Tuning the emission properties of cyclometalated platinum(II) complexes by intramolecular electron-sink/arylethynylated ligands and its application for enhanced luminescent oxygen sensing[†]

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We have synthesized five novel cyclometalated Pt(II) complexes (aryl-ppy)Pt(acac) (ppy = 2-phenyl pyridine, aryl = N-butyl naphthalimide (NI) ethynylene for **Pt-1**, N-butyl naphthalimide (NI)–CH₂ -CO- for Pt-2, 4-cyanophenyl $-CH_2-CO-$ for Pt-3, naphthal ethynylene for Pt-4 and naphthal-diketo for **Pt-5**). For the first time, π -conjugation of the *ppy* ligands was extended *via* the C=C bond. Deep red/near IR emission (638 nm-700 nm) was observed for the complex containing naphthalimide ethynylene subunit (Pt-1), whereas the close analogue Pt-2 (in which the linker between the NI and the ppy subunit is a -CH₂CO- group) shows a relatively blue-shifted emission (540 nm-570 nm) but much longer luminescent lifetime ($\tau = 25.5 \ \mu s$) than Pt-1 ($\tau = 6.6 \ \mu s$). Simultaneous fluorescence/ phosphorescence emissions were observed for Pt-1 and Pt-2, but other complexes show sole phosphorescent emission. The red-shifted phosphorescence of the complexes compared to the model complex ppyPt(acac) (486 nm) was attributed to either the significant electron-sink effect of the NI fragment (Pt-1) (for which the electron withdrawing effect is stronger than the previously reported fluoren-9-one), or the extended π -conjugation of the *ppy* ligand (*via* C=C bond) (*e.g.* Pt-4). The substantial tuning of the emission color and the luminescent lifetimes ($0.86 \,\mu\text{s}$ -25.5 μs) of the complexes were rationalized by theoretical calculations (DFT/TDDFT), *i.e.* the emissive triplet excited states were assigned as the normal ³MLCT state (give smaller τ values) or the novel ligand-localized ³IL emissive state (give larger τ values). With tuning the luminescent lifetimes, the luminescent O₂ sensitivity of the complexes was improved by 117-fold (Stern–Volmer quenching constants $K_{SV} = 0.234$ Torr⁻¹ for Pt-2 *vs.* $K_{SV} = 0.002 \text{ Torr}^{-1}$ for **Pt-5**).

Introduction

Cyclometalated Pt(II)/Ir(III) complexes have attracted much attention due to their applications as phosphorescent emitters in organic light emitting diodes (OLEDs).^{1–22} The emissive excited state of these complexes are intra-ligand or metal-to-ligand-charge-transfer triplet states (³IL/³MLCT). Concerning the application for OLEDs, one of the critical issues is to tune the emission color of the complexes.⁵ To this end, the routine molecular tailoring approach is to attach electron-donating substituents on the phenyl group of the 2-phenylpyridine (*ppy*) ligand (where HOMO is localized), or electron-withdrawing

groups to the pyridine group of the *ppy* moiety (where the LUMO is localized), thus the energy gap between the HOMO and LUMO will be decreased and a red-shifted emission will be observed.⁴ However, this methodology shows limited capability to tune the emission wavelength.⁴ Alternatively the *ppy* ligand is substituted with heterocyclic compounds, such as coumarin *etc.*, to tune the emission wavelength.^{4,8}

Recently we have been interested in luminescent transition metal complexes and the exploration of their potential to be used as molecular sensing materials, such as O2 sensors.^{23,24} Most of the O₂ sensors are based on the quenching of the phosphorescence of transition metal complexes by O2, such as Ru(II) polyimine complexes (luminescent lifetime τ in μ s range), etc.^{6,7,23–25} The ideal lumophores, however, will be those that show longer τ values, which lead to higher sensitivity.23,24 The lifetimes of Ru(II) polyimine complexes can be tuned with the introduction of specific organic chromophores, such as pyrene.^{24a} Recently cyclometalated Ir(III) complexes have been used for O₂ sensing.²⁵ However, very few efforts have been made to tune the emission lifetimes of the cyclometalated Pt(II)/Ir(III) complexes. Moreover, lumophores that show simultaneous fluorescence/phosphorescence dual emission will have more potential when used as O2 sensing materials.22,23 This kind of signal transduction for O2 sensing is superior to the emission intensity-based sensors, which

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is liable to be affected by many experimental uncertainties, such as the photobleaching of the dyes, the drifting of the excitation power, *etc.*^{6,7,22,26,27}

Inspired by the aforementioned challenge as well as the recent progress of cyclometalated Pt(II) complexes and the O₂ sensing materials,^{8,12,14,19,20,22,28} herein we set out to explore new strategies to tune the emission color of cyclometalated complexes by changing the electronic structure of the excited states with an intramolecular electron sink,^{5d} and to study the applications of these phosphorescent materials for luminescent O₂ sensing.

Herein we synthesized five new cyclometalated Pt (II) complexes with arylethynylene subunits on the ppy ligands.⁵ To the best of our knowledge, this is the first time that ethynylated ligands ($-C \equiv C_{-}$) were used to extend the π -conjugation of the ppy ligands of cyclometalated Pt(II) complexes.⁴ We used an electron sink to tune the emission color of the complexes. It should be pointed out that reports on tuning the emission color of cyclometalated Pt complexes with an electron-sink are limited,^{5d} thus leaving much room for further investigation. In the metallation procedure of the ethynylene ligands, oxidization of the ethynylene to keto structure was found, and unexpected mono-keto or diketo side-products were isolated. Pt-1 (NI subunit attached to ppy via $-C \equiv C - group$) shows deep red/ near IR emission, which is red-shifted by ca. 150 nm compared to the model complex *ppv*Pt(acac). Interestingly, for the complex with NI attached to the ppy ligand via a methylene-keto group (Pt-2), blue-shifted emission at 538 nm and long luminescent lifetime ($\tau = 25.5 \text{ } \mu \text{s}$) were observed. For **Pt-4**, in which the naphthalene subunit was attached to ppy, emission at 575 nm was observed. We found that the luminescent O₂ sensing of the complexes can be improved by 117-fold with tuning the luminescent lifetimes, these results show substantial improvement compared to recently reported cyclometalated Ir(III) complexes (for O₂ sensing),²⁵ e.g. the new complex Pt-2 shows 66-fold higher oxygen sensitivity than the recently reported Ir(III) complex.25

Results and discussion

Synthesis

4-Bromo-phenylpyridine was prepared with pyridine and 4-bromobenzeneamine (Scheme 1).²⁹ The arylethynylated *ppy* ligands were prepared by Pd catalyzed Sonogashira coupling reactions. It should be pointed out that more functionalized NI moieties can be prepared readily, *e.g.* simply by using functionalized amines.^{30,31} During the metalation of the ethylnylated ligands with K₂PtCl₄, complexes with keto groups (**Pt-2**, **Pt-3** and **Pt-5**) were obtained, due to the Pt(II) catalyzed oxidation of the C=C bonds.³² All the complexes were obtained in satisfying yields.

Crystal structures of complexes containing ethynyl and α -diketo linker: Pt-1 and Pt-5

For **Pt-1**, the ethynylene linker is distorted, the C9–C12–C13 bond angle is 171.2° (Fig. 1). The NI moiety takes a coplanar geometry with the *ppy* moiety, and ensures efficient electronic communication between the two parts. A distorted square planar geometry was found for the Pt coordination center. The O–Pt

bond lengths are in the range 2.006–2.092 Å. The C(7)–Pt(1) bond length is 1.877 Å, which is slightly shorter than the typical C–Pt bond length.¹⁹ The N(1)–Pt(1) bond length is 1.991 Å. The coordination angles, O(2)–Pt(1)–O(1) and C(7)–Pt(1)–N(1), are 91.8° and 80.4°, respectively, which are close to the typical Pt(II) coordination geometries.¹⁹ No Pt^{II}…Pt^{II} interaction was found in the crystal structure.

A *trans* skewed geometry was found for the α -diketo moiety of **Pt-5**, with a torsion angle of O(4)–C(18)–C(17)–O(3) = 85.2°, which is in agreement with α -diketo compounds (Fig. 1b).³³ Coordination angles O(2)–Pt(1)–O(1) and C(6)–Pt(1)–N(1) are 92.3° and 81.8°, respectively. The O–Pt bond lengths are in the range 1.974–2.071 Å. The C(6)–Pt(1) and N(1)–Pt(1) bond lengths are 1.937 Å and 1.970 Å, respectively. Similar to **Pt-1**, there is no significant Pt(II)…Pt(II) interaction in the crystal structure of **Pt-5**.

Photophysical properties

For L-2 and L-3, the UV-vis absorption bands are centered in the UV range (Fig. 2). For L-1, however, strong absorption in the visible region was observed. These absorptions are due to the π - π * transitions of the chromophores.

With metallation, new absorption bands at lower energy (*ca.* 400 nm) developed, which are due to the $S_0 \rightarrow {}^1MLCT$ transition. The molar extinction coefficients ($\varepsilon = 0.41-3.4 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$) are in agreement with the 1MLCT absorption feature of the *ppy*Pt (acac) complexes.^{4,5,8} The intense absorptions in the UV range are due to the ligand centered ${}^1\pi-\pi^*$ transitions. These assignments were supported by our TDDFT calculations.

For **Pt-1**, intensive absorption in the visible range was observed (beyond 400 nm), with ε up to 33700 cm⁻¹ mol⁻¹ dm³. We propose the ¹MLCT absorption bands (as a shoulder at 430 nm) are buried in the intensive absorption band of NI π – π * transitions, which is supported by the TDDFT calculations (ESI†). The high ε value of **Pt-1** in the visible range is beneficial for further luminescent biosensing or bioimaging applications.³⁴⁻⁴⁰

Emission at 575 nm was observed for **Pt-4**, which is red-shifted by *ca.* 100 nm *vs. ppy*Pt(acac) (486 nm) (Fig. 3c).⁸ The emission is substantially quenched in air (reduced to 97.2% compared to that in N₂), which indicates a long luminescent lifetime ($\tau = 15.8 \text{ } \mu$ s).^{6,23,24}

To the best of our knowledge, this is the first report of tuning the emission color of cyclometalated Pt(II) complexes with extension of the π -conjugation of a *ppy* ligand *via* C \equiv C triple bonds (by Sonogashira coupling reaction, a well-established organic synthetic methodology). This approach can be generalized to prepare novel cyclometalated Pt(II) complexes to tune the emission properties of the complexes.

However, extension of the π -conjugation of the *ppy* ligand does not necessarily guarantee luminescence. For example, a cyclometalated Pt(II) complex with an arylethylene (C=C double bonds) modified *ppy* ligand is non-luminescent,⁴¹ probably due to the significant *cis/trans* isomerization of the C=C double bonds, as a result the luminescence is completely quenched. In our case C=C triple bonds are rigid and an ideal conjugated linker for efficient through-bond energy transfer, *i.e.* electronic communication between the fluorophores at both ends of the C=C bonds.^{34,36,42,43}



Scheme 1 Synthesis of the cyclometalated Pt complexes Pt-1, Pt-2, Pt-3, Pt-4 and Pt-5. The structures of the parent complex *ppy*Pt(acac) and the polymer diisopropyl substituted cardo poly(aryl ether ketone) (IMPEK – C) are also shown. (a) *n*-Butylamine, ethanol, 60 °C, 6 h; (b) trimethylsilylacetylene, Pd(PPh₃)₄, CuI, NEt₃, reflux, 8 h; (c) Bu₄NF, THF, rt; (d) Pd(PPh₃)₂Cl₂, PPh₃, CuI, NEt₃, ethanol, 60 °C, 6 h; (e) K₂PtCl₄, 2-ethoxyethanol/ water = 3 : 1 (v/v), 80 °C; (f) Hacac, Na₂CO₃, 2-ethoxyethanol, 100 °C; (g) NaNO₂, HCl, KI, 0–5 °C; (h) 2-(4'-bromophenyl) pyridine, Pd(PPh₃)₄, toluene, (i-Pr)₂NH, reflux, 8 h.



Fig. 1 ORTEP drawing of the complexes (a) **Pt-1** and (b) **Pt-5** with thermal ellipsoids shown at the 50% probability level. All H atoms are omitted for clarity.



Fig. 2 UV-Vis absorption spectra of (a) the ligands **L-1**, **L-2** and **L-3** and (b) the complexes **Pt-1**, **Pt-2**, **Pt-3**, **Pt-4**, **Pt-5**. 1.0×10^{-5} mol L⁻¹ of the ligands and the complexes in dichloromethane. 20 °C.

Pt-5 emits at 560 nm (Fig. 3d). The O₂ sensitivity of **Pt-5** is lower than **Pt-4** (Fig. 3c), due to the shorter τ value of **Pt-5** (0.86 μ s) than **Pt-4** (15.8 μ s) (Table 1). The HOMO and LUMO energy levels of **Pt-5** are calculated as -5.63 eV and -2.18 eV,

respectively (Fig. 4). It should be pointed out that the emission of **Pt-5** are against the traditional photophysics of the cyclometalated complexes, *i.e.* blue-shifted emission will be expected if an electron-withdrawing moiety is attached to the phenyl group of the *ppy* ligand, where the HOMO is localized.⁴

Compared to **Pt-4** ($\lambda_{em} = 575$ nm), emission at 638 nm was observed for **Pt-1**, the Stokes shift is up to 248 nm. The structured emission band, large Stokes shift and long luminescent lifetime (6.6 µs) indicate the phosphorescence feature of the emission. Notably the emission wavelength is red-shifted by *ca*. 152 nm compared to *ppy*Pt(acac).⁸ The red-shifted emission of **Pt-1** is also unexpected,⁸ which infers that the emissive state is different from the normal *ppy*Pt(acac) complexes. DFT/TDDFT calculations indicate that the ³IL/³MLCT excited state with *ppy* \rightarrow NI electron transfer is responsible for the red-shifted emission of **Pt-1**, *i.e.* the NI moiety serves as an electron-sink (electron acceptor) in the excited state. We noticed the NI moiety is a stronger electron sink than the previously reported fluoren-9one because the emission of **Pt-1** is more red-shifted and the luminescent lifetime of **Pt-1** is longer.^{5d}

Interestingly, besides the major emission at 638 nm, minor emission bands at 455 nm and 530 nm were also observed for **Pt-1**. The structureless feature, the small Stokes shift (65 nm) and the short luminescence lifetime (3.2 ns) attribute the emission at 455 nm to fluorescence. The emission at 530 nm is sensitive to O_2 , thus we attribute this emission band to the normal triplet ³MLCT state. This kind of uni-chromophore fluorescence/phosphorescence dual emission is rare for cyclometalated Pt/Ir complexes.^{4,19,44} We noticed that the decomposition of **Pt-1** gives similar emission at *ca*. 450 nm (possibly due to the emission of the free ligand). The emission of **Pt-1** and **Pt-2** were studied immediately after column purification and the purity of the complexes was checked by HPLC (see ESI[†]).

The $-C \equiv C$ - triple bond in **Pt-2** is oxidized to a keto structure, thus the π -conjugation in the ligand is disrupted. Emission at 538 nm was found for **Pt-2**, *vs.* 638 nm of **Pt-1**. We attribute the emission at 538 nm to the normal ³MLCT emissive state. The blue-shifted emission of **Pt-2** compared to **Pt-1** indicates that the π -conjugated NI-*ppy* fragment is necessary for the red-shifted emission in the red/near IR range. A minor fluorescence emission band at 386 nm was found for **Pt-2**. Thus, fluorescence/phosphorescence dual emission was observed for **Pt-2**. The dual emission of the complexes were used for ratiometric luminescent oxygen sensing, since the fluorescence emission is not sensitive to oxygen but the phosphorescence is (see ESI†). We attribute the dual emission of **Pt-2** to its isolated fluorophore and phosphore, which may lead to non-efficient ISC. The structural analogue **Pt-3** gives only phosphorescence emission.

The effect of the aryl-ethynyls, *i.e.* the NI moiety, the extended π -conjugation and the α -diketo group, on the energy level of the HOMO and LUMO orbitals is summarized (Fig. 4).

The LUMO of **Pt-1** is calculated as -2.56 eV, compared to the LUMO energy level of -1.58 eV for *ppy*Pt(acac) (Fig. 4). Both complexes show similar HOMO energy levels, *i.e.* -5.63 eV and -5.41 eV, respectively. These results indicate that NI fragment serves as an electron-sink and the LUMO is significantly stabilized (Fig. 4).

The HOMO and LUMO energy level of **Pt-2** is calculated as -5.74 eV and -2.23 eV, respectively. Compared to **Pt-1**, the

Fig. 3 Emission of the complexes in solution under a difference atmosphere of nitrogen, air and oxygen. (a) **Pt-1**, $\lambda ex = 390$ nm. (b) **Pt-2**, $\lambda ex = 350$ nm. (c) **Pt-4**, $\lambda ex = 369$ nm, (d) **Pt-5**, $\lambda ex = 400$ nm. The solution is purged with N₂ or O₂ for about 20 min before measurement. 1.0×10^{-5} mol dm⁻³ in dichloromethane. 20 °C. The asterisk (*) in b indicates the second order transition of the monochromator of the fluorescence spectrometer.

LUMO is less stabilized (Fig. 4). Thus we propose the π -conjugation is essential for the electron-sink effect of NI.

The energy levels of HOMO and LUMO of **Pt-4** were calculated as -5.22 eV and -1.90 eV, respectively (Fig. 4). For *ppy*Pt(acac), the HOMO/LUMO energy levels were calculated as -5.41 eV and -1.58 eV, respectively. The π -conjugation destabilizes the HOMO but stabilizes the LUMO, thus the HOMO–LUMO energy gap is decreased.

We can clearly see that the LUMO orbital can be significantly stabilized by the electron-sink effect of the electronwithdrawing fragments appended on the *ppy* ligand (*e.g.* Pt-1). The location of the LUMO orbital of the complexes can be changed by the substituents. For example, the LUMO is predominantly distributed on NI moiety (Pt-1), not the pyridine moiety for typical *ppy*Pt(acac) complex. Furthermore, an elevated HOMO and decreased LUMO were found for the complex containing a π -conjugated *ppy* ligand (Pt-4), thus a decreased HOMO–LUMO energy gap resulted. These findings will be helpful for the design of new phosphorescent cyclometalated Pt complexes.

Table 1 Photophysical parameters of the ligands and the platinum complexes

| | | | Emission properties ^a | | | | |
|------|----------------------|---|----------------------------------|--|---------------------|----------------------------------|--|
| | λ_{abs}/nm^a | $\varepsilon 	imes 10^{-4}$ /cm ⁻¹ mol ⁻¹ dm ³ | $\lambda_{\rm em}{}^a$ | Φ (%) | I_0 / I_{100}^{d} | $	au^e$ | |
| L-1 | 247/301/382 (399s) | 4.48/2.53/3.81(3.56) | 455 | $40.0\%^{b}$ | 1.2 | 1.7 ns | |
| L-2 | 229/321 | 2.07/5.58 | 373 | 68.6% ^b | 1.2 | 0.8 ns | |
| L-3 | 235/334 (352s) | 5.34/4.77(3.98) | 383 | $73.9\%^{b}$ | 1.1 | 1.4 ns | |
| Pt-1 | 243/296/390 | 5.20/2.38/3.37 | 455/638 | 0.06 [%] /1.1 [%] ^c | 109.0 | 455 nm: 3.2 ns 640 nm: 6.6 us | |
| Pt-2 | 240/293/336/357/400 | 5.46/2.28/2.32/1.73/0.412 | 386/538 | 0.38 ^b /18.2 ^c | 126.7 | 386 nm: 25 ns 538 nm: 25.5 μs | |
| Pt-3 | 240/255/292/396 | 3.17/3.23/2.76/0.51 | 536 | $32.3\%^{c}$ | 44.9 | 5.4 μs | |
| Pt-4 | 234/339 (352s) | 3.81/2.51(2.39) | 575 | $9.1\%^{c}$ | 117.0 | 15.8 µs | |
| Pt-5 | 253/297/321/335/400 | 4.67/3.41/2.77/2.68/0.63 | 560 | 4.5% ^c | 6.8 | 0.86 µs | |

^{*a*} In deaerated DCM solution (1.0×10^{-5} mol dm⁻³). s stands for shoulder absorption peaks. ^{*b*} Result of deaerated solution, with quinine sulfate as the standard ($\Phi = 0.547$ in 0.05 M sulfuric acid). Estimated error limit is 5%. ^{*c*} Result of deaerated solution, with complex (Phen)Ru(bpy)₂ ($\Phi = 0.06$ in MeCN) as the standard. Estimated error limit is 5%. ^{*d*} The emission intensity ratio of the complexes under N₂ and O₂ atmosphere. ^{*e*} Luminescent lifetimes.

Fig. 4 Energy levels of the frontier molecular orbitals (HOMO and LUMO) of the complexes: effect of the electron-donating and electron-withdrawing group. The HOMO and LUMO energy gaps are also shown. Calculated by DFT at the B3LYP/6-31G(d)/LanL2DZ level using Gaussian 09.

The photophysical properties of the ligands and the complexes were summarized in Table 1. The luminescent lifetime of **Pt-1** is longer than that of **Pt-3** (Table 1). This is probably due to the more significant ³IL component of the emissive state of **Pt-1**.²³ which is supported by the TDDFT calculations. We noticed a cyclometalated Pt complex with electron-deficient fluoren-9one attached to the *ppy* ligand shows two emission band, both were assigned as ³MLCT emission.^{5d} In the case of **Pt-1** and **Pt-2**, however, fluorescence/phosphorescence dual emission was observed and the separation of the fluorescence/phosphorescence emission band (by 200 nm) is more significant, which is beneficial for luminescent ratiometric O₂ sensing.^{6,7}

We investigated the UV-vis absorption as well as the photoluminescence emission spectra of the complexes at different concentrations and no self-quenching was observed. All the results infer that there is no significant Pt^{II}...Pt^{II} interaction for these complexes in solution (see ESI[†]).⁴⁵⁻⁴⁷

Rationalize the photophysical properties of the *ppy*Pt(acac) complexes with DFT/TDDFT calculation: assignment of the UV-vis absorption and the emissive triplet excited states

Recently, density functional theory (DFT) and time-dependent DFT (TD-DFT) were used in the study of photophysical properties of the luminophores.^{24*a*-*d*,34,48-57} Herein we performed DFT calculations to study the photophysical properties of the complexes.

A distorted planar square Pt coordination center was found for Pt-1, with a Pt–O bond length in the range 2.037–2.141 Å (Fig. 5). Pt–N and Pt–C bond lengths are calculated as 2.024 Å and 1.985 Å, respectively, which are in good agreement with the single crystal structures (Fig. 1). The NI moiety takes a coplanar geometry with the *ppy* plan, which is consistent with the single crystal structure of **Pt-1** (Fig. 1).

The HOMO of **Pt-1** is localized on the phenyl group of *ppy*, the NI group and the Pt atom (Fig. 5). Interestingly, LUMO is distributed on NI, which is different from *ppy*Pt(acac), for which the LUMO is predominantly localized on the pyridine group of *ppy*.^{4,54,8} These results infer that the NI group acts as electron

trap, the electronic structure of the excited state of the complex is perturbed compared to *ppy*Pt(acac).

To study the UV-vis absorption, the singlet excited states were calculated (ESI[†]). The vertical excitation energy of $S_0 \rightarrow S_1$ transition is 452 nm, which is in good agreement with the UV-vis absorption (*ca.* 430 nm). The transition is ¹IL (*ppy* \rightarrow naph-thalimide) and ¹MLCT (Pt \rightarrow *ppy* and Pt \rightarrow naphthalimide) and NI moiety contributes significantly to this transition.

The triplet excited states of **Pt-1** were investigated (Table 2), to study the emission. The calculated $S_0 \rightarrow T_1$ energy difference is 666 nm, which is in good agreement with the experimental results ($\lambda_{em} = 638 \text{ nm}$).¹² The T_1 state can be recognized with a ³IL/³MLCT mixed feature, *i.e. ppy* \rightarrow NI, Pt \rightarrow *ppy*, Pt \rightarrow NI and acac \rightarrow NI electron transfer, with the NI as the electron acceptor. These results indicate that the NI group serves as an electron-sink for the emissive excited state (T_1), the LUMO is localized on NI, not pyridine moiety.

The geometry of **Pt-2** is different from that of **Pt-1** (Fig. 5). The NI group takes an orthogonal orientation toward the *ppy* coordination plan. The LUMO is localized on the *ppy* fragment, not the NI group. This means that without π -conjugation, the electron-sink effect of the NI group in **Pt-2** is much weaker than that in **Pt-1**. For **Pt-2**, the HOMO is mainly distributed on the Pt, the acac ligand and the phenyl group of the *ppy* ligand.

TDDFT indicates the $S_0 \rightarrow S_1$ transition energy of **Pt-2** is 423 nm (ESI[†]), which is close to the experimental result (400 nm). Furthermore, the small oscillator strength (*f*) (0.0498) of S_1 state indicates that the absorption is much weaker than that of **Pt-1** (S_1 state of **Pt-1** has a much higher *f* value of 0.4456, ESI[†]). This theoretical prediction is proved by the UV-vis absorptions (Fig. 2). The energy gap of $S_0 - T_1$ of **Pt-2** is calculated as 541 nm (Table 2), which is close to the experimental results ($\lambda_{em} =$ 538 nm, Fig. 3).¹² The main transitions of the T_1 state are ³IL (NI localized), ³LLCT (NI $\rightarrow ppy$), ³MLCT (Pt \rightarrow NI) and ³LLCT ($ppy \rightarrow$ NI). The significant ³IL component of the T_1 state of **Pt-2** infers that the luminescent lifetime will be extended.²⁴ An equilibrium between the ³MLCT and ³IL states probably exists. This prediction was verified by the τ value of **Pt-2** (25.5 µs), which is longer than **Pt-1** (6.6 µs) (Table 1).

No ³IL character was found for the T₁ state of **Pt-3** (see ESI[†]). Thus, we expect a relatively short luminescent lifetime and higher luminescent quantum yield for **Pt-3**.^{8,24} These expectations were supported by the experimental results (Table 1). The luminescent lifetime of **Pt-3** is determined as 5.4 μ s, *vs.* 25.5 μ s for **Pt-2**.

For **Pt-4**, the pyridine fragment of the *ppy* ligand serves as the electron acceptor, which is different from **Pt-1**. The T_1 state of **Pt-4** can be assigned as a ³IL transition (naphthal \rightarrow pyridine).

The rationalization of the photophysical properties of the complexes demonstrate the potential of DFT/TDDFT calculations for the rational design of luminescent transition metal complexes with predetermined photophysical properties.

Oxygen sensing in polymer films: quantification of the sensitivity towards O_2

Much attention has been paid to luminescent oxygen sensing.^{58–65} However, very few cyclometalated Pt(II) or Ir(III) complexes have been used for luminescent oxygen sensing. Previously a cyclometalated Ir(III) complex as a luminscent O₂ sensing

Fig. 5 Frontier molecular orbitals of (a) Pt-1 and (b) Pt-2. H stands for HOMO and L stands for LUMO. Calculated by DFT at the B3LYP/6-31G(d)/LanL2DZ level using Gaussian 09.

material was reported.²⁵ Herein we studied the luminescent O_2 sensing properties of the new complexes, which have longer luminescent lifetimes than the recently reported oxygen sensing cyclometalated Ir(III) complex ($\tau = 4.3 \ \mu s$).²³ Furthermore, the emission wavelength of the complexes is longer than the reported Ir complex for O_2 sensing.²⁵

For practical O_2 sensors, phosphorescent dyes are usually embedded in solid matrixes, such as polymer films.^{6,7,23,24} We demonstrated that a IMPEK-C polymer (the structures are shown in Scheme 1) is an ideal matrix for O_2 sensing, and offers a significant quenching effect and fast response.^{23,24,66} The response time $(t_{\downarrow}95)$ and recovery time $(t_{\uparrow}95)$ are usually used for the evaluation of the response of O₂ sensing films,^{23,24} which are generally accepted as the time for the luminescence intensity changes to reach 95% of the overall variation, when the gas was switched between different O₂ partial pressures, such as from 100% N₂ to 100% O₂, or vice versa.

We found that the $t_{\downarrow}95$ and the $t_{\uparrow}95$ for **Pt-1** is 4 s and 6 s, respectively (Fig. 6a). Short response and recovery times are usually found for O₂ sensors with porous supporting materials,

Table 2Electronic excitation energies (eV), main configurations and CI coefficients of the low-lying triplet electronically excited states of complexes Pt-1 and Pt-2, calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ, based on the DFT//B3LYP/6-31G(d)/LanL2DZ Optimized Ground State Geometries

| | | TDDFT//B3LYP/6-31G(d) | | | | | |
|------|-----------------------|-----------------------|--------------|----------------------------------|-----------------|------------------|--|
| | Electronic transition | Energy ^a | f^b | Composition ^{<i>c</i>} | CI^d | Character | |
| Pt-1 | $S_0 \rightarrow T_1$ | 1.86 eV 666 nm | 0.0000^{e} | $H - 4 \rightarrow L (15\%)$ | 0.1478 | ILCT | |
| | | | | $H - 4 \rightarrow L + 1 (15\%)$ | 0.1493 | ILCT | |
| | | | | $H - 2 \rightarrow L (21\%)$ | 0.2110 | MLCT, LLCT, ILCT | |
| | | | | $H - 1 \rightarrow L (34\%)$ | 0.3419 | MLCT, LLCT, ILCT | |
| | | | | H→ L (63%) | 0.6331 | MLCT, ILCT | |
| Pt-2 | $S_0 \rightarrow T_1$ | 2.29 eV 541 nm | 0.0000^{e} | $H - 2 \rightarrow L + 1 (71\%)$ | 0.7118 | MLCT | |
| | | | | $H - 2 \rightarrow L (21\%)$ | 0.2058 | LLCT, MLCT | |
| | | | | $H - 1 \rightarrow L + 1 (16\%)$ | 0.1585 | ILCT, LLCT | |
| | | | | $H = 3 \rightarrow L + 1$ (16%) | 0 1 5 3 0 | MLCT | |

^{*a*} Only the selected low-lying excited states are presented. ^{*b*} Oscillator strength. ^{*c*} H stands for HOMO and L stands for LUMO. The relative percentage contributions (absolute values) are listed in parentheses (derived from the log files with software GaussSum 2.1). Only the main configurations are presented. ^{*d*} The CI coefficients are in absolute values. ^{*e*} No spin-orbital coupling effect was considered, thus the *f* values are zero.

Fig. 6 Phosphorescent emission intensity response of the complexes to step variations of O_2 concentration levels (a) emission change of Pt-1 film vs. O_2/N_2 saturation switch, $\lambda_{ex} = 430$ nm, $\lambda_{em} = 640$ nm. (b) Dynamic response of the Pt-1 film vs. small steps of variation of O_2 partial pressure, $\lambda_{ex} = 430$ nm, $\lambda_{em} = 640$ nm. (c) Dynamic response of the Pt-2 film vs. small steps of variation of O_2 partial pressure, $\lambda_{ex} = 400$ nm, $\lambda_{em} = 529$ nm. (d) Fitting of the oxygen sensing property of the IMPEK-C films of complexes based on the two site model (eqn (1)).

such as MCM-41 or organically modified gel (ormosils).^{5,67-70} Our strategy for the film preparation (dissolving and casting) is straight forward and it is ideal for practical O_2 sensing applications. Furthermore, the emission of the **Pt-1** film was quenched by increasing the O_2 partial pressure (Fig. 6b).

The sensitivity of **Pt-2** toward O_2 is much higher than that of **Pt-1** (Fig. 6c). For example, the emission of **Pt-2** sensing film is significantly quenched under 3.5% O_2 .

The sensitivity of **Pt-3** towards O₂ is lower than **Pt-1**, with 3.5% O₂, the emission of **Pt-3** was quenched by *ca.* 19.5% (see ESI†). The recovery time of **Pt-3** is short (5.3 s). The O₂ sensing property of **Pt-4** and **Pt-5** were also studied, fast response and recovery time were observed (see ESI†). **Pt-4** is more significantly quenched compared to **Pt-5**, which is in agreement with the longer luminescent lifetime of **Pt-4** ($\tau = 15.8 \,\mu$ s) than **Pt-5** ($\tau = 0.86 \,\mu$ s).

It should be pointed out the photo-stability of the complexes is excellent, *i.e.* the emission response of the sensing films is fully reversible, even with long periods of continuous irradiation with UV light (Fig. 6). No decomposition of the films was observed. Previously we found that the O_2 sensing films of PtOEP show slightly decreased emission intensity after long periods of continuous irradiation, possibly due to the decomposition of the PtOEP complexes.²³

For heterogeneous O₂ sensing films, a modified Stern–Volmer or two-site model is required for fitting the quenching data.^{23,69} In the two-site model, the O₂-sensitive dyes are considered as two different portions, which are defined as f_1 and f_2 , respectively $(f_1 + f_2 = 1)$. Each portion has a different accessibility to O₂, thus the two portions show different quenching constants (K_{SV1} and K_{SV2} , eqn (1)).

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

In order to quantitatively compare the O₂ sensing property of the complexes, the O₂ sensing data was fitted with the two-site model (Fig. 6d) and the fitting results are summarized in Table 3. Complex **Pt-2** is the best one for O₂ sensing among the complexes studied herein, *i.e.* with the highest quenching constant ($K_{SV}^{app} =$ 0.234 Torr⁻¹, or 0.31 mbar⁻¹), which is 117-fold of **Pt-5**. The order of the sensitivity of the complexes (the magnitude of the K_{SV}^{app} values) are in line with the order of the luminescent lifetimes of the complexes (Table 1). Furthermore, the O₂ sensitivity of the new complexes is generally high, in particular **Pt-2** is 66-fold higher than the previously reported cyclometalated Ir(III) complex for O₂ sensing purpose ($\tau = 4.3 \,\mu$ s and quenching constant $K_{sv} = 4.7 \times 10^{-3} \, \text{mbar}^{-1}$), which is prepared with *ppy* ligands capped with diphenylamine moieties.²⁵

Conclusions

In conclusion, we have synthesized a series of novel cyclometalated Pt(II) (acac) complexes based on aryl-ethynylated *ppy* ligands. To our knowledge, this is the first time that aryl ethynylenes (C \equiv C)

were used to extend the π -conjugation of the *ppy* ligand to perturb the electronic structures of the emissive excited states, and thus to tune the photophysical properties, such as the emission color and the luminescent lifetimes of the cyclometalated Pt(II) complexes. All the complexes show room temperature phosphorescence in fluid solution. The complex with ethynylated naphthalimide (NI) on the ppy ligand (Pt-1) shows unexpected red-shifted emission in the deep red/near IR range (638-800 nm), which is red-shifted by up to 150 nm compared to the parent complex ppyPt(acac) ($\lambda_{em} =$ 486 nm). Interestingly, complex Pt-2, with disrupted π -conjugation between the NI and the ppy subunits, shows emission at much shorter wavelength ($\lambda_{em} = 538$ nm). The drastically red-shifted emission of Pt-1 was rationalized by the DFT/TDDFT calculations, which indicates a significant electron-sink effect of the NI moiety in Pt-1, but not in Pt-2. The luminescent lifetimes of the complexes were tuned from 0.86 µs to 25.5 µs, correspondingly the luminescent O₂ sensing can be improved by 117-fold (Stern-Volmer quenching constants $K_{SV} = 0.234 \text{ Torr}^{-1}$ for **Pt-2** vs. $K_{SV} =$ $0.002 \,\mathrm{Torr}^{-1}$ for Pt-5). Our emission color tuning strategy by using electron-sink or C \equiv C bridged π -conjugated ligand to perturb the electronic structure of the excited states of the complexes, extension of the π -conjugation of the *ppy* ligand *via* aryl-ethynylene moieties, and the assignment of the electronic structures of the emissive excited states of the complexes with DFT/TDDFT calculations will be useful for design and application of novel luminescent transition metal complexes.

Table 3 Parameters of O_2 sensing film with IMPEK-C as supportingmatrix (fitting result of the data in Fig. 6 with the two site model, eqn (1))

| | f_1^a | f_2^a | $K_{\rm SV1}{}^b$ | $K_{\rm SV2}{}^b$ | r2 ^c | $K_{\rm SV}$ app d | $K_{\rm SV}$ app e | pO ₂ /Torr |
|------|---------|---------|-------------------|-------------------|-----------------|-----------------------|-----------------------|-----------------------|
| Pt-1 | 0.265 | 0.735 | 0.062 | 0.000 | 0.9998 | 0.016 | 0.021 | 62.5 |
| Pt-2 | 0.382 | 0.618 | 0.613 | 0.000 | 0.9954 | 0.234 | 0.312 | 4.3 |
| Pt-3 | 0.321 | 0.680 | 0.008 | 0.000 | 0.9993 | 0.003 | 0.004 | 333.0 |
| Pt-4 | 0.596 | 0.404 | 0.037 | 0.000 | 0.9990 | 0.022 | 0.029 | 45.5 |
| Pt-5 | 0.242 | 0.758 | 0.008 | 0.000 | 0.9997 | 0.002 | 0.003 | 500.0 |

^{*a*} The respective ratio of the two portion of the dyes. ^{*b*} The quenching constants of the two portions. ^{*c*} The determination coefficients. ^{*d*} Weighted quenching constant, K_{SV} ^{app} = $f_1 \times K_{SV1} + f_2 \times K_{SV2}$. In Torr⁻¹. ^{*e*} In mbar⁻¹. 1 Torr = 1.3332 mbar. ^{*f*} The oxygen partial pressure at which the initial emission intensity of film is quenched by 50%, and can be calculated as $1/K_{SV}$. In Torr.

Experimental

General information

NMR spectra were recorded on a 400 MHz Varian Unity Inova NMR spectrophotometer. Mass spectra were recorded with Q-TOF Micro MS spectrometer. UV-vis absorption spectra were measured with a HP8453 UV-visible spectrophotometer. Fluorescence spectra were recorded on JASCO FP-6500 or a Sanco 970 CRT spectrofluorometer. Phosphorescence quantum yields were measured with reference (Phen)Ru(bpy)₂ ($\Phi = 0.06$ in MeCN). Luminescent lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument.

L-1

Under Ar, 4-bromo-1,8-naphthalimide (276.4 mg, 0.837 mmol), 2-(4-ethynylphenyl)pyridine (150 mg, 0.837 mmol), dry ethanol

(6 mL) and triethylamine (2 mL) were mixed together. Then Pd(PPh₃)₂Cl₂ (0.042 mmol, 29.3 mg, 5 mol%), PPh₃ (0.042 mmol, 10.2 mg, 5 mol%) and CuI (8.0 mg, 0.042 mmol, 5 mol%) were added. The reaction mixture was heated at 60 °C and stirred under argon for 6 h. After completion of the reaction, the mixture was cooled to room temperature and the vellow precipitate was collected by filtration, and the crude product was purified with column chromatography (silica gel, CH₂Cl₂ as the elute) to give 300.0 mg yellow solid (83.3%). ¹H NMR (400 MHz, $CDCl_3$): 8.76 (d, 2H, J = 8.3 Hz), 8.65 (d, 1H, J = 7.2 Hz), 8.57 (d, 1H, J = 7.8 Hz), 8.11 (d, 2H, J = 8.3 Hz), 7.98 (d, 1H, J =7.5 Hz), 7.85 (t, 1H, J = 7.8 Hz), 7.79 (d, 4H, J = 8.5 Hz), 7.31–7.28 (m, 1H), 4.19 (t, 2H, J = 7.5 Hz), 1.77–1.69 (m, 2H), 1.51-1.42 (m, 2H), 0.99 (t, 3H, J = 7.3 Hz). ¹³C NMR (100 MHz, 130.82, 130.36, 128.10, 127.48, 127.01, 123.07, 122.75, 122.26, 30.23, 120.68, 98.92. 87.50, 40.34, 20.40,13.85 ESI-HRMS ($[C_{29}H_{22}N_2O_2 + H]^+$): calcd, m/z = 431.1760, found, m/z = 431.1769.

Pt-1 and Pt-2

Compound L-1 (260 mg, 0.6044 mmol) was dissolved in mixed solvent of 2-ethoxyethanol (6 mL) and water (2 mL), then K₂PtCl₄ (125.4 mg, 0.302 mmol) was added, the mixture was heated at 80 °C for 16 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water (20 mL) and the precipitate was collected and washed with water (4 \times 20 mL). The precipitate was reacted with Hacac (90.7 mg, 0.907 mmol) in the presence of Na₂CO₃ (320 mg, 3.02 mmol) in 2-ethoxyethanol (6 mL) at 100 °C for 16 h under argon atmosphere. The mixture was poured into water, the precipitate was purified with column chromatography (silica gel, CH_2Cl_2 as eluent), the first band was collected to afford the product Pt-1 as a yellow solid in 10.0% yield (22.0 mg). After the compound Pt-1 was collected, the eluent was changed to DCM/MeOH (100:1, v/v), and a yellow band of Pt-2 was collected. A yellow solid was obtained, yield: 10.9% (25.0 mg).

Pt-1

¹H NMR (400 MHz, CDCl₃): 9.04 (d, 1H, J = 5.8 Hz), 8.81 (d, 1H, J = 8.5 Hz), 8.63 (d, 1H, J = 7.3 Hz), 8.56 (d, 1H, J =7.8 Hz), 7.97 (d, 1H, J = 7.6 Hz), 7.87–7.80 (m, 3H), 7.66 (d, 1H, J = 8.1 Hz), 7.48 (d, 1H, J = 8.0 Hz), 7.42 (d, 1H, J = 7.8 Hz), 7.18 (t, 1H, J = 6.5 Hz), 5.51 (s, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 4.19 (t, 2H, J = 7.5Hz), 1.77–1.68 (m, 2H), 1.51–1.42 (m, 2H), 0.99 (t, 3H, J = 7.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 185.95, 184.26, 167.22, 164.10, 163.83, 147.49, 145.83, 138.59, 138.27, 133.49, 132.61, 131.76, 131.48, 130.64, 130.38, 128.13, 128.05, 127.26, 122.98, 122.63, 122.35, 121.94, 121.84, 118.93, 102.65, 100.59, 87.29, 40.43, 30.25, 29.58, 28.23, 27.21, 20.41, 13.85. MALDI-MS: ([C₃₄H₂₈N₂O₄Pt]⁺) calcd, m/z = 723.1697, found, m/z = 723.1633.

Pt-2

¹H NMR (400 MHz, CDCl₃):9.04 (d, 1H, J = 5.8 Hz), 8.62 (d, 1H, J = 7.3 Hz), 8.58 (d, 1H, J = 7.6 Hz), 8.37 (s, 1H), 8.27 (d, 1H, J = 8.5 Hz), 7.90 (t, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 8.0 Hz), 7.75–7.69 (m, 3H), 7.57 (d, 1H, J = 8.2 Hz), 7.26–7.23 (m, 1H), 5.52 (s, 1H), 4.96 (s, 2H), 4.19 (t, 2H, J = 7.5 Hz), 2.05 (s, 3H), 2.02 (s, 3H), 1.76–1.68 (m, 2H), 1.50–1.41 (m, 2H), 0.98 (t, 3H, J = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 196.86, 186.24, 184.18, 164.31, 164.13, 147.74, 139.63, 138.56, 135.67, 131.01, 130.95, 130.69, 130.29, 129.30, 128.59, 126.99, 123.91, 123.24, 123.03, 122.68, 122.06, 119.54, 102.76, 43.65, 40.22, 30.22, 28.26, 27.21, 20.39, 13.87. MALDI-MS: (C₃₄H₃₀N₂O₅Pt) calcd, m/z = 741.1803, found, m/z = 741.1853.

L-2

argon atmosphere, 2-(4'-bromophenyl) Under pyridine (386.9 mg, 1.655 mmol), 4-ethynylbenzonitrile (5) (210 mg, 1.66 mmol), a mixed deoxygenated solvent of dry ethanol (6 mL) and triethylamine (2 mL) was mixed together. Then Pd(PPh₃)₂Cl₂ (57.9 mg, 0.093 mmol, 5 mol %), PPh₃ (19.7 mg, 0.093 mmol, 5 mol%) and CuI (15.7 mg, 0.093 mmol, 5 mol%) was added. The reaction mixture was heated at 60 °C and stirred under argon for 6 h. After completion of the reaction, the mixture was cooled to room temperature. The solvent was removed under reduced pressure, water was added and the mixture was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layer was dried over anhydrous Na₂SO₄. After removal the solvent, the crude product was purified with column chromatography (silica gel, CH_2Cl_2 :petroleum ether = 2 : 1, v/v), light yellow solid was abstained (210.0 mg, 45.3%). ¹H NMR (400 MHz, CDCl₃) 8.74 (d, 1H, J = 3.5 Hz), 8.06 (d, 2H, J = 8.1 Hz), 7.83–7.77 (m, 2H) 7.67–7.61 (m, 6H) 7.29 (t, 1H, J = 5.5 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 156.08, 149.53, 139.43, 137.27, 132.26, 132.10, 128.12, 126.99, 122.92, 122.69, 120.83, 118.52, 111.58, 99.99, 93.61, 89.02. ESI-HRMS: $([C_{20}H_{12}N_2 + H]^+)$ calcd, m/z =281.1079, found, m/z = 281.1083.

Pt-3

L-2 (130.0 mg, 0.464 mmol) was dissolved in mixed solvent of 2-ethoxyethanol (6 mL) and water (2 mL), then K_2PtCl_4 (96.3 mg, 0.232 mmol) was added, the mixture was heated at 80 °C for 16 h under argon atmosphere. After cooling to room temperature, it was added to water (20 mL) and the precipitate was washed with water (4 \times 20 mL) and dried under vacuum. The precipitate was then treated with Hacac (69.6 mg, 0.696 mmol), in the presence of Na_2CO_3 (245.9 mg, 2.32 mmol), in 2-ethoxyethanol (6 mL) at 100 °C for 16 h under argon atmosphere. The mixture was then poured into water, the precipitate was purified with column chromatography (silica gel, CH_2Cl_2 as an eluent) to afford the product as a yellow solid in 22.8% yield (32.0 mg). ¹H NMR (400 MHz, CDCl₃) 9.06 (d, 1H, J = 5.7 Hz), 8.22 (s, 1H), 7.87 (t, 1H, J = 7.8 Hz), 7.73–7.71 (m, 2H), 7.63 (d, 2H, J = 8.1 Hz), 7.52 (d, 1H, J = 8.2 Hz), 7.43 (d, 2H, J = 8.1 Hz), 7.22 (t, 1H, J = 6.8 Hz), 5.52 (s, 1H), 4.42 (s, 2H), 2.05 (s, 3H), 2.03 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 197.04, 186.25, 184.10, 166.69, 149.76, 147.71, 140.62, 139.11, 135.75, 132.28, 130.58, 130.42, 123.84, 122.94, 122.60, 119.48, 118.89, 110.76, 102.71, 45.56, 28.24, 27.20. MALDI-MS: $([C_{25}H_{20}N_2O_3Pt + H]^-)$ calcd, m/z = 592.1205, found, m/z = 592.1495.

L-3

2-(4'-bromophenyl)pyridine Under argon atmosphere, (459.6 mg, 1.97 mmol), 1-ethynylnaphthalene (6) (300.0 mg, 1.97 mmol), a mixed deaerated solvent of toluene (10 mL) and $(i-Pr)_2NH$ (10 mL) was mixed together. Then Pd(PPh₃)₄ (71.9 mg, 0.06 mmol), CuI (24.6 mg, 0.12 mmol) were added. Then the mixture was refluxed for about 8 h. The reaction mixture was cooled to r.t. and the solvent was removed under reduced pressure. Water was added and the mixture was extracted with dichloromethane. The combined organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent the crude product was purified with column chromatography (silica gel, DCM:hexane = 1 : 1, v/v) A pale solid was obtained, 200.0 mg, yield 33.3%. ¹H NMR (400 MHz, CDCl₃): 8.73 (d, 1H, J = 4.8 Hz), 8.48 (d, 1H, J = 8.3 Hz), 8.07 (d, 2H, J = 8.1 Hz), 7.86 (t, 2H, J = 8.0 Hz), 7.80–7.75(m, 5H), 7.62 (t, 1H, J =7.0 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.8 Hz), 7.27-7.24 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 156.42, 149.61, 138.86, 137.05, 133.23, 132.08, 130.49, 128.91, 128.34, 126.89, 126.48, 126.21, 125.30, 124.10, 122.44, 120.79, 120.67, 94.19, 88.92. ESI-HRMS: calcd ($[C_{23}H_{15}N + H]^+$), m/z =306.1283, found, m/z = 306.1289.

Pt-4 and Pt-5

L-3 (110.0 mg, 0.36 mmol) was dissolved in mixed solvent of 2-ethoxyethanol (6 mL) and water (2 mL), then K₂PtCl₄ (74.8 mg, 0.18 mmol) was added, the mixture was heated at 80 °C for 16 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water (20 mL) and the precipitate was washed with water (4×20 mL) and dried under vacuum. The precipitate was treated with Hacac (54.0 mg, 0.54 mmol), in the presence of Na₂CO₃ (190.8 mg, 1.80 mmol), in 2-ethoxyethanol (6 mL) as solvent at 100 °C for 16 h under argon atmosphere. The mixture was poured into water, the precipitate was purified with column chromatography (silica gel, CH₂Cl₂ as the eluent). The first band was collected to afford the product **Pt-4** as a yellow solid in 13.9% yield (15.0 mg, 0.025 mmol), and the second band was collected to afford the product **Pt-5** as a yellow solid, 25.0 mg. Yield: 22.0%.

Pt-4. ¹H NMR (400 MHz, CDCl₃): 9.02 (d, 1H, J = 5.7 Hz), 8.53 (d, 1H, J = 8.4 Hz), 7.87–7.78 (m, 5H), 7.63–7.58 (m, 2H), 7.53 (t, 1H, J = 7.7 Hz), 7.46 (t, 2H, J = 8.0 Hz), 7.40 (d, 1H, J =8.1Hz), 7.13 (t, 1H, J = 6.6 Hz), 5.50 (s, 1H), 2.07 (s, 3H), 2.02 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 185.94, 184.47, 167.60, 147.54, 145.02, 138.47, 138.36, 133.51, 133.37, 130.48, 128.77, 128.42, 127.19, 126.84, 126.62, 126.54, 125.48, 123.77, 122.81, 121.67, 121.42, 118.93, 102.80, 95.82, 88.68, 29.89, 28.44, 27.40. MALDI-MS: calcd ([C₂₈H₂₁NO₂Pt + H]⁺), m/z =599.1298, found, m/z = 599.1258.

Pt-5. ¹H NMR (400 MHz, CDCl₃): 9.38 (d, 1H, J = 8.7 Hz), 9.06 (d, 1H, J = 5.5 Hz), 8.21 (d, 1H, J = 1.5 Hz), 8.11 (d, 1H, J = 8.3 Hz), 8.01 (d, 1H, J = 7.2 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.88 (t, 1H, J = 8.1 Hz), 7.76 (t, 1H, J = 8.0 Hz), 7.71 (t, 2H, J =8.3 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.55 (d, 1H, J = 8.0 Hz), 7.49 (t, 1H, J = 7.8 Hz), 7.23 (t, 1H, J = 7.0 Hz), 5.41 (s, 1H), 1.99 (s, 3H), 1.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 198.33, 195.93, 186.04, 184.69, 166.71, 151.34, 147.97, 139.74, 138.59, 135.15, 134.30, 132.89, 132.16, 131.08, 129.40, 129.05, 128.86, 127.09, 126.34, 125.45, 124.74, 123.07, 122.97, 119.86, 102.69, 29.88, 28.32, 26.95. MALDI-MS: calcd ([C₂₈H₂₁NO₄Pt]⁻), *m*/*z* = 630.1118, found, *m*/*z* = 630.1169.

X-Ray structural analysis

Single-crystal X-ray diffraction data were obtained on a Bruker SMART APEX CCD diffractometer using a graphite monochromated MoKa ($\lambda = 0.71073$ Å) using the SMART and SAINT programs. The data were collected using the x/2h scan mode and corrected for Lorentz and polarization effects, during data reduction using Shelxtl 97 software the absorption effect was corrected for as well. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication material. The CCDC number for **Pt-1** and **Pt-5** are 762732, and 762731, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 122336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Oxygen sensing films

Typical film preparation is as following. 10.0 mg of IMPEK-C polymer was dissolved in 0.5 mL chloroform, then 0.4 mL of cyclometalated platinum complexes solution in DCM (1.0×10^{-3} mol dm⁻³) was added into the solution. After thorough mixing, about 0.2 mL of the solution was coated on a silica glass disk (diameter: 1.6 cm). The solvent was evaporated at r.t. and a transparent film was obtained. The thickness of the film of complex **Pt-1** was estimated as 12 µm, by the weight of the film (2.8 mg) and the density of the polymer (1.14 g cm⁻³). The thickness of the film of **Pt-1**, **Pt-2**, **Pt-3**, **Pt-4** and **Pt-5** were estimated with the same method as 12 µm, 18 µm, 13 µm, 20 µm and 10 µm, respectively.

DFT calculations

The structures of the complexes were optimized using density functional theory (DFT) with B3LYP functional and 6-31G(d)/LanL2DZ basis set. The excited state related calculations were carried out with the Time dependent DFT (TD-DFT) with the ground state geometry. 6-31G(d) basis set were employed for C, H, N and O LanL2DZ basis set was used for Pt (II). There are no imaginary frequencies for all optimized structures. All these calculations were performed with Gaussian 09.⁷¹

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