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Accessing the long-lived emissive ³IL triplet excited states of coumarin fluorophores by direct cyclometallation and its application for oxygen sensing and upconversion[†]

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We studied four cyclometallated Pt(II) complexes, in which the thiazo-coumarin ligands (Pt-2, Pt-3 and Pt-4) or the phenylthiazo ligand (Pt-1) were directly cycloplatinated. Pt-2 shows intense absorption in visible region but other complexes show blue-shifted absorption. Room temperature phosphorescence was observed for all the complexes, and the emission wavelength is dependent on the size of the π -conjugation, not the intramolecular charge transfer (ICT) feature of the C^{Λ} ligands. Pt-2 shows longer phosphorescence lifetime ($\tau = 20.3 \,\mu$ s) than other complexes (below 2.0 μ s). Furthermore, Pt-2 shows phosphorescence quantum yield $\Phi = 0.37$, whereas **Pt-3** and **Pt-4** show much smaller Φ values (0.03 and 0.01, respectively). DFT/TDDFT calculations indicate ³IL triplet excited states for the complexes. The complexes were used as for luminescence O2 sensing and triplet-triplet-annihilation (TTA) based upconversion. Stern–Volmer quenching constant $K_{sv} = 0.026 \text{ Torr}^{-1}$ was observed for **Pt-2**, ca. 89-fold of that of **Pt-3**. TTA upconversion is achieved with **Pt-2** ($\lambda_{em} = 400$ nm with $\lambda_{ex} =$ 473 nm, anti-Stokes shift is 0.47 eV, excitation power density is at 70 mW cm⁻²). The upconversion quantum yield with Pt-2 as triplet sensitizer is up to 15.4%. The TTET efficiency ($K_{sv} = 1.33 \times 10^5$ M⁻¹, $k_{\rm q} = 6.57 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. DPA as quencher) of **Pt-2** is 34-fold of the model complex [Ru(dmb)₃][PF₆]₂. Our results show that the ³IL state can be readily accessed by direct cyclometallation of organic fluorophores and this approach will be useful for preparation and applications of transition metal complexes that show intense absorption in visible region and the long-lived emissive ³IL excited states.

Introduction

Cyclometalated Pt(II) complexes with C^{N} ligands,¹⁻¹⁵ and N^{N} Pt(II) bisacetylide complexes,¹⁶⁻³¹ have attracted much attention. The emissive excited state of these complexes are usually ³MLCT/³IL (metal-to-ligand-charge transfer, or intraligand). The long-lived triplet excited states of these organometallics are in particular interesting because many of the applications of transition metal complexes are closely related to the triplet excited states, such as electroluminescence or the luminescent O₂ sensing.^{1,12-15} Furthermore, very often the applications can be enhanced with the long-lived triplet excited states, such as in efficient photo-induced charge separation (for dye sensitized solar cell or artificial photosynthesis),^{24,32-34} lifetime-based molecular probe (*e.g.* luminescent oxygen sensing or thiol probes),^{14-15,35-37} photocatalysis,³⁸ sensitization of singlet oxygen (for photodynamic

therapy),39 and more recently triplet-triplet-annihilation (TTA) based upconversions.⁴⁰⁻⁴⁴ The principle photophysics involved in most of the applications is the triplet-triplet-energy-transfer (TTET) process.^{14,34} In this case longer triplet excited state lifetime will improve the TTET efficiency.14,34 However, the intrinsic lifetimes of the triplet excited state of the typical cyclometallated Pt(II) complexes are less than 2 µs.^{1,5,9,45-46} Furthermore, the absorption of typical cyclometalated Pt(II) complexes are weak in visible region. Thus, preparation of Pt(II) complexes that show intense absorption in visible region and long-lived triplet excited states is important for improvement of the applications of these materials. Surprisingly no systematic studies have been carried out to enhance the visible-light absorption of the C^N cyclometalated Pt(II) complexes and to extend the triplet excited state lifetimes of the cyclometallated Pt(II) complexes. Furthermore, we noticed the cyclometalated Pt(II) complexes have not been used for oxygen sensing and upconversions.

It has been shown that the excited state lifetime of Ru(II) and $N^{\Lambda}N$ Pt(II) bisacetylide complexes can be substantially prolonged, especially by tuning the triplet excited states of the complexes.^{14,18,27,35,47–53} One approach to prolong the triplet excited state lifetime is to access the ³IL excited state, which usually shows longer lifetime than the ³MLCT excited state.^{16,26–28} Previously

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Scheme 1 Synthesis of the cyclometalated Pt(II) complexes Pt-3 and Pt-4. The molecular structures of the known complexes Pt-1 and Pt-2 and the polymer used for oxygen sensing (IMPEK-C), and the triplet acceptor/annihilator 9,10-diphenylanthracene (DPA) used in the upconversion are also shown. (i) piperidine (0.05 eq.), MeOH, reflux 4–5 h. (ii) a) PtCl₂ (1.6 eq.), 2-methoxyethanol/benzonitrile 140 °C, 1 h; b) Hacac (9.0 eq.), EtN₃ (9.0 eq.) r.t. overnight. (iii) a) *tert*-BuLi, THP, 0 °C, 4 h; b) THP/DMF (1:1, v/v), r.t., overnight, HCl.

coumarin was used as $C^{\Lambda}N$ ligand to prepare cyclometalated Pt(II) acac complexes, phosphorescence lifetime up to 20.3 µs was observed (**Pt-2**, Scheme 1).⁹ However, the previous investigation on **Pt-2** was limited to the photophysical properties such as the

emission wavelength and lifetimes, no detailed study has been carried out to reveal the component of the T_1 state. Furthermore, the characteristic photophysics of **Pt-2**, such as the intense absorption in visible region, high phosphorescence quantum yield

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and long-lived triplet excited state, have never been employed for applications.

We have been interested in photophysics of luminescent transition metal complexes.^{12,13} Inspired by some pioneering works,^{51,53} we prolonged the triplet excited state lifetime of Ru(II) complexes,^{35,54} tuned the emission properties of cyclometalated Pt(II) with naphthalimide,¹⁴ and prepared phosphorescent molecular probes for detection of thiols.³⁶ We also prepared complexes with long lived ³IL excited states for Pt(II) bisacetylide complexes.⁵⁵

Herein we prepared two new cyclometallated Pt(II) acac complexes with the coumarin subunits directly cyclometallated (Pt-3 and Pt-4, Scheme 1), with the aim to access the visible-light harvesting Pt(II) complexes that show long-lived triplet excited states, and to study the relationship between the molecular structure and the emission properties. Room temperature phosphorescence were observed for all the complexes. The complex with the diethylamino appendant on the coumarin moiety (Pt-2) gives the longest luminescent lifetimes, whereas the complexes without the diethylamino substituents give short luminescent lifetimes (Pt-3 and Pt-4). The emissive triplet excites states of the complexes with coumarin subunits (Pt-2, Pt-3 and Pt-4) were assigned as ³IL (intraligand) excited state. We investigated the tripletenergy-transfer of the ³IL excited state of these complexes, *i.e.* for luminescent O₂ sensing and triplet-triplet annihilation (TTA) based upconversion.

Experimental

Materials and reagents

Ethyl 2-(2'-benzothiazolyl) acetate and $[Ru(dmb)_3](PF_6)_2$ were prepared according to literature procedure.^{56,57} *Tert*-butyllithium (1.6 M in pentane) and PtCl₂ were purchased from J&K Chemical Ltd. Other chemicals are analytical pure and were used as received without further purification. Solvents were dried and distilled 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. Luminescent lifetimes were measured on Horiba Jobin Yvon Fluoro Max-4 (TCSPC). Elemental analysis was performed with vario EL III. The melting points were measured with X-4 Melting-point Apparatus. Flow cell coupled to a fluorospectrometer was used in the luminescent O_2 sensing.³⁵

Synthesis of L-3. Under N₂, salicylaldehyde (580.0 mg, 4.75 mmol) was dissolved in anhydrous methanol (70 mL). 2-(2'benzothiazolyl) acetate (1.05 g, 4.75 mmol) and $24 \,\mu\text{L}$ (0.24 mmol) of piperidine were added, and the solution was heated to reflux. Precipitate appeared after 15 min. The mixture was refluxed for a further 5 h. After cooling to room temperature, water (15 mL) was added and the mixture was stirred for 15 min. The precipitate was collected, washed with water and cold methanol (10 mL), then dried under vacuum. A yellow solid was obtained, 1.12 g, yield: 84.4%. ¹H NMR (400 MHz, CDCl₃): δ 9.09 (s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.47–7.44 (m, 2H), 7.40 (t, J = 7.6 Hz, 1H). EI-HRMS m/z: calcd for C₁₆H₉NO₂S ([M]⁺) 279.0354, found 279.0363. M.p. 220.9–222.0 °C

Synthesis of Pt-3. PtCl₂ (129.0 mg, 0.49 mmol) was dissolved in 1 mL of benzonitrile by heating at 160 °C for several minutes. L-3 (80.0 mg, 0.31 mmol) in 2-ethoxyethanol (6 mL) and benzonitrile (18 mL) was added via syringe. The mixture was heated for 1 h at 140 °C. The solution was cooled and diluted with 7 mL of acetone. Then, 276 µL of Hacac and 361 µL of triethylamine were added and the solution was stirred overnight at r.t. Then 25 mL of hexane were added and the precipitate was collected by filtration. The product was purified by column chromatography (silica gel, CH_2Cl_2 : triethylamine = 100 : 2, v/v). Orange solid was obtained, 30.0 mg, 17.7%. Decomposition temperature: 270 °C. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: δ 9.16 (d, J = 8.4 Hz, 1H), 8.98 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.51–7.38 (m, 2H), 7.22–7.20 (m, 2H), 5.57 (s, 1H), 2.04 (s, 3H), 1.96 (s, 3H). MALDI-HRMS m/z: calcd for C₂₁H₁₅NO₄SPt ([M]+) 572.0370, found 572.0391. Anal. Calcd. For C21H15NO4PtS: C, 44.06; H, 2.64; N, 2.45; Found: C, 44.17; H, 2.79; N, 2.42.

Synthesis of 2-Hydroxy-3-naphthaldehyde58

Under N₂, 2-naphthol (1.73 g, 12 mmol) was dissolved in dry tetrahydropyran (6 mL). To the stirred solution, *t*-BuLi (18 mL, 1.6 M in pentane) was added dropwise *via* a syringe at r.t. in *ca*. 12 min, then the solution was stirred for 4 h. At 0 °C, to the solution was added the mixture of DMF (6 mL) and THP (6 mL), then stirred overnight at room temperature. HCl (5.0%) was added to adjust the pH to 5 ~ 6. Then the mixture was extracted with ether (3 × 50 mL). The organic phase was dried over anhydrous Na₂SO₄. The product was purified by column chromatography (silica gel, CH₂Cl₂: hexane = 1 : 1, v/v). Yellow powder was obtained, 0.20 g, yield: 9.7%. M.p. 84.7–85.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.32 (s, 1H), 10.10 (s, 1H), 8.16 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.29 (s, 1H). TOF-HRMS *m/z*: calcd for C₁₁H₇O₂ ([M – H]⁻) 171.0446, found 171.0441.

Synthesis of L-4. Under N₂, 3-hydroxy-2-naphthaldehyde (100.0 mg, 0.58 mmol) was dissolved in anhydrous methanol (9 mL). 2-(2'-benzothiazolyl) acetate (128.6 mg, 0.13 mmol) and $3 \,\mu L$ (0.03 mmol) of piperidine were added, and the solution was refluxed. Precipitate appeared after 0.5 h; the solution was refluxed for 4 h. After cooling to r.t., water (10 mL) was added and the mixture stirred for 15 min. Precipitate was collected with filtration, washed with water and cold methanol (10 mL), and dried under vacuum. An orange solid was obtained, 0.13 g, yield: 70.1%. M.p.: 288.6–299.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.18 (s, 1H), 8.24 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.80 (s, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.56–7.51 (m, 2H), 7.43 (t, J = 8.0 Hz, 1H). ¹³C NMR (100 M Hz, CDCl₃) δ 160.1, 152.7, 150.0, 141.6, 137.2, 135.5, 130.7, 130.6, 129.3, 129.0, 127.9, 126.73, 126.4, 125.7, 123.2, 121.9, 120.9, 119.1, 113.0. ES-HRMS m/z: calcd for C₂₀H₁₂NO₂S ([M]⁺) 330.0589, found 330.0592.

Synthesis of Pt-4. Under N_2 , PtCl₂ (103.0 mg, 0.39 mmol) was dissolved in 1 mL of benzonitrile by heating at 160 °C for several

minutes. L-4 (80.0 mg, 0.24 mmol) in 2-ethoxyethanol (6 mL) and benzonitrile (3 mL) was added *via* syringe. The mixture was stirred for 1 h at 140 °C. The solution was cooled. 353 µL of Hacac and 462 µL of triethylamine were added and the solution was stirred overnight at r.t. Then 10 mL of hexane was added and the precipitate was collected with filtration. The crude product was washed with CH₂Cl₂ and hexane. An orange solid was obtained, 40.3 mg, 27.0%. M.p. > 300 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.81 (s, 1H), 8.96 (d, *J* = 7.6 Hz, 1H), 7.76–7.70 (m, 3H), 7.51–7.52 (m, 2H), 7.42–7.37 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 5.57 (s, 1H), 2.02 (s, 3H), 1.99 (s, 3H). MALDI-HRMS *m/z*: calcd for C₂₅H₁₇NO₄NaSPt ([M+Na]⁺) 645.0424, found 645.0375. Anal. Calcd. For C₂₅H₁₇NO₄PtS (0.33 CH₂Cl₂): C, 46.76; H, 2.74; N, 2.15; Found: C, 46.83; H, 3.16; N, 2.06.

Computational Methods. All calculations were performed using Gaussian 09 W (Gaussian, Inc.).⁵⁹ The gas phase geometry optimizations were calculated using B3LYP functional with the 6-31G(d) basis set. The excitation energy was calculated with the time-dependent DFT (TDDFT) method based on the optimized singlet ground state geometry. The spin-density of the triplet state was calculated with the energy minimized T_1 state geometries.

Upconversions. Diode pumped solid state laser was used as the excitation source for the upconversions. The samples were purged with N₂ 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 standard ($\Phi =$ 0.10 in CH₂Cl₂) and the quantum yields were calculated with eqn (1),⁴¹ where Φ_{unk} , A_{unk} , I_{unk} and η_{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.

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

Results and discussions

Design and synthesis of the complexes

Pt-1 and **Pt-2** were reported to show high phosphorescence quantum yields.⁹ **Pt-2** shows exceptionally long phosphorescence lifetime (27.9 μs).⁹ However, the diversity of the complex structure with directly cyclometallated fluorophore is very limited. Thus, **Pt-3** with coumarin subunit is designed, in which the coumarin subunit is without the electron-donating diethylamino group (Scheme 1). We also designed a complex containing coumarin with larger π-conjugated scaffold (**Pt-4**, Scheme 1). Thus we can reveal the relation between the molecular structure of the coumarin chromophore and the phosphorescence property of the complexes.

The synthesis of the ligands followed the routine procedure (Scheme 1). The *o*-aminothiophenol and ethyl cyanoacetate were used to prepare the ethyl 2-(2'-benzothiazolyl) acetate. The ligand for cyclometallation was synthesized through the piperidine-catalyzed Knoevenagel condensation with substituted *o*-hydroxy aldehydes and ethyl 2-(2'-benzothiazolyl) acetate under mild conditions. 2-hydroxyl-3-naphthalaldehyde is used for synthesis of

coumarin ligand (L-4) of Pt-4, instead of using the commercially available 2-hydroxyl-1-naphthalaldehyde, to avoid steric hindrance of the cyclometallation. The coumarin ligands were treated with $PtCl_2$ and then with Hacac. The compounds were obtained with moderate to satisfying yields (Scheme 1). Complexes Pt-1 and Pt-2 were prepared for comparison.⁹

UV-vis absorption/emission spectra of the ligands and the complexes

Ligand L-1 shows absorption in UV region (290 nm). Conversely, the ligands with coumarin subunit show absorption in visible range. For example, L-2 shows intense absorption at 464 nm (ε = 50600 M⁻¹ cm⁻¹). Interestingly, the coumarin ligand with large π -conjugation (L-4) does not show red-shifted absorption compared to L-2. The red-shifted absorption of L-2 may be due to the more significant intramolecular charge transfer (ICT) feature of the ligand.

Compared to the absorption of ligands, the Pt(II) complexes generally show bathochromically shifted absorptions (Fig. 1b). The absorption of the complexes in the visible region are due to the $S_0 \rightarrow {}^1MLCT/{}^1IL$ transitions.^{1,9} Absorption bands of the ligand $\pi - \pi$ transition are at *ca.* 380 nm. **Pt-2** shows intense absorption at 496 nm ($\varepsilon = 47800 \text{ M}^{-1} \text{ cm}^{-1}$). This significant light-harvesting ability is ideal for applications.



Fig. 1 UV-vis absorption spectra of (a) the ligands and (b) the Pt(II) complexes. In CH₂Cl₂ ($c = 1.0 \times 10^{-5}$ M; 25 °C).

The emission maxima of the ligands are dependent on the π -conjugation and the ICT character of the ligands (Fig. 2a). For example, L-4 with large π -conjugation shows the red-shifted emission than L-3. However, L-2 shows red-shifted emission at 497 nm compared to L-3 and L-4. This result indicates that the fluorescence emission of the ligands is mainly dependent on the ICT feature fluorophore (Table 1). For example, L-2 shows quantum yield up to 0.613, conversely L-3 and L-4 show much lower quantum yield of 0.175% and 0.026%, respectively.

| | $\lambda_{ m abs}~({ m nm})^a$ | λ_{ex} (nm) | $\lambda_{\rm em} \ ({\rm nm})^b$ | ${\varPhi_{\mathrm{f}}}^{c}$ | ${\varPhi_{\mathrm{p}}}^d$ | au (ns) | $k_{\mathrm{r}} (\mathrm{s}^{\scriptscriptstyle -1})^{e}$ | $k_{\mathrm{nr}} (\mathrm{s}^{-1})^{e}$ |
|------|--|------------------------------|-----------------------------------|------------------------------|----------------------------|----------------------|--|--|
| L-1 | 299 (1.77) | 313 | 363 | 0.009 | h | 0.91 ns | 9.9×10^{6} | 1.1×10^{9} |
| L-2 | 448 (5.03), 464 (5.06) | 475 | 497 | 0.613 | h | 2.52 ns | 2.4×10^{8} | 1.5×10^{8} |
| L-3 | 364 (3.76) | 389 | 452 | 0.175 | h | 1.21 ns | 1.4×10^{8} | 6.8×10^{8} |
| L-4 | 289 (0.17), 300 (0.14), 376 (0.37) | 402 | 475 | 0.026 | h | 2.39 ns | 1.1×10^{7} | 4.1×10^{8} |
| Pt-1 | 256 (2.31), 316 (1.80), 331 (1.63), 385 (0.76) | 404 | 543, 585 | h | 0.36 | 0.34 µs | 1.1×10^{6} | 1.87×10^{6} |
| Pt-2 | 302 (1.31), 389 (2.18), 469 (3.84), 496 (4.78) | 476 | 596, 646 | h | 0.37 ^f | 20.3 µs ^g | 1.8×10^{4} | 3.0×10^{4} |
| Pt-3 | 281 (1.61), 346 (1.21), 364 (1.42), 404 (1.18), 443 (0.69), 472 (0.50) | 476 | 597, 650 | h | 0.03 | 1.59 μs | 1.9×10^{4} | 3.8×10^{5} |
| Pt-4 | 259 (3.66), 301 (1.99), 370 (2.11), 414 (1.55), 455 (1.21), 487 (0.86) | 472 | 629, 686 | h | 0.01 | 1.28 µs | 9.6×10^{3} | 7.7×10^{5} |

Table 1 Photophysical parameters of platinum complexes Pt-1–Pt-4 and the ligands L-1–L-4 (the data of the known complexes Pt-1 and Pt-2 are presented for comparison)

^{*a*} Extinction coefficients (10⁴ M⁻¹ cm⁻¹) are shown in parentheses. ^{*b*} Asterisks indicate emission peaks appearing as shoulders or weak bands. ^{*c*} Quantum yield of fluorescence in CH₂Cl₂. ^{*d*} Quantum yield of phosphorescence in CH₂Cl₂. ^{*e*} radiative deactivation rate constant (k_{n}) and non-radiative deactivation rate constant (k_{n}). $k_{r} = \phi_{em}/\tau_{em}$; $k_{nr} = 1/\tau_{em}(1 - \Phi_{em})$. It is assumed that the emitting excited state is produced *vis* ¹MLCT/¹IL \rightarrow ³MLCT/³IL with unit efficiency. ^{*f*} literature value is 0.25 µs in 2-methyltetrahydrofuran solutions. ^{*s*} *k* literature value is 27.9 µs, in 2-methyltetrahydrofuran. ^{*s*} Not applicable.



Fig. 2 Normalized emission spectra of (a) the ligands and (b) the complexes. The known complexes Pt-1 and Pt-2 were studied for comparison. In CH₂Cl₂ ($c = 1.0 \times 10^{-5}$ M; 25 °C).

Room temperature (r.t.) emissions beyond 500 nm were found for the complexes, especially for **Pt-2**, which shows emission bands at 596 nm (Fig. 2b). **Pt-4** gives more red-shifted emission at 629 nm. R.t. phosphorescence in deep-red and near-IR region is in particularly interesting because these materials can be used as emitters for optical fiber communications.⁶⁰ The large Stokes shifts of the emissions, and the significant quenching of O_2 on the emission support the assignment of the emission as phosphorescence.^{1,61,62}

Interestingly, **Pt-3** and **Pt-2** show the same emission wavelength, despite the drastically different ICT feature of the ligands, as well as the different fluorescence emission of the ligands (Fig. 2a). **Pt-4**, the complex with the large π -conjugation ligand, however, shows the most red-shifted emission (by 33 nm compared to **Pt-2** and

Pt-3). Interestingly, ligand **L-4** emits at shorter wavelength than **L-2** (Fig. 2a).

The efficiency of the light-harvesting of coumarin-containing complexes is dependent on the relative energy levels of the ¹IL state of the ligand and the ¹MLCT state of the complex.^{52,60,63} In order to study the light-harvesting effect of the coumarin-containing complexes, the excitation spectra of the complexes were also studied and were compared with the UV-vis absorption spectra of the complexes (ESI[†]). We found that the excitation spectra of the complexes are superimposable to the UV-vis absorption, which indicate efficient energy transfer between ¹IL/¹MLCT state and the ³MLCT state.⁶³

The photophysical properties of the ligands and complexes were summarized in Table 1. Notably **Pt-1** and **Pt-2** show high room temperature phosphorescence quantum yield, up to 0.362 and 0.371, respectively.⁹

Pt-2 shows the longest luminescent lifetimes among the complexes studied (τ = 20.3 µs).⁹ Without the diethylamino substituent, **Pt-3** and **Pt-4** show much shorter luminescent lifetimes (τ = 1.59 µs and 1.28 µs, respectively). We noticed that a cyclometallated Ir(III) complexes with the same coumarin ligand of **Pt-2** was reported.⁶⁴ However, that Ir(III) complex show shorter luminescent lifetime (τ = 11.3 µs).⁶⁴

³IL Triplet excited state: assignment of the emissive excited states of the cyclometallated complexes with DFT/TDDFT calculations

The electronic structure of the lowest-lying triplet excited states of the transition metal complexes can be revealed with the DFT calculations, thus components of the emissive triplet excited states (³IL or ³MLCT) can be assigned, and the emission property of the complexes can be predicted to some extent.^{12-14,35–36,65–72}

Firstly the ground state geometry of **Pt-2** was optimized with DFT calculations. Planar square coordination geometry was found for the Pt(II) centers (Fig. 3). The coumarin and acac auxiliary ligands take co-planar geometry. Thus large π -conjugation was expected for this complex.

The frontier molecular orbitals were examined (Fig. 3). Coumarin contributes significantly to both the HOMO and LUMO. The Pt(II) atom contributes only slightly to the HOMO and LUMO. In order to investigate the UV-Vis absorption, the singlet excited states of Pt-2 were studied with the TDDFT calculations (Table 2). Large oscillator strength was observed for the



Fig. 3 Frontier molecular orbitals of **Pt-2**. Calculated at the B3LYP/6-31G((d)/LanL2DZ level using Gaussian 09W.

 $S_0 \rightarrow S_1$ transition (f = 0.5457), thus we expect intense absorption is correlated to the $S_0 \rightarrow S_1$ transition, which is supported by the experimental results (Fig. 1b). The calculated S_1 state is with excitation energy of 427 nm, which is close to the absorption at 469 nm (Fig. 1b). Thus the absorption at 427 nm is assigned as ¹IL/¹MLCT, based on the distribution of the electron density of the molecular orbitals (Fig. 3).

The triplet excited states of **Pt-2** were also studied with the TDDFT calculations based on the optimized ground state geometry (Table 2). The calculated $S_0 \rightarrow T_1$ energy gap is 2.17 eV (572 nm), which is close to the emission wavelength at 596 nm (Fig. 2b). The T_1 state can be assigned as ³IL state, mixed with ³MLCT feature. Thus the long phosphorescence lifetime of **Pt-2** may be due to the ³IL T_1 state.

Pt-1 was also studied with DFT/TDDFT calculations (ESI[†]). The calculated $S_0 \rightarrow T_1$ energy gap is 505 nm, which is close to the experimental emission at 543 nm (Fig. 2b).⁷³ However, we found significant contribution of the Pt(II) ion to the HOMO and LUMO of **Pt-1**. Thus we expect **Pt-1** will show shorter phosphorescence lifetime than that of **Pt-2**.³⁵

The singlet excited states of **Pt-4** were also studied with DFT/TDDFT calculations. The geometry of the **Pt-4** was optimized and the frontier molecular orbitals were presented in Fig. 4. The HOMO and LUMO orbitals are localized on coumarin ligand with minor contribution from Pt(II).



Fig. 4 Frontier molecular orbitals of **Pt-4**. Calculated at the B3LYP/6-31G((d)/LanL2DZ level using Gaussian 09W.

The singlet excited state of **Pt-4** was studied (Table 3). The $S_0 \rightarrow S_1$ excitation energy is calculated as 429 nm, with much smaller oscillator strength (f = 0.2797), which indicate weak absorption compared to **Pt-2** (for which the *f* value is larger).

The calculated $S_0 \rightarrow T_1$ energy gap is 2.02 eV (Table 3), which is much smaller than that of **Pt-2**. Indeed we observed emission at 629 nm for **Pt-4**, which is red-shifted by 33 nm compared to **Pt-2**. Minor involvement of the Pt(II) is found for the T_1 state. Based on the electronic composition of the transition, the T_1 state can be assigned as ³IL state.

We studied the spin density of T_1 state (Fig. 5). The spin density contours of the complexes are localized on the thiazo ligands. The Pt(II) ions contribute to the spin density. For the acac ligands, however, no contribution was found. This result indicates that the triplet state are independent on the acac ligands, and it is the $C^{\Lambda}N$ cyclometalation ligands that dictate the photophysical properties of the complexes.^{5,45}

Enhanced phosphorescent O₂ sensing

Luminescent O_2 sensing is based the quantitative relation between the quenched phosphorescence of transition metal complexes and the O_2 partial pressure,^{61,62,74} We have been interested in luminescent O_2 sensing and we found that the long-lived ³IL state is more sensitive O_2 sensing than the ³MLCT state.^{14,35,75} Usually Ru(II) polypyridine complexes or Pt(II) porphyrin complexes were

Table 2 Electronic excitation energies (ev) and corresponding oscillator strengths (f), main configurations and CI coefficients of the low-lying electronically excited states of complex Pt-2, calculated by TDDFT, based on the ground state geometries

| | Electronic transition | TDDFT//B3LYP/6-31G(d) | | | | | | |
|---------|-----------------------|-----------------------|---------|--------------------------|-----------------|------------------------|--|--|
| | | Energy ^a | f^{b} | Composition ^e | CI^d | Character ^e | | |
| Singlet | $S_0 \rightarrow S_1$ | 2.90 eV 427 nm | 0.5457 | $H-2 \rightarrow L$ | 0.1461 | LLCT & MLCT | | |
| | | | | $H \rightarrow L$ | 0.6257 | IL | | |
| | $S_0 \rightarrow S_3$ | 3.38 eV 353 nm | 0.1753 | $H-6\rightarrow L$ | 0.1077 | | | |
| | | | | $H-2 \rightarrow L$ | 0.1467 | LLCT & MLCT | | |
| | | | | $H-1 \rightarrow L$ | 0.6266 | IL & LLCT | | |
| | | | | $H \rightarrow L$ | 0.1208 | IL | | |
| | | | | $H \rightarrow L+1$ | 0.1170 | LLCT | | |
| | $S_0 \rightarrow S_5$ | 3.60 eV 345 nm | 0.1365 | $H-6\rightarrow L$ | 0.1242 | | | |
| | | | | $H-2 \rightarrow L$ | 0.6182 | LLCT & MLCT | | |
| | | | | $H-1 \rightarrow L$ | 0 1873 | IL & LLCT | | |
| | | | | H→L. | 0 1120 | II. | | |
| Triplet | $S_a \rightarrow T_a$ | 2 17 eV 572 nm | 0.0000 | $H_{-2} \rightarrow I$ | 0.1206 | LLCT & MLCT | | |
| mpier | | 2.17 CV 372 min | 0.0000 | $H \rightarrow L$ | 0.7351 | IL | | |

^{*a*} Only the selected low-lying excited states are presented. ^{*b*} Oscillator strength. ^{*c*} H stands for HOMO and L stands for LUMO. Only the main configurations are presented. ^{*d*} The CI coefficients are in absolute values. ^{*e*} IL: intraligand, LLCT: ligand-to-ligand charge transfer, MLCT: metal-to-ligand charge transfer. ^{*f*} No spin-orbital coupling effect was considered, thus the *f* values are zero.

Table 3 Electronic excitation energies (eV) and corresponding oscillator strengths (*f*), main configurations and CI coefficients of the low-lying electronically excited states of complex **Pt-4**, calculated by TDDFT based on the optimized ground state geometries

| | | TDDFT//B3LYP/6-31G(d) | | | | | | |
|---------|---|------------------------------------|------------------|--|----------------------------|------------------------|--|--|
| | Electronic transition | Energy ^a f ^b | | Composition ^e | CI^d | Character ^e | | |
| Singlet | $S_0 \rightarrow S_1$ | 2.89 eV 429 nm | 0.2797 | $\begin{array}{c} H-2 \rightarrow L \\ H \rightarrow L \end{array}$ | 0.1261 | LLCT IL | | |
| | $\begin{array}{c} \mathbf{S}_0 \rightarrow \mathbf{S}_3 \\ \mathbf{S}_0 \rightarrow \mathbf{S}_5 \end{array}$ | 3.29 eV 376 nm 3.65 eV 340 nm | 0.1294 0.1920 | $ \begin{array}{c} H \rightarrow L \\ H - 2 \rightarrow L \\ H - 6 \rightarrow L \end{array} $ | 0.6636 0.1153 | LLCT | | |
| | $S_0 \rightarrow S_{15}$ | 4.21 eV 294 nm | 0.1418 | $\begin{array}{c} H-3 \rightarrow L \\ H-9 \rightarrow L \end{array}$ | 0.6396 0.1232 | LLCT | | |
| Triplet | S T | 2.02 eV 615 nm | 0.0000 | $\begin{array}{c} H - 6 \rightarrow L \\ H \rightarrow L + 2 \\ H - 1 \rightarrow L + 2 \end{array}$ | 0.5036 0.3527 0.1738 | IL IL & MI CT | | |
| mplet | $3_0 \rightarrow 1_1$ | 2.02 CV 015 mm | 0.0000 | $\begin{array}{c} H=1 \rightarrow L+2 \\ H\rightarrow L \\ H\rightarrow L+2 \end{array}$ | 0.1738 0.7411 0.1328 | IL & MECT IL IL | | |

^{*a*} Only the selected low-lying excited states are presented. ^{*b*} Oscillator strength. ^{*c*} H stands for HOMO and L stands for LUMO. Only the main configurations are presented. ^{*d*} The CI coefficients are in absolute values. ^{*e*} IL: intraligand, LLCT: ligand-to-ligand charge transfer, MLCT: metal-to-ligand charge transfer. ^{*f*} No spin-orbital coupling effect was considered, thus the *f* values are zero.



Fig. 5 Spin density surfaces of the T_1 excited state of Pt-1, Pt-2, Pt-3 and Pt-4. Based on the optimized triplet state geometry.

used for the O₂ sensing.^{61,62,64} However, to the best of knowledge, little O₂ sensing has been performed with cyclometallated Pt(II) complexes.^{1,46} Thus the O₂ sensing properties of the complexes were studied in detail. For **Pt-2**, the intense absorption in visible region ($\varepsilon = 47800 \text{ M}^{-1} \text{ cm}^{-1}$ at 496 nm), long phosphorescence lifetime ($\tau =$ 20.3 µs) and the high phosphorescence quantum yield (0.371) are ideal for application for O₂ sensing. Firstly the O₂ sensitivities of the complexes were studied in solution (Fig. 6 and ESI†). For **Pt-1**, the phosphorescence was quenched by 89.2% in air compared to that in N₂. The emission is almost completely quenched in neat O₂. For **Pt-2**, however, the emission in air is almost completely quenched (Fig. 6a), For **Pt-3**, however, the quenching effect is lower than that of **Pt-2**. For example, the emission of **Pt-2** is



Fig. 6 Emission spectra of (a) **Pt-2**, $\lambda_{ex} = 476$ nm, and (b) **Pt-3**, $\lambda_{ex} = 476$ nm. In CH₂Cl₂ solution saturated with air, oxygen and nitrogen, respectively. $c = 1.0 \times 10^{-5}$ M, 25 °C.

quenched by 98.9% in air, compared to 73.6% for **Pt-3**. **Pt-4** shows lower O_2 sensitivity than **Pt-2** (ESI[†]).

In order to quantitatively compare the O_2 sensing property of the complexes, the O_2 sensing in polymer films were studied (Fig. 7). **Pt-4** was not studied in the film due to its poor emission property. Two type of sensing experiments were carried out, *i.e.* the phosphorescence response of the films toward the switch between N_2 and O_2 (Fig. 7a, b), and the dynamic response of the sensing films toward step variation of the O_2 partial pressure (Fig. 8c, d). The response time t_495 and recovery time $t_{\uparrow}95$ were used to characterize the response dynamics. Fast response (0.6 s) and recovery (0.9 s) were observed for the sensing films. For **Pt-1**, we found the quenching of the phosphorescence is not significant, *e.g.* the emission is quenched by 23.9% in neat O_2 (ESI†). For **Pt-2**, however, the sensitivity is much higher, *e.g.* the emission intensity is quenched by 91.3% in O_2 (Fig. 7a). **Pt-3** shows much lower sensitivity for oxygen sensing (Fig. 7b).

800 N a.u. Ν 800 N a.u. Emission intensity intensity / 600 600 3.5% O 3.5% 4.3% 6.8% 4.3% 400 400 10% 10% Emission 5% O 200 ⁄20%. 200 Pt-2 10% O, air С Pt-2 30% `30% 50% 0 а 0 0 Ó 1200 1600 400 800 400 800 1200 1600 0 Time / s Time / s 908 r. a.u. 800 N air 0 intensity 70 % O_{2 50} % O₂ 600 N, ntensity / 600 400 % 80% 90% 400 Emission Emission 200 200 Pt-3 b d Pt-3 0 0 400 800 1200 1600 0 400 1200 1600 800 0 Time / s Time / s

Fig. 7 Phosphorescence response of the complexes to step variations of O₂ concentration. (a) and (c) Pt-2, $\lambda_{ex} = 476$ nm, $\lambda_{em} = 650$ nm. (b) and (d) Pt-3. $\lambda_{ex} = 476$ nm, $\lambda_{em} = 596$ nm. 25 °C.



Fig. 8 Two-sites model plots for sensing film of **Pt-1**, **Pt-2** and **Pt-3** in IMPEK-C. Intensity ratios $I_0/I vs. O_2$ partial pressure (Torr).

The response of the films toward small step of O_2 partial pressure variation was also studied (Fig. 7c, d). The response of **Pt-1**, **Pt-3** are small (Fig. 7b and ESI[†]) but the response of **Pt-2** is more significant (Fig. 7c). The phosphorescence of the sensing films are fully reversible, *i.e.* the emission intensity is fully recovered even after long time of continuous irradiation, indicating good photostability of the complexes, which is ideal for O_2 sensing applications.^{61,62} Significant photobleaching (photodecomposition) was observed for a previously reported Ir(III) complex (the UV-vis absorbance decreased by *ca.* 80% within 20 min of irradiation).⁶⁴ For **Pt-2**, no photobleaching was observed even with 30 min continuous irradiation (Fig. 7).

 O_2 sensing with the polymer films (a heterogeneous system) can be described by the two-site model.^{61,62,76,77} In this model, the dye molecules are considered to be distributed in two different microenvironments in the polymer film, which are defined as f_1 and f_2 , respectively ($f_1 + f_2 = 1$), each portion is with different O_2 accessibility, *i.e.* the two portions show different quenching constants (K_{SV1} and K_{SV2} , eqn (2)).

$$\frac{I_0}{I} = \frac{1}{\frac{f_1}{1 + K_{SV1}p_{O_2}} + \frac{f_2}{1 + K_{SV2}p_{O_2}}}$$
(2)

The O₂ sensing data (Fig. 7 and ESI[†]) were fitted with eqn (2) (Fig. 8). The quenching constants obtained from the fitting were listed in Table 4. The quenching constant of **Pt-2** is 13.6-fold of that **Pt-1**. We compared the O₂ sensing of **Pt-2** with a recently reported cyclometalated Ir(III) complexes (with triphenylamine caped 2-phenylpyridine ligand).⁴⁶ The K_{sv} of **Pt-2** is 7.4-fold of the triphenylamine caped cyclometalated Ir(III) complexes. We noticed that a cyclometallated Ir(III) complexes with the coumarin ligand was used for O₂ sensing.⁶⁴ However, that Ir(III) complex show much shorter phosphorescence lifetime (11.3 µs) than **Pt-2**. The O₂ sensitivity of **Pt-2** is *ca.* 8.0-fold of the Ir(III) complex (for which $K_{sv} = 0.0032$ Torr⁻¹).⁶⁴

Enhanced triplet-triplet-annihilation based upconversion

Triplet-triplet-annihilation (TTA) based upconversion has attracted much attention (eqn (3)),⁷⁸⁻⁸⁰ and is believed to be promising for practical applications, such as to improve the efficiency of dye-sensitized solar cells.^{78,81}

³Sensitizer* + Acceptor \rightarrow Sensitizer + ³Acceptor* (TTET) (3)

| Table 4 | Parameters of O ₂ sensing film of complex Pt-1, Pt-2 and Pt-3 |
|---------|--|
| with IM | PEK-C as supporting matrix (fitting result of the two site model) |

| | f_1^a | f_2^a | $K_{SV1}{}^{b}$ | K_{SV2}^{b} | $K_{ m SV}{}^{ m app \ c}$ | pO_2^d |
|------|---------|---------|-----------------|---------------|----------------------------|----------|
| Pt-1 | 0.7503 | 0.2497 | 0.0001 | 0.0073 | 0.00190 | 526.9 |
| Pt-2 | 0.9146 | 0.0854 | 0.0282 | 0.0004 | 0.02583 | 38.7 |
| Pt-3 | 0.8781 | 0.1219 | 0.0000 | 0.0024 | 0.00029 | 3418.1 |

^{*a*} Ratio of the two portions of dyes. ^{*b*} Quenching constants of the two portions. ^{*c*} Weighted quenching constant, $K_{SV}^{app} = f_1K_{SV1} + f_2K_{SV2}$. ^{*d*} The oxygen partial pressure at which the initial emission intensity of the film is quenched by 50% and calculated as $1/K_{SV}$. In Torr.

 3 Acceptor* + 3 Acceptor* \rightarrow 1 Acceptor* + Acceptor (TTA)

¹Acceptor * \rightarrow Acceptor + hv (emission of fluorescence)

This modular upconversion is in particular promising for applications because the excitation and emission wavelength can be tuned by independent selection of the sensitizer and the annihilator (see ESI for the Jablonski diagram which demonstrates the photophysical processes[†]).⁴⁰⁻⁴⁴

However, the present understanding of the photophysics involved in TTA based upconversion is still premature. Little is known on the effect of the excited state lifetimes on the upconversion efficiency.⁷⁹ It is important to use complexes with intense visible-light absorption capability and long-lived triplet excited states for the TTA based upconversion, but the related reports are rare.

Firstly, the emission spectra of the complexes with 473 nm laser excitation were studied (Fig. 9a). Only **Pt-2** gives intense emission. Weak emission was observed for other complexes, which is due to either the poor absorption in the 473 nm region (**Pt-1**) or low phosphorescence quantum yield (**Pt-3**, **Pt-4** and $[Ru(dmb)_3]^{2+}$). [Ru(dmb)₃]²⁺ gives very weak emission, which is one ninth of **Pt-2** (Fig. 9a).



Fig. 9 (a) Emission of **Pt-1**, **Pt-2**, **Pt-3**, **Pt-4** and $[\text{Ru}(\text{dmb})_3]^{2+}$ (1.0 × 10⁻⁵ M) with excitation by 473 nm laser (5 mW). (b) Emission of the upconverted fluorescence of 9,10-diphenylanthracene (DPA, 4.3 × 10⁻⁵ M) and the residual photoluminescence of **Pt-1**, **Pt-2**, **Pt-3**, **Pt-4** and $[\text{Ru}(\text{dmb})_3][\text{PF}_{6]_2}$ (1.0 × 10⁻⁵ M) in the upconversion experiments. Excitation by 473 nm laser (5 mW). The asterisks denote the scattered laser at 473 nm. 25 °C.

Next, 9,10-diphenylanthracene (DPA) was added into the solution of the complexes and the emission of the mixtures upon 473 nm laser excitation were studied (Fig. 9b). The phosphorescence of **Pt-2** was quenched in the presence of DPA. Concurrently, the characteristic blue fluorescence emission of DPA was observed

| Table 5 | Luminescence lifetimes (τ), Stern–Volmer quenching constants |
|--------------------|--|
| $(K_{\rm sv})$ and | l bimolecular quenching constants (k_q) of the Pt-2, Pt-3, Pt-4 and |
| [Ru(dmb) | ₃] ²⁺ complexes. In deaerated CH ₂ Cl ₂ . 25 °C |

| | τ/µs | $K_{\rm sv}/10^3 {\rm M}^{-1}$ | $k_{\rm q}/10^9~{ m M}^{-1}~{ m s}^{-1}$ | $\Phi_{ m UC}/\%$ |
|---------------------------------------|------|--------------------------------|--|-------------------|
| Pt-2 | 20.3 | 133.46 | 6.57 | 15.4 |
| Pt-3 | 1.59 | 8.22 | 5.17 | 5.3 |
| Pt-4 | 1.28 | 8.20 | 6.40 | 2.8 |
| [Ru(dmb) ₃] ²⁺ | 0.84 | 3.93 | 4.68 | 1.2 |

(Fig. 9b). For $[Ru(dmb)_3][PF_6]_2$, however, the phosphorescence is not quenched and no significant upconverted fluorescence was observed (Fig. 9b). Irradiation of DPA alone at 473 nm does not produce any emission. Little upconverted emissions were observed with **Pt-1**, **Pt-3** and **Pt-4**.

It should be pointed out that upconversion is dependent on the experimental conditions, such as sensitizer/acceptor concentrations, excitation power and excitation wavelength, *etc.* However, our results show that the upconversion threshold for **Pt-2** is much lower than that of other complexes.

The concentration of the DPA in our upconversion is much lower than that in literatures $(10^{-4} \text{ M-}0.1 \text{ M})$.^{43,44,79,82} The lowthreshold of the upconversion with **Pt-2** demonstrated the significant effect of light-harvesting and the long-lived ³IL triplet excited state of the sensitizer on the upconversion. Upconversion with 532 nm laser excitation was also investigated and similar results were observed (ESI[†]).

The key step for TTA upconversion is TTET (see the Jablonski diagram in ESI[†]). In order to study the TTET quantitatively, the quenching effect of DPA on the phosphorescence of sensitizers were studied and the Stern–Volmer quenching curves were constructed (Fig. 10).^{61,62,79}



Fig. 10 Stern–Volmer plots generated from intensity quenching of complex [Ru(dmb)₃]²⁺, Pt-2, Pt-3, Pt-4 photoluminescence measured as a function of DPA concentration in CH₂Cl₂. The concentrations of all the complexes are 1.0×10^{-5} mol dm⁻³. $\lambda_{ex} = 473$ nm. 25 °C.

Stern–Volmer quenching constant $K_{\rm sv} = 1.33 \times 10^5 \, {\rm M}^{-1}$ was observed for **Pt-2**, which is at least of 33-fold of [Ru(dmb)₃][PF₆]₂ ($K_{\rm sv} = 3.93 \times 10^3 \, {\rm M}^{-1}$), a benchmark triplet sensitizer for TTA upconversion. This is due to the longer T₁ state lifetime and the significant light-harvesting effect of **Pt-2** than that of [Ru(dmb)₃][PF₆]₂. The Stern–Volmer constant of **Pt-2** is also much higher than **Pt-3** and **Pt-4** (Table 5).

The upconversion quantum yields were determined. The model complex $[Ru(dmb)_3][PF_6]_2$ shows a low quantum yield of 1.2%. For **Pt-3** and **Pt-4**, higher quantum efficiency of 5.3% and 2.8% were observed, respectively. Complex **Pt-2** shows intense absorption

in visible region (Fig. 1b) and the longest triplet excited lifetime among the complexes studied (20.3 μ s, Table 1). An upconversion quantum yield of 15.4% was observed. This high efficiency exceeds the theoretical maximum of 11.1% and is among highest values ever reported. Recently it was proposed that molecular encounters with spin manifold other than triplet is also effective for the upconverted fluorescence.⁴² Herein **Pt-2** is an example that upconversion quantum efficiency higher than the theoretical maximum can be achieved. The high upconversion quantum yield of **Pt-2** is due to its intense absorption and its long-lived triplet state.

The emission of the complexes alone and the upconversion with 473 nm laser excitation were visible with the unaided eye (Fig. 11). For the complexes alone (Fig. 11a), the phosphorescences were observed with 473 nm laser excitation. **Pt-2** gives the strongest emission (saturation was observed for the digital photography). **Pt-4** shows the weakest emission but with deep-red color (the longest emission wavelength, Fig. 2b). With addition of the annihilator/acceptor into the solution, the upconverted blue fluorescence of DPA were observed for **Pt-2**, **Pt-3** and **Pt-4**, among which **Pt-2** shows the most intense blue emission (Fig. 11b).



Fig. 11 The photographs of (a) the emission of the complexes alone and (b) the upconversion, *i.e.* emission of the mixed solution of sensitizers and DPA. 473 nm laser excitation (5 mW). In deaerated CH₃Cl₂. *c*[sensitizers] = 1.0×10^{-5} M. *c*[DPA] = 4.3×10^{-5} M. 25 °C.

Conclusions

We have studied the phosphorescence of cyclometallated Pt(II) complexes that with the thiazo-coumarin ligand directly cyclometallated. Room temperature phosphorescences were observed for all the complexes. The emission wavelength of the complexes are dependent on the extent of the π -conjugation of the ligands, but the fluorescence emission of the ligands is more sensitive to the ICT feature of the ligands. The emissive excited state of the complexes were assigned as ³IL triplet excited state with DFT/TDDFT

calculations. The complexes were used for luminescent O₂ sensing and triplet–triplet-annihilation based upconversion. The O₂ sensitivity of the **Pt-2** sensing film is 8.0-fold of a recently reported cyclometallated Ir(III) complex. The TTET efficiency of **Pt-2** in upconversion ($K_{sv} = 1.33 \times 10^5 \text{ M}^{-1}$, $k_q = 6.57 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. DPA as quencher) is 33-fold of [Ru(dmb)₃][PF₆]₂, a benchmark triplet sensitizer for TTA based upconversion. The upconversion quantum yield of **Pt-2**/DPA is up to 15.4%. We propose that the complexes with intense absorption in visible region and long-lived emissive ³IL excited states can be accessed with direct cyclometallation of the organic fluorophores; this approach will be useful for design of new phosphorescent transition metal complexes and for their applications in luminescent O₂ sensing, photocatalysis, triplet–triplet-annihilation based upconversion, *etc.*

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