

Pt(*dbbp*)Cl<sub>2</sub> (50.0 mg, 0.09 mmol), CuI (5.0 mg, 0.09 mmol) and diisopropylamine (1.0 mL) were dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> and DMF (2/3, v/v), the mixture was stirred for 10 min. The mixture was purged with Ar, then product **2** (70.0 mg, 0.27 mmol) was added and the mixture was stirred at room temperature for 24 h. The resulting white solid was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. The residue was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH = 80 : 1, v/v) 23.3 mg, yield: 85%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.40(d, *J* = 4.0 Hz, 2H), 7.92 (s, 2H), 7.79 (s, 2H), 7.73 (d, *J* = 4.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.52 (m, 4H), 1.44 (m, 18H), 1.25 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.57, 163.07, 156.16, 155.08, 152.88, 149.60, 141.91, 128.13, 125.01, 118.25, 109.47, 108.82, 97.49, 96.61, 44.78, 35.74, 29.70, 12.53. HR-MALDI-MS: [C<sub>48</sub>H<sub>52</sub>N<sub>4</sub>O<sub>4</sub>Pt+H]<sup>+</sup>, calculated *m/z* = 944.3715, found *m/z* = 944.3776. Anal. calcd for C<sub>48</sub>H<sub>52</sub>N<sub>4</sub>O<sub>4</sub>Pt(·0.5CH<sub>2</sub>Cl<sub>2</sub>): C, 59.05; H, 5.42; N, 5.68; Found: C, 59.26; H, 5.32; N, 5.62.

**Computational methods.** All calculations were performed using the Gaussian 09 W software (Gaussian, Inc.).<sup>21</sup> The gas phase geometry optimizations were carried out using B3LYP functional with the 6-31G(d) basis set. The vertical excitation energy was calculated with the Time-Dependent DFT (TDDFT) method based on the singlet ground state geometry. The spin-density of the triplet state was calculated with the energy minimized triplet state geometries.

**Upconversions.** A diode pumped laser was used for the upconversions. The solution samples were purged with N<sub>2</sub> or Ar for 15 min before measurement. The upconversion quantum yields were determined with a laser dye 4-dicyanomethylene-6-(*p*-dimethylaminostyryl)-2-methyl-4*H*-pyran (DCM) as the quantum yield standards ( $\Phi = 0.10$  in CH<sub>2</sub>Cl<sub>2</sub>) and the quantum yields were calculated with eqn (1),<sup>11</sup> where  $\Phi_{\text{unk}}$ ,  $A_{\text{unk}}$ ,  $I_{\text{unk}}$  and  $\eta_{\text{unk}}$  represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the samples. The photography of the upconversion were taken with Sumsang NV

5 digital camera. The exposure times are the default values of the camera.

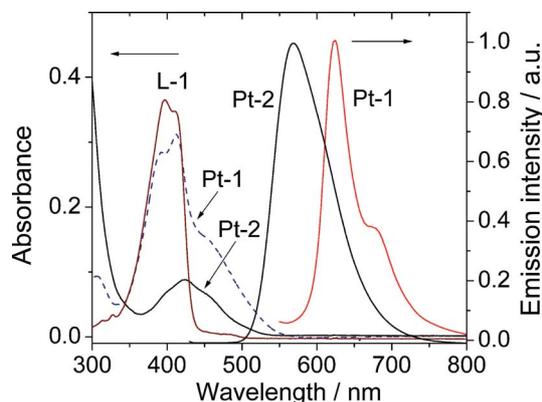
$$\Phi_{\text{unk}} = 2\Phi_{\text{std}} \left( \frac{A_{\text{std}}}{A_{\text{unk}}} \right) \left( \frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left( \frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad (1)$$

## Results and discussion

### Solvents-dependent absorption and emission

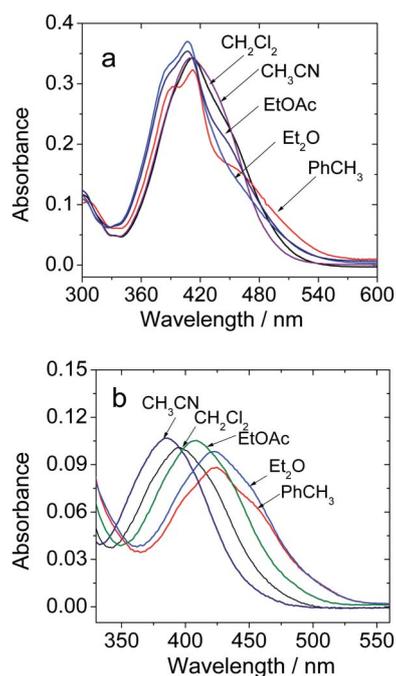
Coumarins are well-known fluorophores that show intense absorption and strong fluorescence, and were widely used as fluorophores for molecular probes or lanthanide luminescence.<sup>22a</sup> Previously coumarin was used as a light-harvesting antenna for lanthanide luminescence,<sup>22b</sup> or a *C*<sup>^</sup>*N* ligand for cyclometalated Ir(III) complexes,<sup>23,24</sup> or Pt(II)/Pd(II) complexes,<sup>25,26</sup> but its room temperature phosphorescence was never reported. Inspired by the related work that <sup>3</sup>IL emission can be observed by connection of arylacetylde to a Pt(II) center, and our own work with naphthalimide,<sup>15</sup> herein we designed a *N*<sup>^</sup>*N* Pt(II) bisacetylde complex with the coumarin acetylde ligand (**Pt-1**, Scheme 1). The  $\pi$ -conjugation framework of coumarin is directly attached to Pt(II) in **Pt-1** thus a significant heavy atom effect is expected, by which the intersystem crossing (ISC) from the singlet excited state to the triplet excited state can be facilitated, thus <sup>3</sup>IL emission is possible.<sup>1</sup> We used a model complex **Pt-2** in our photophysical and photophysical application studies (Scheme 1).

Firstly the UV-vis absorptions of the complexes were studied (Fig. 1). **Pt-2** shows maximal absorption at 424 nm with a moderate molar extinction coefficient ( $\epsilon = 8800 \text{ M}^{-1} \text{ cm}^{-1}$ ). For **Pt-1**, however, the absorption at 424 nm is greatly enhanced ( $\epsilon = 24903 \text{ M}^{-1} \text{ cm}^{-1}$ ). Furthermore, an intense absorption band at 414 nm was observed ( $\epsilon = 32300 \text{ M}^{-1} \text{ cm}^{-1}$ ). By comparison with that of **L-1**, the absorption of **Pt-1** at 414 nm is clearly due to the coumarin ligand, *i.e.* S<sub>0</sub> → <sup>1</sup>IL transition.



**Fig. 1** UV-vis absorption of **L-1**, **Pt-1** and **Pt-2**, and the normalized emission of **Pt-1** and **Pt-2**. *c* = 1.0 × 10<sup>-5</sup> M in toluene, 20 °C.

The absorption feature of **L-1** is recognizable in **Pt-1**. This is different from the normal Pt(II) bisacetylde complexes, which usually show red-shifted absorption compared to the free acetylde ligand.<sup>1,6,7,14</sup> Furthermore, the UV-vis absorption of **Pt-1** is not sensitive to the polarity of the solvents (Fig. 2a). On the contrary, **Pt-2** shows negative solvatochromism (Fig. 2b), indicating that



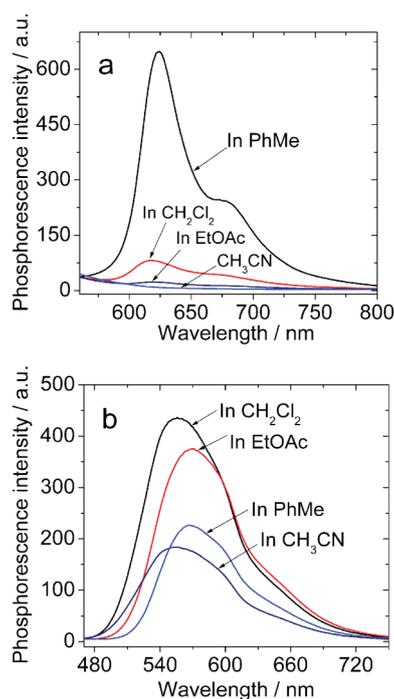
**Fig. 2** UV-Vis absorption spectra of (a) **Pt-1** and (b) **Pt-2** in different solutions.  $c = 1.0 \times 10^{-5}$  M, 20 °C.

CT absorption is the major component of the UV-vis absorption bands of **Pt-2**.<sup>27</sup> All these results infer that the absorption of **Pt-1** is IL in character, not the typical MLCT for Pt(II) bisacetylides complexes.<sup>1</sup>

An emission band at 624 nm with vibrational progression was found for **Pt-1** (Fig. 1). A structured band is characteristic for <sup>3</sup>IL emission.<sup>1,10,12,14,20</sup> On the contrary, structureless emission was observed for **Pt-2** (567 nm). Thus the emission of **Pt-1** was attributed to the <sup>3</sup>IL excited state localized on the coumarin ( $\tau_T = 2.44$   $\mu$ s). A Pt(II) acetylides complex with an ethynyl-flavone ligand was reported to show emission at 570 nm ( $\tau = 21$   $\mu$ s).<sup>28</sup> The phosphorescence quantum yield of **Pt-1** is low ( $\Phi_P = 2.6\%$ ), probably due to the equilibrium of the <sup>3</sup>MLCT state (herein it is non-emissive) with the <sup>3</sup>IL excited state.<sup>29</sup> It is known that Pt(II) bisacetylides complexes with an electron-donating acetylides ligand are non-phosphorescent.<sup>30,31</sup> **Pt-1** is phosphorescent in the solid state (ESI†).

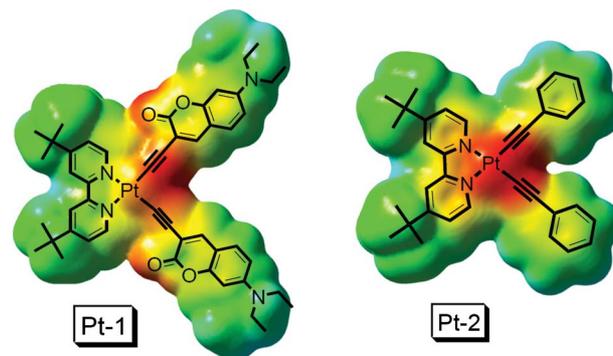
The emission of **Pt-1** is strongly solvent polarity dependent (Fig. 3a). It is highly emissive in toluene but the phosphorescence is significantly quenched in polar solvents, such as in ethyl acetate or in methylene dichloride, and it becomes non-phosphorescent in acetonitrile. We propose that the non-luminescent <sup>3</sup>MLCT excited state will be more significantly stabilized in polar solvents than <sup>3</sup>IL states (<sup>3</sup>MLCT becomes lower in energy than <sup>3</sup>IL excited state), thus **Pt-1** is non-phosphorescent in CH<sub>3</sub>CN.<sup>16</sup> The emission of **Pt-2** is relatively less solvent polarity-dependent (Fig. 3b).

Previously it was found that the phosphorescence of the 2-(4'-nitrophenyl)pyridine Pt(II) (acac) complex can be quenched by a weak Lewis base, such as toluene, dichloromethane, *etc.*, due to the strong positively charged Pt(II) center of the complex.<sup>32</sup> In order to exclude the exciplex quenching of **Pt-1** by the polar solvents (Lewis bases), the electrostatic potential surfaces of the complexes **Pt-1** and **Pt-2** at the T<sub>1</sub> state were studied (Fig. 4). The red-colored



**Fig. 3** Emission spectra of (a) **Pt-1** ( $\lambda_{ex} = 474$  nm) and (b) **Pt-2** ( $\lambda_{ex} = 403$  nm) in different solutions. Under N<sub>2</sub> atmosphere.  $c = 1.0 \times 10^{-5}$  M, 20 °C.

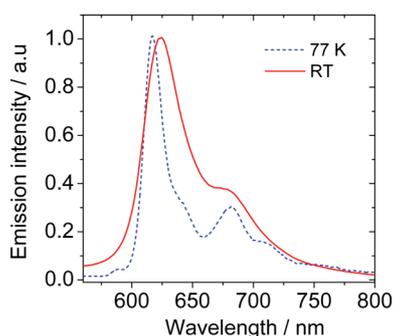
area in **Pt-2** defines a region of high electron density at the metal center, while the corresponding green area depicts a diminished electronic density. For **Pt-1**, a similar profile was observed, *i.e.* the Pt(II) center has higher electron density than the other areas of the complex (Fig. 4), thus the Lewis base quenching mechanism is not applicable to **Pt-1**.<sup>32</sup>



**Fig. 4** Potential surfaces of electron density for the T<sub>1</sub> excited state of **Pt-1** (left) and **Pt-2** (right). The red color represents areas of high electron density and the green color indicates areas with diminished electron density (isovalue = 0.0004). Calculated at B3LYP/3-21G level with the T<sub>1</sub> state geometry with Gaussian 09W.

#### 77 K emission, nanosecond time-resolved transient absorption and spin density of the complexes: assignment of the <sup>3</sup>IL features of the T<sub>1</sub> state

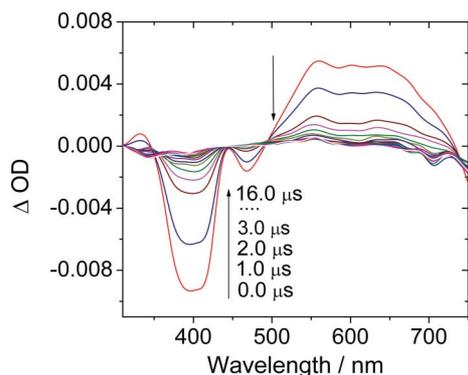
The emission of **Pt-1** at 77 K shows more significant vibration progression than the emission spectrum at RT. Notably the thermally induced Stokes shift is very small ( $\Delta E_s = 182$  cm<sup>-1</sup>) (Fig. 5), a small  $\Delta E_s$  is an established evidence for the <sup>3</sup>IL emission.



**Fig. 5** Photoluminescence spectra of **Pt-1** at RT (in toluene) and 77 K (in EtOH–MeOH, 4: 1, v/v).  $\lambda_{\text{ex}} = 414$  nm.

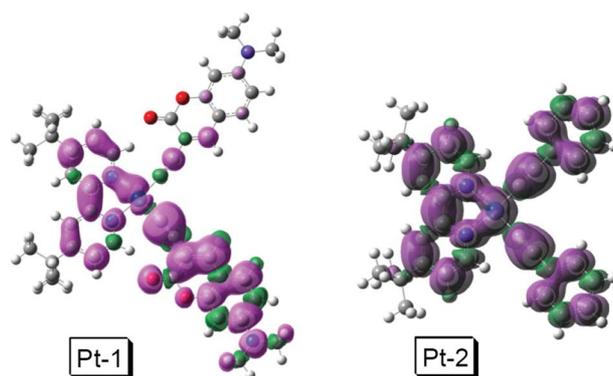
In contrast, substantial a  $\Delta E_s$  value of  $2470 \text{ cm}^{-1}$  (0.31 eV) was reported for the model complex **Pt-2**, for which the emissive  $T_1$  state is MLCT.<sup>8b</sup>

In order to prove the  $^3\text{IL}$  feature of the triplet excited state of **Pt-1**, nanosecond time-resolved transient absorption spectroscopy was studied (Fig. 6). Significant bleaching at 400 nm was observed for **Pt-1** upon pulsed laser excitation, which unambiguously proved the coumarin localized  $^3\text{IL}$  excited state. Minor bleaching was observed at 470 nm. Transient absorption was observed in the range of 500 nm–700 nm. The transients of **Pt-1** are drastically different from that of the model complex **Pt-2**.<sup>33</sup> **Pt-2** did not show any transient absorption in the range of 500 nm–700 nm.<sup>17,20,34</sup>



**Fig. 6** Transient absorption spectra of **Pt-1** after pulsed laser excitation ( $\lambda_{\text{ex}} = 532$  nm).  $c = 1.5 \times 10^{-5}$  M in toluene, 20 °C.

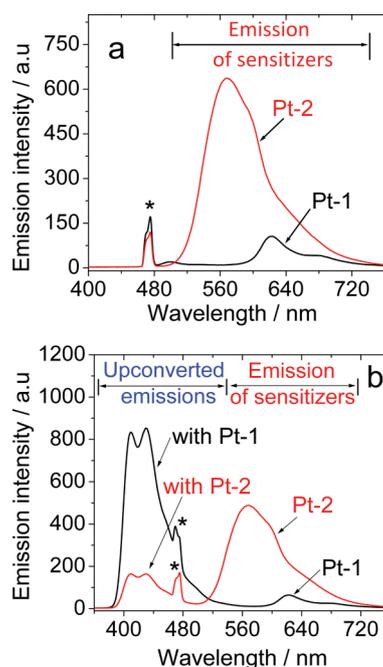
The isosurfaces of the spin density of  $T_1$  state of **Pt-1** support the IL feature of the  $T_1$  state (Fig. 7). For **Pt-2**, the spin density surface is localized on the phenyl acetylide ligands, the Pt(II) center and the dbbpy ligand. This spin density distribution is in line with the known  $^3\text{MLCT}/^3\text{LLCT}$  feature of *dbbpy* Pt(II) bisphenylacetylide. For **Pt-1**, the coumarin ligand contributes more significantly to the spin density. We proved that the energy level of the triplet excited state of the coumarin acetylide ( $T_1 = 576$  nm, by DFT calculation) is close to the  $^3\text{MLCT}$  state of the complex (see Supporting Information†), thus the  $^3\text{IL}$  excited state is the  $T_1$  state of **Pt-1**. This assignment was supported by the NBO analysis of the  $T_1$  excited state (see ESI for detailed analysis†).



**Fig. 7** Spin density surfaces for the  $T_1$  excited state of **Pt-1** and **Pt-2**. Calculated at B3LYP/6-31g(d)/LanL2DZ level based on the optimized  $T_1$  state geometry (isovalue = 0.0004), with Gaussian 09W.

### Application of **Pt-1** as triplet sensitizer for triplet–triplet-annihilation upconversion

Next we set out to utilize **Pt-1** for triplet–triplet-annihilation (TTA) based upconversion.<sup>11,34</sup> TTA upconversion requires a triplet sensitizer and an acceptor to accomplish the cascade processes of light-harvesting, triplet–triplet-energy-transfer (TTET), TTA and the upconverted fluorescence emission.<sup>35</sup> This upconversion scheme is particularly promising for application due to its low excitation power (even lower than the terrestrial solar radiation level,  $0.1 \text{ W cm}^{-2}$ , AM 1.5G).<sup>36,37</sup> Furthermore, the excitation/emission wavelength of TTA upconversion can be readily optimized by independent selection of the triplet sensitizers and acceptors. Currently the triplet sensitizers of TTA upconversion are limited to porphyrin Pt(II)/Pd(II) complexes.<sup>35–37</sup> However, it

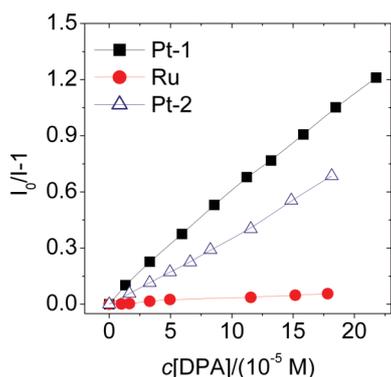


**Fig. 8** Triplet–triplet-annihilation upconversion with **Pt-1** and **Pt-2** as triplet sensitizers. (a) Emission of the sensitizers **Pt-1** and **Pt-2** alone. (b) Emission of **Pt-1** and **Pt-2** in the presence of DPA. Excited with 473 nm laser (5 mW).  $c_{\text{sensitizers}} = 1.0 \times 10^{-5}$  M,  $c_{\text{DPA}} = 1.32 \times 10^{-4}$  M. 20 °C. The asterisks indicate the scattered 473 nm laser.

is difficult to modify the porphyrin complexes to optimize the excitation/emission wavelength. Thus new sensitizers have to be developed. Herein we used **Pt-1** as the triplet sensitizer for TTA upconversion.

The emission of **Pt-1** is much weaker than **Pt-2** with 473 nm laser excitation (Fig. 8a). DPA was selected as the triplet acceptor.<sup>11,38</sup> In the presence of DPA, upconverted fluorescence (400 nm–550 nm) was observed upon selective excitation of the sensitizers at 473 nm. Irradiation of DPA alone at 473 nm did not produce any emission, and thus verified the upconverted emission with **Pt-1** or **Pt-2** as the triplet sensitizers. Upconversion quantum yields ( $\Phi_{UC}$ ) of 14.1% and 8.9% were determined for **Pt-1** and **Pt-2** under our experimental conditions, respectively (Table 2).

Notably, the peak area of the quenched phosphorescence of **Pt-1** by DPA is not significant, although the upconverted fluorescence is significant. For **Pt-2**, the upconversion is accompanied with quenching of the phosphorescence. We propose a non-emissive portion of the **Pt-1** sensitizers that in the triplet excited state is involved in TTET. It should be pointed out that <sup>3</sup>IL is weakly phosphorescent ( $\Phi_P = 2.6\%$ ). This is the first time that sensitizer molecules at excited states that are otherwise non-emissive were proposed to be involved in the TTA upconversion. The efficiency of the TTET process of the TTA upconversion was studied. The Stern–Volmer quenching constants of  $5.56 \times 10^3 \text{ M}^{-1}$  and  $3.77 \times 10^3 \text{ M}^{-1}$  were determined for **Pt-1** and **Pt-2**, respectively (Fig. 9 and Table 2).



**Fig. 9** Stern–Volmer plots generated from the phosphorescence intensity quenching of complex **Ru-1** ( $\lambda_{ex} = 474 \text{ nm}$ ), **Pt-1** ( $\lambda_{ex} = 474 \text{ nm}$ ), **Pt-2** ( $\lambda_{ex} = 403 \text{ nm}$ ) as a function of DPA concentration. In toluene,  $c = 1.0 \times 10^{-5} \text{ M}$ ,  $20^\circ \text{C}$ .

The upconversion quantum yield of **Pt-1** is among the highest values ever reported.<sup>35</sup> Considering the large molar extinction coefficient, the absolute upconverted fluorescence emission of **Pt-1** is ca. 5-fold of **Pt-2**. Recently [Pt(tpy)(C≡CPh)]ClO<sub>4</sub> (where tpy = 4'-p-tolylterpyridine) was reported for TTA based upconversion.<sup>39</sup> However, the  $\Phi_{UC}$  is only 1.1%, despite its long phosphorescence lifetime (4.6  $\mu\text{s}$ ).<sup>39</sup> Using Pt(II) acetylide complexes as triplet sensitizers for TTA upconversion is attractive because the photophysical properties of the Pt(II) complex sensitizers, such as the excitation wavelength, can be readily optimized by using different acetylide ligands.

**Table 1** Photophysical parameters of **L-1**, **Pt-1** and **Pt-2**

	$\lambda_{abs}^a$	$\epsilon^b$	$\lambda_{em}^c$	$\Phi^d$	$\tau_L^e$	$\tau_T (\mu\text{s})^f$
<b>L-1</b>	397	3.66	443	84.2%	2.8 ns	—
<b>Pt-1</b>	414	3.23	624	2.6%	2.52 $\mu\text{s}$	2.44
<b>Pt-2</b>	424	0.88	567	42.2%	1.27 $\mu\text{s}$	—

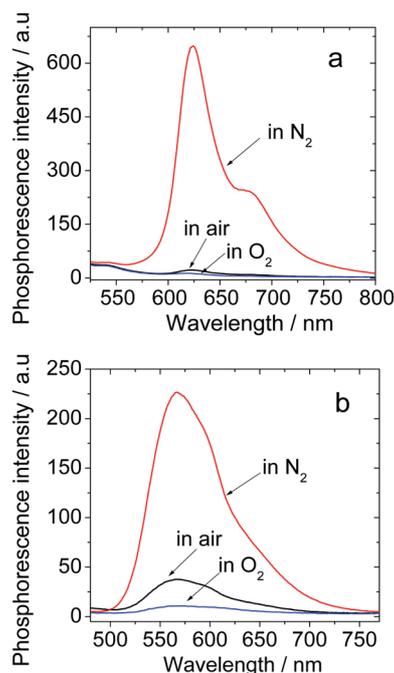
<sup>a</sup> In toluene ( $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ). <sup>b</sup> Molar extinction coefficient at the absorption maxima.  $\epsilon$ :  $10^4 / \text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ . <sup>c</sup> In toluene. <sup>d</sup> In toluene, with [Ru(bpy)<sub>2</sub>(phen)][PF<sub>6</sub>]<sub>2</sub> as standard ( $\Phi = 0.06$  in deaerated acetonitrile). <sup>e</sup> Luminescence lifetime. In toluene. <sup>f</sup> Triplet state lifetime, measured by time-resolved transient absorption.  $1.5 \times 10^{-5} \text{ mol dm}^{-3}$  in toluene.

**Table 2** Stern–Volmer quenching constant ( $K_{SV}$ ) and bimolecular quenching constants ( $k_q$ ) of **Pt-1** and **Pt-2** for TTET with DPA as acceptor and the upconversion quantum yields ( $\Phi_{UC}$ ).  $20^\circ \text{C}$

	$K_{sv} / (10^3 \text{ M}^{-1})$	$k_q / (10^9 \text{ M}^{-1} \text{ s}^{-1})$	$\Phi_{UC}$
<b>Pt-1</b>	5.56	2.21	14.1%
<b>Pt-2</b>	3.77	2.97	8.9%

### Application of the complexes for luminescent oxygen sensing

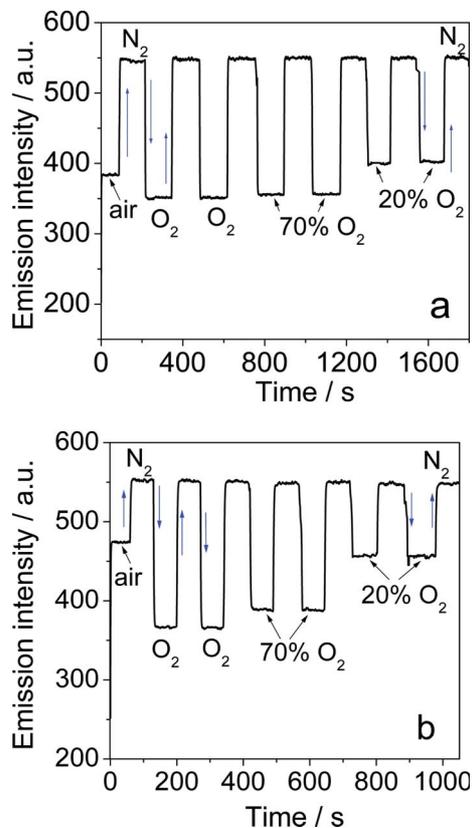
Firstly the sensitivity of the complex to oxygen in toluene solution was studied (Fig. 10). **Pt-1** is strongly phosphorescent in nitrogen saturated solution (Fig. 10a). The emission is quenched under air atmosphere or in oxygen saturated solution. Thus the phosphorescence of **Pt-1** is sensitive to O<sub>2</sub>. For **Pt-2**, however, the emission under air atmosphere is still significant compared to that under N<sub>2</sub> atmosphere. These results indicate that the phosphorescence lifetime of **Pt-1** is longer than that of **Pt-2** (Table 1).



**Fig. 10** Emission spectra of (a) **Pt-1** ( $\lambda_{ex} = 474 \text{ nm}$ ) and (b) **Pt-2** ( $\lambda_{ex} = 403 \text{ nm}$ ) in toluene saturated with air, oxygen and nitrogen.  $c = 1.0 \times 10^{-5} \text{ M}$ ,  $20^\circ \text{C}$ .

For practical applications the O<sub>2</sub> sensing will be performed with the complexes embedded in solid supporting matrix, such

as in polymer films.<sup>40</sup> We selected a polymer IMPEK-C as the supporting matrix and the oxygen sensing with the films was studied with a flow-cell, which is coupled to a spectrometer with an optical fiber bundle.<sup>12</sup> Two kinds of experiment were performed. The first one is to test the response of the films to the saturation switch between the O<sub>2</sub> and N<sub>2</sub> (Fig. 11). Fast response and recovery was observed with the films. Both  $t_{\downarrow 95}$  and  $t_{\uparrow 95}$  are 4 s.



**Fig. 11** Phosphorescence intensity response of the oxygen sensing films toward O<sub>2</sub>/N<sub>2</sub> switches. (a) **Pt-1**,  $\lambda_{\text{ex}} = 412$  nm,  $\lambda_{\text{em}} = 624.3$  nm. (b) **Pt-2**,  $\lambda_{\text{ex}} = 424$  nm,  $\lambda_{\text{em}} = 567$  nm. 20 °C.

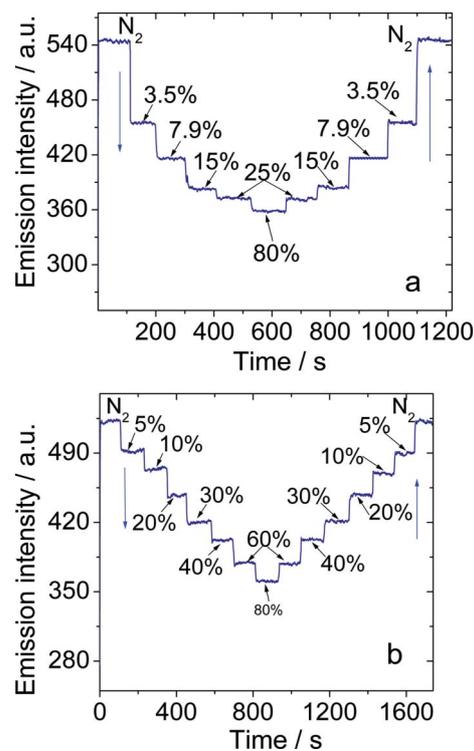
Good photostability were observed for the complexes, *i.e.* the phosphorescence of the complexes is fully recovered after exposure to continuous irradiation during the O<sub>2</sub> sensing experiments, which is ideal for practical applications. Previously a cyclometalated Ir(III) complex were used for O<sub>2</sub> sensing but it was unstable toward photoexcitation.<sup>23</sup>

In order to quantitatively evaluate the O<sub>2</sub> sensitivity of the complexes, the response of the phosphorescence of the sensing films toward small steps of variation of O<sub>2</sub> partial pressure were studied (Fig. 12). **Pt-1** is more significantly quenched than **Pt-2**.

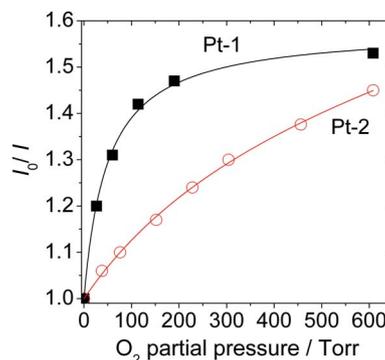
The oxygen sensing data of **Pt-1** and **Pt-2** were fitted with the two-sites model (Fig. 13 and ESI†).<sup>10</sup> The Stern–Volmer quenching constants of **Pt-1** and **Pt-2** were determined as 0.012 and 0.001 Torr<sup>-1</sup>, respectively. Thus the oxygen sensitivity of **Pt-1** is 12-fold of **Pt-2**.

## Conclusions

In conclusion, a diimine Pt(II) bis(coumarin acetylide) complex was prepared, in which the fluorophore of coumarin was directly



**Fig. 12** Phosphorescence intensity response of the complexes to O<sub>2</sub>/N<sub>2</sub> switches. (a) **Pt-1**,  $\lambda_{\text{ex}} = 412$  nm,  $\lambda_{\text{em}} = 624.3$  nm. (b) **Pt-2**,  $\lambda_{\text{ex}} = 424$  nm,  $\lambda_{\text{em}} = 567$  nm. 20 °C.



**Fig. 13** Two-sites model plots for sensing film of **Pt-1** and **Pt-2** in IMPEK-C. Intensity ratios  $I_0/I$  vs. O<sub>2</sub> partial pressure (Torr). 20 °C.

connected to a Pt(II) center. The complex shows enhanced UV-vis absorption ( $\epsilon = 32\,300$  M<sup>-1</sup> cm<sup>-1</sup> at 414 nm), red-emission at 625 nm, phosphorescence lifetime ( $\tau_p$ ) of 2.44  $\mu$ s and quantum yield ( $\Phi_p$ ) of 2.6%. The phosphorescence of the complex is dependent on the polarity of the solvents. Coumarin-localized intraligand emissive triplet excited (<sup>3</sup>IL) was proposed to be responsible for the emission of the complex. To the best of our knowledge, this is the first time that the room temperature phosphorescence of coumarin was observed. The complex was used as triplet sensitizer for triplet–triplet-annihilation based upconversion and upconversion quantum yield ( $\Phi_{\text{UC}}$ ) up to 14.1% was observed. We propose that sensitizer molecules at the triplet excited state that are otherwise non-emissive were involved in the triplet–triplet-energy-transfer (TTET) process. The complexes were also used for another TTET process, *i.e.* luminescent oxygen sensing. The

Stern–Volmer quenching constant of the coumarin-containing complex is 12-fold of the model complex. Good photostability was observed for the complexes during the luminescent oxygen sensing experiments. Our strategy of directly attaching a fluorophore to Pt(II) atom *via* an acetylide linker to access Pt(II) complexes with intense absorption in the visible region and long-lived emissive <sup>3</sup>IL excited state (ligand phosphorescence) will be useful for design of light-harvesting transition metal complexes and for applications in photovoltaics, in photocatalysis and in upconversions materials, *etc.*

## Acknowledgements

We thank the NSFC (20972024 and 21073028), the Fundamental Research Funds for the Central Universities (DUT10ZD212 and DUT11LK19), Ministry of Education (SRFDP-200801410004 and NCET-08-0077), the Royal Society (UK) and NSFC (China-UK Cost-Share Science Networks, 21011130154), the Education Department of Liaoning Province (2009T015) and State Key Laboratory of Fine Chemicals (KF0802) for financial support.

## Notes and references

- 1 J. A. G. Williams, *Top. Curr. Chem.*, 2007, **281**, 205.
- 2 (a) M. Hissler, A. Harriman, A. Khatyr and R. Ziessel, *Chem.–Eur. J.*, 1999, **5**, 3366; (b) F. Nastasi, F. Puntoriero, S. Campagna, J.-H. Olivier and R. Ziessel, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7392.
- 3 (a) Y. Liu and K. Schanze, *Inorg. Chem.*, 2005, **44**, 4055; (b) C. She, A. A. Rachford, X. Wang, S. Goeb, A. O. El-Ballouli, F. N. Castellano and J. T. Hupp, *Phys. Chem. Chem. Phys.*, 2009, **11**, 8586; (c) S. C. F. Kui, Y.-C. Law, G. S. M. Tong, W. Lu, M.-Y. Yuen and C.-M. Che, *Chem. Sci.*, 2011, **2**, 221.
- 4 (a) T. J. Wadas, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2003, **42**, 3772; (b) J. Ni, L.-Y. Zhang, H.-M. Wen and Z.-N. Chen, *Chem. Commun.*, 2009, 3801; (c) P.-H. Lanoë, H. L. Bozec, J. A. Gareth Williams, J.-L. Fillaut and V. Guerschais, *Dalton Trans.*, 2010, **39**, 707; (d) G.-J. Zhou and W.-Y. Wong, *Chem. Soc. Rev.*, 2011, **40**, 254.
- 5 I. V. Sazanovich, M. A. H. Alamiry, J. Best, R. D. Bennett, O. V. Bouganov, E. S. Davies, V. P. Grivin, A. J. H. M. Meijer, V. F. Plyusnin, K. L. Ronayne, A. H. Shelton, S. A. Tikhomirov, M. Towrie and J. A. Weinstein, *Inorg. Chem.*, 2008, **47**, 10432.
- 6 C. E. Whittle, J. A. Weinstein, M. W. George and K. S. Schanze, *Inorg. Chem.*, 2001, **40**, 4053.
- 7 M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2000, **39**, 447.
- 8 (a) J. A. Aligo, L. Smith, J. L. Eglin and L. E. Pence, *Inorg. Chem.*, 2005, **44**, 4001; (b) I. E. Pomestchenko and F. N. Castellano, *J. Phys. Chem. A*, 2004, **108**, 3485.
- 9 A. A. Rachford, S. Goeb and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 2766.
- 10 S. Ji, W. Wu, W. Wu, P. Song, K. Han, Z. Wang, S. Liu, H. Guo and J. Zhao, *J. Mater. Chem.*, 2010, **20**, 1953.
- 11 S. Ji, W. Wu, W. Wu, H. Guo and J. Zhao, *Angew. Chem., Int. Ed.*, 2011, **50**, 1626.
- 12 W. Wu, W. Wu, S. Ji, H. Guo, P. Song, K. Han, L. Chi, J. Shao and J. Zhao, *J. Mater. Chem.*, 2010, **20**, 9775.
- 13 W. Wu, W. Wu, S. Ji, H. Guo and J. Zhao, *Eur. J. Inorg. Chem.*, 2010, 4470.
- 14 Maria L. Muro-Small Guo, S. M. Ji, J. Z. Zhao and Felix N. Castellano, *Inorg. Chem.*, 2010, **49**, 6802.
- 15 H. Guo, S. Ji, W. Wu, W. Wu, J. Shao and J. Zhao, *Analyst*, 2010, **135**, 2832.
- 16 S. Goeb, A. A. Rachford and F. N. Castellano, *Chem. Commun.*, 2008, 814.
- 17 S. Goeb Rachford, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2008, **47**, 4348.
- 18 Q. Yang, L. Wu, Z. Wu, L. Zhang and C. Tung, *Inorg. Chem.*, 2002, **41**, 5653.
- 19 I. E. Pomestchenko, C. R. Luman, M. Hissler, R. Ziessel and Felix N. Castellano, *Inorg. Chem.*, 2003, **42**, 1394.
- 20 E. O. Danilov, I. E. Pomestchenko, S. Kinayyigit, P. L. Gentili, M. Hissler, R. Ziessel and F. N. Castellano, *J. Phys. Chem. A*, 2005, **109**, 2465.
- 21 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. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *GAUSSIAN 09 (Revision A.1)*, Gaussian, Inc., Wallingford, CT, 2009.
- 22 (a) N. C. Lim, J. V. Schuster, M. C. Porto, M. A. Tanudra, L. L. Yao, H. C. Freake and C. Bruckner, *Inorg. Chem.*, 2005, **44**, 2018; (b) J. Yao, W. Dou, W. Liu and J. Zheng, *Inorg. Chem. Commun.*, 2009, **12**, 430.
- 23 S. M. Borisov and I. Klimant, *Anal. Chem.*, 2007, **79**, 7501.
- 24 C. Ulbricht, N. Rehmman, E. Holder, D. Hertel, K. Meerholz and U. S. Schubert, *Macromol. Chem. Phys.*, 2009, **210**, 531.
- 25 J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2002, **41**, 3055.
- 26 O. A. Rodionova, M. V. Puzyk and K. P. Balashev, *Opt. Spectrosc.*, 2008, **105**, 62.
- 27 F. N. Castellano, I. E. Pomestchenko, E. Shikhova, F. Hua, M. L. Muro and N. Rajapakse, *Coord. Chem. Rev.*, 2006, **250**, 1819.
- 28 P. H. Lanoë, J. L. Fillaut, L. Toupet, J. A. G. Williams, H. L. Bozec and V. Guerschais, *Chem. Commun.*, 2008, 4333.
- 29 N. Armaroli, *ChemPhysChem*, 2008, **9**, 371.
- 30 F. Q. Guo and W. F. Sun, *Inorg. Chem.*, 2005, **44**, 4055.
- 31 X. Han, L. Z. Wu, G. Si, J. Pan, Q. Z. Yang, L. P. Zhang and C. H. Tung, *Chem.–Eur. J.*, 2007, **13**, 1231.
- 32 M. D. Perez, P. I. Djurovich, A. Hassan, G. Y. Cheng, T. J. Stewart, K. Aznavour, R. Bauz and M. E. Thompson, *Chem. Commun.*, 2009, 4215.
- 33 J. E. McGarrah and R. Eisenberg, *Inorg. Chem.*, 2003, **42**, 4355.
- 34 F. Hua, S. Kinayyigit, A. A. Rachford, E. A. Shikhova, S. Goeb, J. R. Cable, C. J. Adams, K. Kirschbaum, A. A. Pinkerton and F. N. Castellano, *Inorg. Chem.*, 2007, **46**, 8771.
- 35 T. N. Singh-Rachford and F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560.
- 36 A. Monguzzi, J. Mezyk, F. Scotognella, R. Tubino and F. Meinardi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 195112–1.
- 37 A. Monguzzi, R. Tubino and F. Meinardi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 155122–1.
- 38 R. R. Islangulov, D. V. Kozlov and F. N. Castellano, *Chem. Commun.*, 2005, 3776.
- 39 P. W. Du and R. Eisenberg, *Chem. Sci.*, 2010, **1**, 502.
- 40 (a) O. Wolfbeis and R. Narayanaswamy, *Optical sensors: Industrial, Environmental and Diagnostic Applications*, Springer-Verlag, Berlin-Heidelberg, 2004; (b) J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic, New York, 2nd edn, 1999.