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## **Observation of Room-Temperature Deep-Red/Near-IR Phosphorescence of** Pyrene with Cycloplatinated Complexes: An Experimental and Theoretical Study

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Pyrene-containing cyclometallated Pt<sup>II</sup> complexes, with the pyrene moiety directly cyclometallated (Pt-1) or connected to a 2-phenylpyridine (ppy) ligand through a C-C (Pt-2) or C≡C bond (Pt-3), and a control complex with a phenyl group attached to the ppy ligand (Pt-4) have been prepared. Roomtemperature deep-red/near-IR (NIR) phosphorescence emission (650-800 nm) was observed for Pt-1, Pt-2 and Pt-3, whereas Pt-4 showed emission at 528 nm. We found that Pt-2, in which the pyrene moiety is not directly cyclometallated, shows intense pyrene-based phosphorescence, which contrasts with a previous report that direct cyclometallation is necessary for the observation of the phosphorescence of pyrene in cyclometallated complexes. Besides the phosphorescence emission in the deep-red/near-IR range, a fluorescence

### Introduction

Cyclometallated Pt<sup>II</sup>/Ir<sup>III</sup> complexes such as [(ppy)Pt-(acac)] (ppy = 2-phenylpyridine, acac = acetylacetonato) have attracted considerable attention due to their applications in electroluminescence.<sup>[1-9]</sup> Some of the cyclometallated Pt<sup>II</sup> complexes are luminescent in fluid solution at room temperature (r.t.).<sup>[1]</sup> The emissive excited states of these complexes are usually <sup>3</sup>IL/<sup>3</sup>MLCT (phenyl-)pyridine, Pt→pyridine) triplet states.<sup>[1]</sup> These complexes are ideal phosphores for organic light-emitting diodes (OLEDs) because 75% of the excitons in the electroluminescence, which show triplet-spin manifold, cannot be utilized by fluorescent materials. Concerning the photoluminescence with cyclometallated complexes, the population of the triplet state is a result of the heavy-atom effect of Pt or Ir, through which the singlet $\rightarrow$ triplet intersystem crossing (ISC) is facilitated  $(S_1 \rightarrow T_1)$ , and thus phosphorescence can be observed. Usually the singlet excited state is completely quenched by

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promising. the ISC process and thus no fluorescence can be detected for these cyclometallated complexes. Cyclometallated complexes usually give emission in the blue-green range depending on the structures of the ligands.<sup>[1,6]</sup> For example, the emission of [(ppy)Pt(acac)] was observed at 486 nm.<sup>[5]</sup> However, emission at longer wavelengths is also desired, for example, emission at longer wavelengths (deep-red/near-IR range) is important for optical communication and biomedical imaging. Unfortunately it is difficult to access deep-red/ near-IR emission through cyclometallated complexes, especially with PtII.[1]

emission band at higher energy was observed. Thus, these

complexes can be described as unichromophore multi-emissive materials. Normal <sup>3</sup>MLCT/<sup>3</sup>IL emission at 528 nm was

observed for Pt-4. The UV/Vis absorption and phosphores-

cence emissions of the complexes were rationalized by DFT/ TDDFT calculations. Theoretical calculations propose py-

rene-localized  $T_1$  states (<sup>3</sup>IL) for Pt-1, Pt-2 and Pt-3, which is

supported by the experimental results. The complexes were

used in luminescent O<sub>2</sub>-sensing experiments. These studies

will be helpful in the development of room-temperature

phosphorescent materials and their application as lumines-

cent molecular sensing or electroluminescent materials are

On the other hand, luminescent molecular sensors or chemosensors usually employ fluorescent chromophores such as pyrene.<sup>[10–12]</sup> Pyrene is a versatile fluorophore and has been extensively used in fluorescent chemosensors. However, the phosphorescence emission of pyrene has not been employed in luminescent molecular sensors. Phosphorescence usually exhibits larger Stokes shifts, red-shifted emission and much longer luminescent lifetimes compared with fluorescence emission.<sup>[10]</sup> These photophysical properties are ideal for luminescent molecular sensor applications.<sup>[10,11]</sup> However, room-temperature phosphorescence of aromatic fluorophores is difficult to obtain because the weak spin-orbit coupling effect of the aromatic fluorophores ( $\pi$ - $\pi$ \* transitions) and the large singlet-triplet energy gap makes  $S_1 \rightarrow T_1$  ISC difficult. As a result, very few aromatic polycyclic hydrocarbons show room-temperature



phosphorescence and usually the phosphorescence can only be observed at low temperatures in a rigid matrix.<sup>[10]</sup>

Recently, we studied the room-temperature phosphorescence of heavy-transition-metal complexes such as Ru<sup>II</sup>.<sup>[13–15]</sup> There are only very limited reports on the observation of room-temperature phosphorescence emission of pyrene<sup>[16]</sup> and its application as sensing materials, such as in luminescent oxygen sensing.<sup>[14,17–20]</sup>

Inspired by the recent elegant work on cyclometallated Pt complexes and to tackle the aforementioned challenges,<sup>[1,5,11,17,18,21]</sup> we set out to tune the emission colour of cyclometallated  $Pt^{II}$  complexes from the typical green to deep-red/near-IR in order to achieve the room-temperature phosphorescence of pyrene. The design rationale of these complexes lies in the notion that room-temperature phosphorescence of polycyclic aromatic hydrocarbons can be facilitated by the heavy-atom effect of Pt. Thus, <sup>3</sup>IL emission will be accessible with a strong spin-orbit coupling effect. Following this line, we designed and prepared complex Pt-1 in which the pyrene moiety is directly metallated by  $Pt^{II}$ (Scheme 1). As a similar model complex, Pt-2 was synthesized with the pyrene moiety appended to the 4-position of the ppy ligand and not directly cyclometallated. A complex with a pyrene-ethynyl moiety attached to ppy was also prepared (Pt-3). A complex with a phenyl group attached to the ppy ligand (Pt-4) was prepared to study the effect of structure on the photophysics of the complexes. Room-temperature phosphorescence in the deep-red and near-IR range (650-800 nm) was observed for Pt-1, Pt-2 and Pt-3. The emission bands were assigned to the ligand-centred (<sup>3</sup>IL) phosphorescence of pyrene appends. **Pt-1** shows emission bands that are red-shifted by 50 nm relative to those of a previously reported cycloplatinated pyrene.<sup>[16]</sup> In particular, <sup>3</sup>IL emission (phosphorescence of pyrene) was observed for Pt-2 in which the pyrene is not directly cyclometallated. These results contrast those of a previous report that the phosphorescence of pyrene requires direct cyclometallation.<sup>[16,22]</sup> In the case of new complex Pt-2, intense pyrene-derived r.t. phosphorescence was observed without direct cyclometallation of the pyrene moiety. In addition to the phosphorescence bands in the near-IR range, emissions at higher energy were observed for Pt-1, Pt-2 and Pt-3. These emission bands were assigned to the fluorescence emission of the ligand, similarly to a previous report.<sup>[16]</sup> Based on the experimental results, a frustrated ISC process, that is, from the pyrene-localized <sup>1</sup>IL to the <sup>1</sup>MLCT and <sup>3</sup>MLCT states, was proposed to be responsible for the unichromophore fluorescence/phosphorescence multi-emissions. The photophysics of the complexes were studied by performing theoretical calculations based on density functional theory (DFT) and time-dependent DFT (TDDFT), which clearly indicate pyrene-localized triplet excited states for Pt-1, Pt-2 and Pt-3. The complexes were used in luminescent O<sub>2</sub>-sensing experiments. Our strategy for achieving the deep-red/near-IR emission of pyrene through the use of cyclometallated Pt<sup>II</sup> complexes, the application of the complexes in luminescent O<sub>2</sub>-sensing, as well as the assignment of the emissive triplet excited states by using DFT/TDDFT

calculations will be useful in the future design of functional cyclometallated Pt complexes with predetermined photophysical properties, such as the <sup>3</sup>IL emissive state (r.t. phosphorescence of the ligands), to achieve room-temperature phosphorescence of organic chromophores.

## **Results and Discussions**

### Design and Synthesis of the Complexes

The design rationale of the complexes lies in the notion that the r.t. phosphorescence of pyrene may be switched on by the heavy-atom effect of Pt.<sup>[16]</sup> Thus, complex Pt-1 was designed with a view to the direct metallation of the pyrene moiety. The C^N ligand of Pt-1 was synthesized by Suzuki coupling reaction between 1-pyreneboronic acid and 2-bromopyridine. Then the ligand 2-pyrenylpyridine was metallated with [K<sub>2</sub>PtCl<sub>4</sub>]. The auxiliary ligand acetylacetonate (acac) was introduced in the presence of Na<sub>2</sub>CO<sub>3</sub> (Scheme 1). To investigate the effect of the direct cycloplatination of the pyrene moiety on the photophysical properties, Pt-2 was designed with the pyrene moiety appended at the 4-position of the ppy group through a C–C single bond (pyrene is not directly cycloplatinated). First, 4-bromo-ppy was synthesized and then the palladium-catalysed Sonogashira coupling reaction was carried out with 1-pyreneboronic acid to prepare ligand L-2.

Previously we found that an ethynylated ligand may impart a significant effect on the photophysics of polypyridyl ruthenium complexes.<sup>[14]</sup> To investigate the effect of  $\pi$  conjugation on the photophysics of the cyclometallated Pt complex, Pt-3 was designed in which ethynylene acts as the linker between the pyrene and the ppy units. Note that we did not use a C=C double bond as the linker to extend the  $\pi$  conjugation of the ppy ligand because the *cis/trans* photoisomerization of the C=C double bond can substantially quench the luminescence of the excited lumophores.<sup>[23]</sup> Instead, the C=C triple bond is a rigid linker and is effective for  $\pi$  conjugation and through-bond electron/energy transfer.<sup>[24]</sup> Note also that the C=C linker may induce complicated yet interesting photophysical properties in the luminescent metal complexes.<sup>[14]</sup> To investigate the effect of the pyrene moiety on the photophysics of the Pt<sup>II</sup> complexes, a model complex Pt-4 was synthesized with a phenyl group attached to the 4-position of the ppy ligand. All the complexes were prepared in satisfactory yields.

As the energy of the triplet excited state  $(T_1)$  of pyrene (ca. 600 nm) is substantially lower than the  $T_1$  state of the [(ppy)Pt(acac)] complex (ca. 485 nm) we expected to observe phosphorescence emission from the pyrene in **Pt-1**, **Pt-2** and **Pt-3**,<sup>[14]</sup> although this is not a guaranteed property.<sup>[16]</sup> For **Pt-4**, however, as the energy of the triplet state of the phenyl group is substantially higher than that of [(ppy)Pt(acac)] (485 nm),<sup>[5]</sup> we do not expect any emission other than the typical <sup>3</sup>IL/<sup>3</sup>MLCT emission of [(ppy)Pt(acac)].



Scheme 1. Synthesis of the cyclometallated Pt complexes. (a) 2-Bromopyridine was used for the synthesis of L-1. 2-(4-Bromophenyl)-pyridine was used for L-2. Base/Pd(PPh<sub>3</sub>)<sub>4</sub> (3.6 mol-%), toluene/EtOH (3:1, v/v), Ar, 90 °C, 20 h. (b) i) K<sub>2</sub>PtCl<sub>4</sub>, 2-ethoxyethanol/water (3:1, v/v), Ar, 80 °C, 20 h; ii) Hacac/Na<sub>2</sub>CO<sub>3</sub>, 2-ethoxyethanol, 100 °C, 20 h. (c) i) Ethynyltrimethylsilane, Pd(PPh<sub>3</sub>)Cl<sub>2</sub> (2 mol-%), CuI (4 mol-%), PPh<sub>3</sub> (4.0 mol-%), NEt<sub>3</sub>/THF (3:1, v/v), Ar, 90 °C, 6 h; ii) K<sub>2</sub>CO<sub>3</sub>, MeOH/diethyl ether (2:1, v/v), r.t., 3 h. (d) Diisopropylamine, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (6 mol-%), CuI (6 mol-%), PPh<sub>3</sub> (12 mol-%), Ar, 90 °C, 4 h.

# UV/Vis Absorption Spectra of the Ligands and the Cyclometallated Pt<sup>II</sup> Complexes

The UV/Vis absorption spectra of the ligands and the complexes were studied (Figure 1). The UV/Vis absorption spectra of the pyrene-containing ligands are different to that of pyrene.<sup>[12,14]</sup> This indicates electronic coupling between the pyrene and the ppy moiety. For example, the absorption bands of **L-1** and **L-2** at 350 nm are red-shifted relative to that of pyrene. Moreover, the absorption bands of **L-1** and **L-2** are structureless, in contrast to the highly structured absorption of pyrene at around 320 nm.<sup>[25,26]</sup> These absorption bands mainly arise from pyrene-localized transitions, which is supported by DFT calculations. For **L-4**, however, the maximal absorption band is at a much shorter wavelength (270 nm).

New absorption bands were observed for the Pt<sup>II</sup> complexes at wavelengths red-shifted in comparison with the C<sup>N</sup> ligands. For example, a structured intense absorption band at 425 nm was observed for **Pt-1**. The spectra of ligand **L-1** is devoid of this absorption band. The absorption of **Pt-1** in the visible range is red-shifted by around 50 nm relative to that of previously reported cycloplatinated pyrene complexes with 1-(diphenylphosphanyl)pyrene or 1,6-



Figure 1. UV/Vis absorption spectra of the ligands and complexes in  $CH_2Cl_2$  ( $c = 1.0 \times 10^{-5} \text{ mol/L}$ , 25 °C).

bis(diphenylphosphanyl)pyrene as ligands.<sup>[16]</sup> We propose the red-shifted absorption of **Pt-1** is a result of perturbation of the molecular orbitals of pyrene by direct platination (with the formation of a Pt–C covalent bond) and transitions such as <sup>1</sup>IL (pyrene $\rightarrow$ pyridine) and <sup>1</sup>MLCT (Pt $\rightarrow$ pyrene/pyridine) are responsible for the red-shifted absorptions. This assumption is supported by DFT calculations, which indicate that the absorption at around 400–470 nm is due to <sup>1</sup>MLCT (Pt $\rightarrow$ pyridine), <sup>1</sup>IL (pyrene-localized) and <sup>1</sup>LLCT (pyrene $\rightarrow$ pyridine) transitions.

For L-2, however, the UV/Vis absorption changes observed upon metallation are different to those of L-1. First, the main absorptions of L-2 persist in the UV/Vis absorption of Pt-2, namely the bands at 280 and 346 nm. Secondly, a new shoulder absorption at around 420 nm appeared for Pt-2 not observed for L-2. We attribute the new absorption at 420 nm to the absorption of the complex (e.g., <sup>3</sup>MLCT), whereas the absorption band at 350 nm is due to the pyrene-localized transition. This assignment is supported by DFT/TDDFT calculations. These results demonstrate that the metallation of L-2 imparts only a minor effect on the UV/Vis absorption of the pyrene moiety in contrast to the case of Pt-1. New absorption bands at 366 and 391 nm appeared for **Pt-4** when compared with the absorption spectrum of L-4. We attribute the new absorption at 391 nm to the Pt complexation effect, that is, to the  ${}^{3}IL/$ <sup>3</sup>MLCT states. The intense absorption of L-4 at 275 nm persists upon cyclometallation.

#### Photoluminescence of the Ligands and Complexes

The emission spectra of the ligands and the cyclometallated complexes were also studied (Figure 2). For the pyrene-containing ligands of L-1 and L-2, structureless emission bands at 393 and 417 nm were observed, respectively. This emission profile is in contrast to the structured emission band of pyrene at 390 nm,<sup>[10,12]</sup> which points to significant electronic coupling between the pyrene and the pyridine or ppy appends. The red-shifted emission of L-2 at 417 nm may be due to the extended  $\pi$ -conjugated framework in comparison with L-1. For L-4, however, the emission was observed at the much shorter wavelength of 348 nm. The slightly more structured emission at 428 nm for L-3 may be due to the attachment of the electron-withdrawing ethynyl moiety on the pyrene.<sup>[12]</sup>

The emissions of the cyclometallated complexes are shown in Figure 2b. First we checked the emission of the model complex **Pt-4**; an emission band at 528 nm was observed. The structured emission profile is a characteristic of [(ppy)Pt(acac)] complexes.<sup>[5]</sup> However, the emission of **Pt-4** is red-shifted by around 40 nm relative to that of the parent complex [(ppy)Pt(acac)].<sup>[5]</sup>

Next we investigated the complex **Pt-1** in which the pyrene moiety is directly cycloplatinated. Interestingly, deepred/near-IR emission at 680 nm (the emission spectrum covers the range of 650 to beyond 800 nm) was observed. The emission band is red-shifted by around 50 nm relative to



Figure 2. Emission spectra of (a) the ligands and (b) the complexes.  $\lambda_{ex}(L-1) = 360 \text{ nm}, \lambda_{ex}(L-2) = 367 \text{ nm}, \lambda_{ex}(L-3) = 367 \text{ nm}, \lambda_{ex}(L-4)$ = 310 nm,  $\lambda_{ex}(Pt-1) = 415 \text{ nm}, \lambda_{ex}(Pt-2) = 433 \text{ nm}, \lambda_{ex}(Pt-3) = 380 \text{ nm}, \lambda_{ex}(Pt-4) = 397 \text{ nm}$  ( $c = 1.0 \times 10^{-5} \text{ mol/L}$  in CH<sub>2</sub>Cl<sub>2</sub>, 25 °C).

the previously reported cycloplatinated complexes with 1diphenylphosphanylpyrene or 1,6-bis(diphenylphosphanyl)pyrene as ligands.<sup>[16]</sup> We propose that the emission at 680 nm is due to a triplet emissive state with a substantial <sup>3</sup>IL component, that is, the pyrene-localized excited state.<sup>[16]</sup> This assignment was supported by DFT/TDDFT calculations. Besides the deep-red/near-IR emission at 680 nm, minor emission bands at higher energies of 577 and 471 nm were also observed for Pt-1. We propose that the emission at 577 nm is due to emission typical of [(ppy)Pt(acac)] complexes. This is supported by the sensitivity of the emission intensity at 577 nm to  $O_2$  (the emission can be completely quenched under aerated conditions). Further, we propose that the emission band at 471 nm is due to the fluorescence of the ligand. Similar fluorescence emission was previously observed for pyrene-derived PtII or AuI complexes.[16,22] The emission intensity of the peak at 471 nm is nearly unaffected by O<sub>2</sub>, which is characteristic of fluorescent emissions; the insensitivity to oxygen is due to the singlet manifold and the short luminescent lifetime of the emission.<sup>[10]</sup>

In contrast to **Pt-1**, the pyrene unit of **Pt-2** is not directly cycloplatinated. The photoluminescence of **Pt-2** shows a structured emission band at 640 nm (Figure 2b), which is blueshifted by around 40 nm relative to that of **Pt-1**. Interestingly, the emission of **Pt-2** is red-shifted by 112 nm relative to that of **Pt-4**. Thus, the deep-red emission is not due to the normal <sup>3</sup>MLCT emission of the [(ppy)Pt(acac)] complexation core. Based on DFT/TDDFT calculations we attribute this emission band to the phosphorescence emission originating from the pyrene-localized triplet state <sup>3</sup>IL and the pyrene-pyridine <sup>3</sup>LLCT mixed with Pt-ppy <sup>3</sup>MLCT

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features. Similar emission was reported for cyclometallated or dangling Pt<sup>II</sup> complexes with 1-diphenylphosphanylpyrene or 1,6-bis(diphenylphosphanyl)pyrene as ligands.<sup>[16]</sup> Note that an intense phosphorescence emission of pyrene is observed for **Pt-2** in which the pyrene moiety is not directly cycloplatinated. Previously it was reported that a pyrenederived complex with a dangling Pt ion shows very weak phosphorescence, but strong fluorescence of the pyrene moiety.<sup>[16]</sup> Emission at a higher energy is also observed for **Pt-2** (485 nm). We attribute the emission to typical [(ppy)-Pt(acac)] emission.<sup>[26]</sup>

Interestingly, emission at 669 nm was observed for Pt-3, which is red-shifted by around 30 nm relative to that of Pt-2. Emission at a much higher energy (430 nm) is also observed for Pt-3. We attribute this emission band to the fluo-

Table 1. Photophysical parameters of the ligands and the cycloplatinated complexes Pt-1-Pt-4.

	$\lambda_{\rm abs} [{\rm nm}] (\varepsilon \ [10^4 { m m}^{-1} { m cm}^{-1}])^{[a]}$	λ <sub>ex</sub> [nm]	λ <sub>em</sub> [nm]	$arPhi_{ m f}^{ m [b]}$	${\varPhi_{\mathrm{p}}}^{[\mathrm{c}]}$	$ au^{[d]}$
L-1	280 (1.56), 345 (1.34)	360	393	0.41	_	3.0 ns
L-2	280 (4.36), 346 (3.83)	367	417	0.68	_	12.5 ns
L-3	285 (2.16), 310 (2.46), 375 (3.16), 398 (3.22)	367	428	0.83	-	1.49 ns
L-4 Pt-1	275 (10.81) 283 (5.64), 357 (2.25), 394 (2.61), 415 (3.43)	310 415	348 471, 577, 680	0.12 _[e]	_ 0.49	1.29 ns 471 nm (3.0 ns), 578 nm (856.2 ns),
Pt-2	280 (4.95), 346 (3.78)	433	485, 640	0.001	0.65	682 nm (6.22 μs) 485 nm (2.4 ns), 640 nm (15.8 μs)
Pt-3	286 (6.79), 350 (9.45)	380	669	_[e]	0.26	_[e]
Pt-4	296 (2.79), 332 (0.16), 366 (0.70), 391 (0.05)	397	528	_[e]	15.0	5.6 µs

[a] Extinction coefficients are shown in parentheses. [b] Quantum yield of fluorescence in aerated  $CH_2Cl_2$ . [c] Quantum yield of phosphorescence in deoxygenated  $CH_2Cl_2$ . The values are multiplied by  $10^2$ . [d] The lifetimes of the ligands were measured in aerated  $CH_2Cl_2$ . The lifetimes of the complexes were measured in deoxygenated  $CH_2Cl_2$ . [e] Not determined.

rescence of the ethynyl ligand (Figure 2, a).<sup>[16]</sup> The principle photophysical data of the ligands and the complexes are compiled in Table 1.

# The Excited States of the Complexes-DFT/TDDFT Calculations

Recently, theoretical calculations, such as the DFT and TDDFT methods, have been used to study the photophysical properties of fluorophores.<sup>[12,27–33]</sup> Investigation of the photophysical properties from a theoretical point of view will be beneficial for the design of new luminophores with predetermined photophysical properties.<sup>[12,14,27]</sup>

The different photophysical properties of the structurally related analogues **Pt-1**, **Pt-2** and **Pt-3** are fascinating and we set out to evaluate the different photophysical properties by theoretical calculations. The ground-state geometry of **Pt-1** was optimized; a square-planar coordination Pt<sup>II</sup> centre was found with the pyrene moiety coplanar with the pyridine group. We found that the frontier orbitals (HOMO/LUMO) of **Pt-1** are basically ligand-localized, that is, pyrene-localized (Figure 3).

The excitation energies calculated for **Pt-1** are in good agreement with experimental observations. For example, the predicted absorptions are located at 439, 421, 351/349 and 285 nm (Table 2). These predicted values are in good agreement with the experimental values of 415, 394, 357 and 283 nm (Figure 1, b). Based on the electronic structures of the transitions, we assigned the absorption bands at 400–450 nm (Figure 1, b) to  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transitions; the orbitals involved are  $H-2\rightarrow L$ ,  $H-1\rightarrow L$ ,  $H\rightarrow L$ ,  $H\rightarrow L+1$ . By examining the distributions of the molecular orbitals, we found that these transitions are pyrene-localized (<sup>1</sup>IL),  $Pt\rightarrow pyrene/pyridine$  (<sup>1</sup>MLCT), pyrene $\rightarrow pyridine$  and acac $\rightarrow pyrene/pyridine$  (<sup>1</sup>LLCT) transitions.

**Pt-1** shows deep-red/near-IR emission in the range of 650–800 nm. To investigate the emissive states, the triplet excited states of **Pt-1** were studied by the TDDFT method. The calculated excitation energy of  $T_1$  is 672 nm. Note that the calculation is based on the ground-state geometry, thus, the anticipated emission will be more red-shifted than the



Figure 3. Frontier molecular orbitals of **Pt-1** calculated by DFT/TDDFT at the B3LYP/6-31G(d)/LanL2DZ level of theory using Gaussian 09.



Table 2. Electronic excitation energies and the corresponding oscillator strengths (f), the main configurations and CI coefficients of the low-lying electronically excited states of complex **Pt-1** calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ based on the DFT//B3LYP/6-31G(d)/LanL2DZ-optimized ground-state geometries.

	Electronic					
	transitions	Energy <sup>[a]</sup>	f <sup>[b]</sup>	Composition <sup>[c]</sup>	CI <sup>[d]</sup>	Character
Singlet	$S_0 \rightarrow S_1$	2.83 eV, 439 nm	0.2998	H–1→L	0.5863	IL & MLCT
				H→L	0.3032	IL
	$S_0 \rightarrow S_2$	2.95 eV, 421 nm	0.3981	H−2→L	0.1614	LLCT & MLCT
				$H-1 \rightarrow L$	0.2663	IL & MLCT
				$H \rightarrow L$	0.5448	IL
				$H \rightarrow L+1$	0.1131	LLCT
	$S_0 \rightarrow S_4$	3.29 eV, 377 nm	0.0261	H−2→L	0.6422	LLCT & MLCT
				$H-1 \rightarrow L$	0.1485	IL & MLCT
				$H \rightarrow L+1$	0.1840	IL
	$S_0 \rightarrow S_5$	3.53 eV, 351 nm	0.0239	H−2→L	0.1070	LLCT & MLCT
				$H-1 \rightarrow L+1$	0.2891	IL
				$H \rightarrow L+1$	0.5989	IL
	$S_0 \rightarrow S_6$	3.56 eV, 349 nm	0.0573	H−2→L	0.1113	LLCT & MLCT
				$H-1 \rightarrow L+1$	0.5843	IL
				$H \rightarrow L+1$	0.2426	IL
	$S_0 \rightarrow S_{18}$	4.35 eV, 285 nm	0.1474	$H-4\rightarrow L+2$	0.4741	LLCT & MLCT
				$H-1\rightarrow L+4$	0.2002	LLCT & MLCT
Triplet	$S_0 \rightarrow T_1$	1.85 eV, 672 nm	$0.0000^{[e]}$	$H-5\rightarrow L+5$	0.1143	LLCT & MLCT
				H−1→L	0.1652	IL & MLCT
				H→L	0.7392	IL
				$H \rightarrow L+1$	0.1943	IL
				$H \rightarrow L+3$	0.1376	LLCT

[a] Only selected low-lying excited states are presented. [b] Oscillator strength. [c] H represents the HOMO and L the LUMO. Only the main configurations are presented. [d] The CI coefficients are absolute values. [e] No spin–orbital coupling effect was considered and thus the f values are zero.

calculated energy gap between  $S_0$  and  $T_1$  triplet excited state (672 nm). Experiments indicated phosphorescence emission at 680 nm.<sup>[34]</sup>

By examining the electronic structures of the excited state and the corresponding molecular orbitals (Table 2 and Figure 3) we found that the T<sub>1</sub> state of **Pt-1** is characterized by pyrene-localized (<sup>3</sup>IL), pyrene $\rightarrow$ pyridine (<sup>3</sup>LLCT) and Pt $\rightarrow$ pyrene/pyridine transitions (<sup>3</sup>MLCT), but that Pt<sup>II</sup> does not contribute significantly to the T<sub>1</sub> state.

Based on these calculations, we anticipate that in contrast to the parent complex [(ppy)Pt(acac)], for which an <sup>3</sup>IL state was proposed (phenyl-)pyridine of the ppy ligand),<sup>[1,5]</sup> Pt-1 will show pyrene-localized emission. This prediction is supported by the experimental results, which show emission bands in the 600-800 nm range.<sup>[16]</sup> The energies of the HOMO and LUMO of Pt-1 were calculated to be -5.14 and -1.96 eV, respectively, which compares with the energies of the HOMO and LUMO of -5.41 and -1.66 eV for Pt-4. We found that the energy of the HOMO of Pt-1 is higher, but the LUMO energy is lower than those of the model complex Pt-4, that is, the HOMO-LUMO energy gap of Pt-1 is smaller than that of Pt-4. Thus, redshifted emission can be expected for Pt-1 when compared with Pt-4. This expectation is supported by the experimental results (Figure 1 and Table 1).

**Pt-2** shows blueshifted emission (by ca. 50 nm) compared with **Pt-1**, but is substantially red-shifted compared with that of **Pt-4**. The structural difference between the two complexes is that the pyrene moiety is not directly cycloplati-

nated in **Pt-2** (Scheme 1). The ground-state geometry of **Pt-2** was optimized (Figure 4) and it was found that the pyrene moiety is tilted by 55° with respect to the Pt coordination plane. The calculated singlet excitation energies are 420, 360, 355, 279 and 276 nm. These values are very similar to the UV/Vis experimental absorption data of 400, 345, 279 and 267 nm. By examining the electronic structures of the S<sub>1</sub> state we found that the absorption bands at 420 nm can be assigned to pyrene $\rightarrow$ ppy (IL), Pt $\rightarrow$ pyrene/ppy (MLCT) and acac $\rightarrow$ pyrene/ppy (LLCT) transitions. For the absorption band at 345 nm, acac $\rightarrow$ pyrene/ppy and Pt $\rightarrow$ pyrene/ ppy features can be indentified, with the pyrene-localized transition (H $\rightarrow$ L+1) being dominant (Table 3 and Figure 4).

To study the emission of the complex, the triplet states of **Pt-2** were also studied using TDDFT calculations (Table 3). The calculated  $S_0-T_1$  energy gap is 612 nm. This value is similar to the experimental results of the phosphorescence emission at 640 nm. By examining the  $T_1$  state, we can attribute the emission band at 640 nm to the pyrene $\rightarrow$ ppy (HOMO $\rightarrow$ LUMO) and pyrene-localized (HOMO $\rightarrow$ LUMO+1) transitions, the Pt atom contributing slightly to these transitions. With a small involvement of the Pt atom in the  $T_1$  state (which is responsible for the emission at 640 nm) we anticipate a longer luminescent lifetime of this emission band compared with the normal emission of the [(ppy)Pt(acac)] complex. The luminescence lifetime of **Pt-2** was determined to be  $\tau = 15.8 \,\mu$ s, which compares with  $\tau = 2.6 \,\mu$ s for [(ppy)Pt(acac)].<sup>[5]</sup> The energies of



Figure 4. Frontier molecular orbitals of **Pt-2** calculated by DFT/TDDFT at the B3LYP/6-31G(d)/LanL2DZ level of theory using Gaussian 09.

Table 3. Electronic excitation energies and the corresponding oscillator strengths (f), the main configurations and CI coefficients of the low-lying electronically excited states of complex **Pt-2** calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ based on the DFT//B3LYP/6-31G(d)/LanL2DZ-optimized ground-state geometries.

	Electronic					
	transitions	Energy <sup>[a]</sup>	<i>f</i> <sup>[b]</sup>	Composition <sup>[c]</sup>	CI <sup>[d]</sup>	Character
Singlet	$S_0 \rightarrow S_1$	2.95 eV, 420 nm	0.3101	H−2→L	0.1141	LLCT & MLCT
-				$H-1 \rightarrow L$	0.1868	LLCT & LMCT
				H→L	0.6307	IL & LLCT
				$H \rightarrow L+1$	0.1084	IL & LLCT
	$S_0 \rightarrow S_4$	3.45 eV, 360 nm	0.1037	H−3→L	0.2278	MLCT
				H−2→L	0.5186	LLCT & MLCT
				$H \rightarrow L+1$	0.3036	IL & LLCT
	$S_0 \rightarrow S_5$	3.50 eV, 355 nm	0.1899	H−2→L	0.2923	LLCT & MLCT
				$H-1 \rightarrow L$	0.1633	LLCT & LMCT
				$H-1 \rightarrow L+1$	0.1968	LLCT
				$H \rightarrow L+1$	0.4911	IL & LLCT
	$S_0 \rightarrow S_{24}$	4.45 eV, 279 nm	0.1412	H–6→L	0.2467	LLCT & MLCT
				$H-5\rightarrow L+1$	0.3926	IL & LLCT
				$H-4\rightarrow L+1$	0.3533	IL & MLCT
	$S_0 \rightarrow S_{25}$	4.50 eV, 276 nm	0.1355	$H-6\rightarrow L$	0.3173	LLCT & MLCT
				$H-5\rightarrow L+1$	0.2711	IL & LLCT
				$H-2\rightarrow L+3$	0.3609	IL
Triplet	$S_0 \rightarrow T_1$	2.03 eV, 612 nm	$0.0000^{[e]}$	H→L	0.5112	IL & LLCT
				$H \rightarrow L+1$	0.5625	IL & LLCT
				$H \rightarrow L+2$	0.1697	LLCT
	$S_0 \rightarrow T_2$	2.56 eV, 484 nm	$0.0000^{[e]}$	$H-5\rightarrow L$	0.1969	IL & LLCT
				H–2→L	0.3386	LLCT & MLCT
				$H-1 \rightarrow L$	0.4325	LLCT & LMCT
				H→L	0.2934	IL & LLCT
				H→L+1	0.2493	IL & LLCT
				$H \rightarrow L+2$	0.1419	LLCT

[a] Only selected low-lying excited states are presented. [b] Oscillator strength. [c] H represents HOMO and L the LUMO. Only the main configurations are presented. [d] The CI coefficients are absolute values. [e] No spin–orbital coupling effect was considered, thus the f values are zero.

the HOMO and LUMO of **Pt-2** were calculated to be -5.06 and -1.74 eV, respectively. The energy of the HOMO orbital is greater than that of the model complex **Pt-4**.

Complex **Pt-3** was studied by a similar method. The ground-state geometry of the complex adopts a coplanar conformation, that is, the pyrene is coplanar with the Pt coordination plane (Figure 5). This geometry ensures efficient  $\pi$  conjugation between the pyrene and the ppy–Pt coordination moiety and thus we expect a longer wavelength of emission for **Pt-3** compared with **Pt-2**. This expectation was proven by the experimental results, which show

the emission of **Pt-3** centred at 669 nm and the emission band of **Pt-2** at 635 nm (Figure 2 and Table 1).

The vertical excitation energies of **Pt-3** were calculated by the TDDFT method. The excitation energies calculated for the singlet excited states are 452, 421, 382 and 324 nm (Table 4). These calculated values are in good agreement with the UV/Vis absorption data (Figure 1).

To study the emissive state of **Pt-3**, the triplet excited states were also studied (Table 4). Based on the electronic configuration of the  $T_1$  excited state, which is responsible for the phosphorescence emission, the  $T_1$  state is charac-



Figure 5. Frontier molecular orbitals of **Pt-3** calculated by DFT/TDDFT at the B3LYP/6-31G(d)/LanL2DZ level of theory using Gaussian 09.

Table 4. Electronic excitation energies and the corresponding oscillator strengths (f), the main configurations and CI coefficients of the low-lying electronically excited states of the complex **Pt-3** calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ based on the DFT//B3LYP/ 6-31G(d)/LanL2DZ-optimized ground-state geometries.

	Electronic TDDFT//B3LYP/6-31G(d)					
	transitions	Energy <sup>[a]</sup>	$f^{[b]}$	Composition <sup>[c]</sup>	CI <sup>[d]</sup>	Character
Singlet	$S_0 \rightarrow S_1$	2.74 eV, 452 nm	1.0803	H→L	0.6402	LC
				$H \rightarrow L+1$	0.1023	LLCT
	$S_0 \rightarrow S_2$	2.95 eV, 421 nm	0.0854	H–4→L	0.1024	MLCT
				$H-1 \rightarrow L$	0.6312	LC
				$H-1\rightarrow L+1$	0.1606	LLCT
	$S_0 \rightarrow S_3$	3.25 eV, 382 nm	0.1744	H−2→L	0.3544	LLCT & MLCT
				$H \rightarrow L+1$	0.5702	LLCT
	$S_0 \rightarrow S_{10}$	3.83 eV, 324 nm	0.1779	$H-5\rightarrow L$	0.2412	MLCT
				H–4→L	0.3905	LC
				$H-2\rightarrow L+1$	0.2493	LLCT
				$H \rightarrow L+3$	0.2464	IL & LLCT
Triplet	$S_0 \rightarrow T_1$	1.78 eV, 697 nm	0.0000 <sup>[e]</sup>	$H-2\rightarrow L+1$	0.1326	LLCT
				H→L	0.6913	LLCT
				$H \rightarrow L+1$	0.3409	LLCT

[a] Only selected low-lying excited states are presented. [b] Oscillator strength. [c] H represents the HOMO and L the LUMO. Only the main configurations are presented. [d] The CI coefficients are absolute values. [e] No spin–orbital coupling effect was considered, thus the f values are zero.

terized by pyrene-localized (<sup>3</sup>IL), pyrene $\rightarrow$ ppy (<sup>3</sup>IL) and Pt $\rightarrow$ ppy (<sup>3</sup>MLCT) transitions. The energies of the HOMO and LUMO of **Pt-3** were calculated to be -5.01 and -2.01 eV, respectively. Compared to **Pt-4**, the HOMO of **Pt-3** is significantly higher and the LUMO is lower and thus we expect red-shifted emission for this complex.

**Pt-4** was designed as a model complex and does not contain the pyrene group. Therefore the normal <sup>3</sup>MLCT/<sup>3</sup>IL emissive state was expected for this complex.<sup>[1,5]</sup> The ground-state geometry of the complex shows the phenyl group tilted by 37° with respect to the ppy coordination plane, which rules out efficient  $\pi$  conjugation (Figure 6). The excited states of **Pt-4** were also studied. The singlet excited states of the complex were found to have the main excitation energies of 403, 361, 326, 305 and 282 nm (Table 5). These values are in good agreement with the experimental results, which show UV/Vis absorption bands at 391, 366, 332 and 296 nm.

By examining the electronic structure of the  $S_1$  state, the transition can be attributed to Pt $\rightarrow$ ppy and phenyl $\rightarrow$ pyridine transitions. In contrast to **Pt-1** and **Pt-2**, no aryl append localized transitions (<sup>1</sup>IL) were found. The triplet states of **Pt-4** were also studied and an excitation energy of 490 nm (T<sub>1</sub>) was found. This value is in good agreement with the experimental result of phosphorescence emission at 527 nm.<sup>[34]</sup> By examining the electronic configuration of the T<sub>1</sub> state and the molecular orbitals, we found that the T<sub>1</sub> state is characterized by ppy-localized phenyl $\rightarrow$ pyridine and Pt $\rightarrow$ ppy transitions, that is, the T<sub>1</sub> state is a mixed <sup>3</sup>MLCT/<sup>3</sup>IL state. Therefore the emissive state (T<sub>1</sub>) of **Pt-4** is characterized by the normal profile of the [(ppy)Pt(acac)] complexes. The HOMO and LUMO energies of **Pt-4** were calculated to be -5.41 and -1.66 eV, respectively.

The energy levels of electroluminescence materials are important for device fabrication. The energies of the HOMOs and LUMOs of the complexes were calculated (Figure 7.) and it is clear that **Pt-4** and the model complex [(ppy)Pt(acac)] share similar HOMO and LUMO energies. For **Pt-1** and **Pt-3**, the energy gaps between the HOMO and the LUMO are smaller than that of complex [(ppy)-Pt(acac)]. This is not surprising as the pyrene moiety is directly cycloplatinated (**Pt-1**) or the pyrenyl-ethynyl conjugated ppy ligand was used (**Pt-3**). The HOMO and LUMO energies of **Pt-2** are very interesting. The pyrene moiety is neither directly cycloplatinated nor  $\pi$ -conjugated to the ppy ligand through a C=C bond, however, the HOMO energy



Figure 6. Frontier molecular orbitals of **Pt-4** calculated by DFT/TDDFT at the B3LYP/6-31G(d)/LanL2DZ level of theory using Gaussian 09.

Table 5. Electronic excitation energies [eV] and the corresponding oscillator strengths (*f*), the main configurations and CI coefficients of the low-lying electronically excited states of complex **Pt-4** calculated by TDDFT//B3LYP/6-31G(d)/LanL2DZ based on the DFT//B3LYP/ 6-31G(d)/LanL2DZ-optimized ground-state geometries.

	Electronic					
	transitions	Energy <sup>[a]</sup>	$f^{[b]}$	Composition <sup>[c]</sup>	CI <sup>[d]</sup>	Character
Singlet	$S_0 \rightarrow S_1$	3.08 eV, 403 nm	0.0612	H−3→L	0.1372	LLCT & MLCT
				$H-2\rightarrow L$	0.1309	LLCT & MLCT
				H→L	0.6448	LLCT
	$S_0 \rightarrow S_2$	3.44 eV, 361 nm	0.0888	H−3→L	0.3300	LLCT & MLCT
				H−2→L	0.1669	LLCT & MLCT
				$H-1 \rightarrow L$	0.5642	LLCT
				$H \rightarrow L$	0.1008	LLCT
	$S_0 \rightarrow S_5$	3.80 eV, 326 nm	0.1936	H−3→L	0.3809	LLCT & MLCT
				H−2→L	0.3147	LLCT & MLCT
				$H-1 \rightarrow L+1$	0.2768	LLCT
				$H-1 \rightarrow L$	0.1633	LLCT
				$H \rightarrow L+1$	0.3287	LLCT
				$H-1 \rightarrow L+1$	0.1968	LLCT
	$S_0 \rightarrow S_8$	4.07 eV, 305 nm	0.1950	H−3→L	0.1500	LLCT & MLCT
				H−2→L	0.1221	LLCT & MLCT
				$H-2\rightarrow L+1$	0.2006	LLCT & MLCT
				$H-1 \rightarrow L+1$	0.5745	LLCT
Triplet	$S_0 \rightarrow T_1$	2.53 eV, 490 nm	0.0000 <sup>[e]</sup>	H−1→L	0.3708	LLCT
				H→L	0.6021	LLCT
				$H \rightarrow L+1$	0.1107	LLCT

[a] Only selected low-lying excited states are presented. [b] Oscillator strength. [c] H represents the HOMO and L the LUMO. Only the main configurations are presented. [d] The CI coefficients are absolute values. [e] No spin–orbital coupling effect was considered, thus the f values are zero.

of **Pt-2** is significantly higher than that of the model complex [(ppy)Pt(acac)] (Figure 7). This increased HOMO energy cannot be rationalized by the electron-donating ability of the pyrenyl group because no such effect was observed for **Pt-4** in which a phenyl ring is attached to the ppy ligand. DFT calculations revealed that the pyrene moiety contributes significantly to the HOMOs (Figure 4) and thus the high HOMO energy of **Pt-2** can be rationalized.

Our theoretical calculations show that the DFT/TDDFT method can be used to study the excited state of the cyclometallated Pt complexes and for assignment of the UV/Vis absorption (singlet excited states) and phosphorescence emissions (triplet excited states). The calculations indicated that the pyrene moiety is involved in the lowest-lying excited states of **Pt-1**, **Pt-2** and **Pt-3**. For **Pt-4**, however, normal <sup>3</sup>MLCT/<sup>3</sup>IL transitions were found. These theoretical predictions are fully supported by the experimental results,



Figure 7. Calculated frontier energy levels of the complexes calculated by DFT/TDDFT at the B3LYP/6-31G(d)/LanL2DZ level of theory using Gaussian 09.

such as the deep-red/near-IR emission and the extended luminescent lifetimes of **Pt-1**, **Pt-2** and **Pt-3**. For **Pt-4**, normal <sup>3</sup>MLCT/<sup>3</sup>IL emission was predicted by the theoretical calculations. Our assignment of the emissive state of the cyclometallated Pt complexes by DFT/TDDFT calculations will be useful in the design of luminescent complexes with predetermined photophysical properties, such as the ligandlocalized triplet excited state (<sup>3</sup>IL).

#### Luminescent O<sub>2</sub>-Sensing with the Emissive Pt Complexes

Recently, luminescent O<sub>2</sub>-sensing has attracted considerable attention.<sup>[11,13,21,35,36]</sup> Phosphorescent dyes, usually transition-metal complexes, are employed for luminescent O<sub>2</sub> sensing as a result of their triplet nature and the long lifetime of their luminescence (in the microsecond range,  $\mu$ s). Typical compounds for this purpose are Pt–porphyrin complexes, for example, PtOEP and Ru<sup>II</sup>–polypyridine complexes.<sup>[13,14,37–39]</sup> To the best of our knowledge, no cyclometallated Pt(acac) complexes have been systematically studied for O<sub>2</sub>-sensing applications. Thus, we carried out a preliminary investigation on the luminescent O<sub>2</sub>-sensing properties of the complexes.

The changes in the emission of the complexes in solution versus variation of  $O_2$  partial pressures were studied (Figure 8). We found the phosphorescence emission band of Pt-1 at 680 nm is sensitive to  $O_2$ . For example, changing from



Figure 8. Luminescent oxygen-sensing properties. Emission spectra of (a) **Pt-2** in CH<sub>2</sub>Cl<sub>2</sub> solution saturated with 0.00, 0.02, 0.08, 0.12, 0.20, 1.00, 1.50, 3.50, 4.30, 21.0 and 100.0% oxygen (mixed gas with N<sub>2</sub>, v/v). (b) Intensity ratios  $F_0/F$  vs. O<sub>2</sub> partial pressure [Torr]. Linear fitting of the O<sub>2</sub>-sensing data of **Pt-1**, **Pt-2**, **Pt-3** and **Pt-4** in CH<sub>2</sub>Cl<sub>2</sub>. The asterisk (\*) in (a) indicates the second-order transition of the monochromator of the fluorescence spectrometer.  $c = 1.0 \times 10^{-5}$  mol/L, 12 °C.



a N<sub>2</sub> atmosphere to 0.20% O<sub>2</sub> will significantly quench the emission by 22.6% (see the Supporting Information).

We noticed the phosphorescence emission of **Pt-2** is highly sensitive to the presence of O<sub>2</sub>. For example, the emission intensity is nearly completely quenched in the presence of 1.0% O<sub>2</sub> (v/v; Figure 8, b). The O<sub>2</sub>-sensing data were fitted to the Stern–Volmer equation (Figure 8, b). Quenching constants of 0.17 and 1.45 Torr<sup>-1</sup> were determined for **Pt-1** and **Pt-2**, respectively. Thus, the emission of **Pt-2** is much more sensitive towards O<sub>2</sub> than **Pt-1**. Similar O<sub>2</sub>-sensing studies were performed for **Pt-3** and **Pt-4** (see the Supporting Information). The quenching constants for **Pt-3** and **Pt-4** were determined to be 1.16 and 0.18 Torr<sup>-1</sup>, respectively.

Our results show that the  $O_2$  sensitivity of the emission of the cycloplatinated complexes is in line with the luminescent lifetimes of the complexes (Table 1). **Pt-2** shows the longest luminescence lifetimes and also shows the most sensitive  $O_2$ -sensing behaviour among the complexes studied herein. **Pt-1** and **Pt-4** have relatively short luminescence lifetimes compared with **Pt-2** and lower sensitivity towards oxygen. Thus, **Pt-1** and **Pt-4** can potentially be used as an electroluminescence material and **Pt-2** can be used as a phosphorescent molecular probes (Table 6).

Table 6. Parameters of  $O_2$  sensing of the complexes Pt-1, Pt-2, Pt-3 and Pt-4 in  $CH_2Cl_2$  (linear fitting result).

	$K_{\rm SV}^{\rm app[a]}$	$pO_2^{[b]}$	r <sup>2[c]</sup>
Pt-1	0.17	5.88	0.99
Pt-2	1.45	0.69	0.98
Pt-3	1.16	0.86	0.99
Pt-4	0.18	5.56	0.99

<sup>[</sup>a] Quenching constant [Torr<sup>-1</sup>]. [b] Oxygen partial pressure at which the initial emission intensity of the film is quenched by 50%, and can be calculated as  $1/K_{SV}$  [c] Determination coefficients.

### Conclusions

We have prepared pyrene-containing cycloplatinated complexes in which the pyrene moiety is directly cycloplatinated (Pt-1) or attached to the ppy ligand through a C-C single bond (Pt-2) or through a  $C \equiv C$  triple bond (Pt-3). A control complex with a phenyl group attached to the ppy ligand (Pt-4), was also prepared. We observed room-temperature deep-red/near-IR phosphorescence emission (650-800 nm) for Pt-1, Pt-2 and Pt-3. Notably, room-temperature phosphorescence emission in the range of 600–700 nm was observed for Pt-2 in which the pyrene moiety is not directly cycloplatinated. This discovery contrasts the results in a previous report on cycloplatinated complexes with 1diphenylphosphanylpyrene or 1,6-bis(diphenylphosphanyl)pyrene as ligands. To the best of our knowledge this is the first report of room-temperature phosphorescence of pyrene without direct cyclometallation. The photophysical properties of the complexes were rationalized by DFT/ TDDFT calculations, which indicate pyrene-localized  $T_1$ states for Pt-1 and Pt-2. Our systematic study of the synthe-

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sis of the pyrene-substituted [(ppy)Pt(acac)] complexes, the observation of the deep-red/near-IR phosphorescence emission of pyrene with **Pt-1**, the observation of the phosphorescence of pyrene without direct cyclometallation on the pyrene moiety and the assignment of the emissive state through DFT/TDDFT calculations will be useful in the development of novel deep-red/near-IR-emitting complexes and for their application as molecular sensors or electroluminescence materials.

## **Experimental Section**

**General:** All the chemicals used were analytically pure and used as received without further purification. NMR spectra were recorded with a 400 MHz Varian Unity Inova spectrometer. Mass spectra were recorded with a Q-TOF Micro MS spectrometer. UV/Vis spectra were recorded with a HP8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded with a JASCO FP-6500 or Sanco 970 CRT spectrofluorimeter. Fluorescence and phosphorescence quantum yields were measured with quinine sulfate ( $\Phi = 54\%$  in 0.5 M H<sub>2</sub>SO<sub>4</sub>) or [Ru(bpy)<sub>2</sub>(phen)]·(PF<sub>6</sub>)<sub>2</sub> as references ( $\Phi = 6.0\%$  in CH<sub>3</sub>CN), respectively. Fluorescence lifetimes were measured with a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument.

**1-Bromopyrene:** A solution of NBS (4.09 g, 23 mmol) in DMF (23 mL) was slowly added to a solution of pyrene (5.11 g, 25 mmol) in DMF (35 mL) at 0 °C. After stirring at room temp. for 24 h, the reaction mixture was poured into ice–water (150 mL) and the was mixture was extracted with diethyl ether. The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent by evaporation the crude white solid was purified by column chromatography (silica gel, petroleum ether). A white solid was obtained; yield 3.5 g, 54.2%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.40$  (d, J = 9.2 Hz, 1 H), 8.20–8.17 (m, 3 H), 8.13 (d, J = 9.2 Hz, 1 H), 8.05–7.95 (m, 4 H) ppm. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>9</sub>Br [M]<sup>+</sup> 279.9888; found 279.9889.

2-(1-Pyrenyl)pyridine (L-1): 2-Bromopyridine (192.8 mg. 1.22 mmol), 1-pyrenylboronic acid (300.0 mg, 1.22 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (52.1 mg, 0.045 mmol), aqueous Ba(OH)<sub>2</sub> (2.286 g, 2.0 M, 60 mL), EtOH (15 mL) and toluene (45 mL) were mixed. The mixture was degassed with argon and heated at reflux for 20 h. After being cooled, the solvent was evaporated under reduced pressure and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried with  $Na_2SO_4$  and then evaporated to dryness. The crude product was purified by column chromatography (silica gel,  $CH_2Cl_2$ /petroleum ether = 2:1, v/v). A light-yellow solid was obtained; yield 0.16 g, 47.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.87 (d, J = 4.4 Hz, 1 H), 8.37 (d, J = 9.2 Hz, 1 H), 8.24 (d, J = 8.0 Hz, 1 H), 8.20–8.14 (m, 3 H), 8.09–8.05 (m, 3 H), 8.00 (t, J = 7.2 Hz, 1 H), 7.86 (t, J = 8.0 Hz, 1 H), 7.70 (d, J = 8.0 Hz, 1 H), 7.36 (t, J = 2.4 Hz, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 159.5$ , 149.7, 136.4, 135.6, 131.5, 131.4, 128.6, 128.0, 127.9, 127.6, 127.4, 126.0, 125.8, 125.4, 125.1, 124.9, 124.8, 122.0 ppm. MS (EI): calcd. for C<sub>21</sub>H<sub>13</sub>N [M]<sup>+</sup> 279.1042; found 279.1048.

**Pt-1:** A mixture of 2-(1-pyrenyl)pyridine (147.0 mg, 0.53 mmol) and  $[K_2PtCl_4]$  (109.2 mg, 0.26 mmol) in 2-ethoxyethanol (6 mL) and water (2 mL) was heated at 80 °C for 20 h. After cooling to room temperature, the mixture was poured into water (20 mL) and the precipitate was collected and washed with water (2×10 mL) and dried under vacuum at 50 °C for 5 h. The precipitate with treated with Hacac (78.9 mg, 0.79 mmol) in the presence of

Na<sub>2</sub>CO<sub>3</sub> (279.0 mg, 2.63 mmol) in 2-ethoxyethanol (6 mL) at 100 °C for 20 h. Water (10 mL) was added and the precipitate was collected and washed with water (2 × 10 mL). After drying in vacuo in an oven, the crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 1:1, v/v). A yellow solid was obtained; yield 43.0 mg, 27.9%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.22 (d, *J* = 8.0 Hz, 1 H), 8.69 (d, *J* = 9.6 Hz, 2 H), 8.39 (d, *J* = 9.2 Hz, 2 H), 8.14–8.00 (m, 5 H), 7.95–7.90 (m, 2 H), 7.15 (t, *J* = 8.0 Hz, 1 H), 5.54 (s, 1 H), 2.13 (s, 3 H), 2.06 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 184.7, 148.4, 138.2, 131.0, 129.8, 128.7, 128.6, 128.4, 127.2, 126.2, 125.6, 125.1, 123.2, 121.9, 120.8, 102.8, 28.5, 27.6 ppm. MS (MALDI-TOF): calcd. for C<sub>26</sub>H<sub>19</sub>NO<sub>2</sub>Pt [M]<sup>+</sup> 572.1064; found 572.1052. C<sub>26</sub>H<sub>19</sub>NO<sub>2</sub>Pt (572.51): calcd. C 54.55, H 3.35, N 2.45; found C 54.84, H 3.55, N 2.31.

2-[4-(1-Pyrenyl)phenyl]pyridine (L-2): 2-(4-Bromophenyl)pyridine (286.0 mg, 1.22 mmol), 1-pyrenylboronic acid (300.0 mg, 1.22 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (52.1 mg, 0.045 mmol), aqueous Ba(OH)<sub>2</sub> (2.286 g, 2.0 M, 60 mL), EtOH (15 mL) and toluene (45 mL) were mixed in a flask. The mixture was degassed with argon and heated at reflux for 20 h. After being cooled, the solvent was evaporated under vacuum and the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub>, dried with  $Na_2SO_4$  and then evaporated to dryness. The crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 2:1, v/v). A light-yellow solid was obtained; yield 0.19 g, 43.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.77 (d, J = 4.4 Hz, 1 H), 8.26-8.17 (m, 6 H), 8.11 (s, 2 H), 8.06-8.00 (m, 3 H), 7.88-7.82 (m, 2 H), 7.76 (t, J = 8.0 Hz, 2 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl3):  $\delta = 157.2, 149.7, 142.3, 138.1, 137.4, 137.3, 131.7, 131.3,$ 131.2, 131.0, 128.7, 127.8, 127.7, 127.6, 127.2, 126.2, 125.4, 125.2, 125.1, 124.9, 122.5, 121.0 ppm. MS (EI): calcd. for C<sub>27</sub>H<sub>17</sub>N [M]<sup>+</sup> 355.1361; found 355.1367.

Pt-2: A mixture of 2-[4-(1-pyrenyl)phenyl]pyridine (155.0 mg, 0.44 mmol) and [K<sub>2</sub>PtCl<sub>4</sub>] (91.0 mg, 0.22 mmol) in 2-ethoxyethanol (6 mL) and water (2 mL) was heated at 80 °C for 20 h. After cooling to room temperature, the mixture was added to water (20 mL) and the precipitate was washed with water  $(2 \times 10 \text{ mL})$  and dried under vacuum in a drying oven at 50 °C for 5 h. The precipitate was treated with Hacac (65.5 mg, 0.65 mmol) in the presence of Na<sub>2</sub>CO<sub>3</sub> (231.0 mg, 2.18 mmol) in 2-ethoxyethanol (6 mL) at 100 °C for 20 h. Water (10 mL) was added and the yellow precipitate was collected and washed with water  $(2 \times 10 \text{ mL})$ . After drying in vacuo in an oven the crude product was purified by column chromatography (silica gel,  $CH_2Cl_2$ /petroleum ether = 1:1, v/v). A yellow solid was obtained; yield 85.0 mg, 60.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.07 (d, J = 5.2 Hz, 1 H), 8.32 (d, J = 8.8 Hz, 1 H), 8.23 (d, J = 8.0 Hz, 2 H), 8.20-7.99 (m, 8 H), 7.89-7.85 (m, 2 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.62 (d, J = 8.0 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 7.72 (t, J = 7.6 Hz, 1 H), 5.45 (s, 1 H), 2.02 (s, 3 H), 1.86 (s, 3 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ = 184.7, 148.4, 138.2, 131.0, 129.8, 128.7, 128.6, 128.4, 127.2, 126.2, 125.6, 125.1, 123.2, 121.9, 120.8, 102.8, 28.5, 27.6 ppm. MS (MALDI-TOF): calcd. for C<sub>32</sub>H<sub>23</sub>NO<sub>2</sub>Pt [M]<sup>+</sup> 648.1377; found 648.1340. C<sub>32</sub>H<sub>23</sub>NO<sub>2</sub>Pt (648.14): calcd. C 59.26, H 3.57, N 2.16; found C 59.09, H 3.84, N 1.85.

**1-Ethynylpyrene:** Under argon, 1-bromopyrene (2.0 g, 3.57 mmol), [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (100 mg, 0.14 mmol), PPh<sub>3</sub> (74.6 mg, 0.28 mmol) and CuI (54.3 mg, 0.28 mmol) were mixed in THF (20 mL) and triethylamine (60 mL). Then trimethylsilylacetylene (414 mg, 4.2 mmol) was added. The system was heated for 6 h at 90 °C. The reaction mixture was cooled to room temperature and filtered. The filtrate was collected and the solvent removed under reduced pres-



sure. The residue was dissolved in *n*-hexane. The remaining solid was filtered off and the filtrate was collected. Then the solvent was removed and a yellow oily was obtained. The yellow oil was dissolved in diethyl ether (20 mL). Then methanol (40 mL) and potassium carbonate (3.2 g) were added. The system was stirred at room temp. for 3 h. The mixture was filtered and the filtrate was revolved to dryness. The residue was purified by column chromatography (silica gel, *n*-hexane/DCM = 50:1, v/v). The third fraction was collected and the solvent was removed. The product was obtained as a cinereous powder; yield 600 mg, 40.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.54 (d, *J* = 8.6 Hz, 1 H), 8.11 (m, 4 H), 8.03 (m, 2 H), 7.97 (m, 2 H), 3.61 (s, 1 H) ppm. MS (EI): calcd. for C<sub>18</sub>H<sub>10</sub> [M]<sup>+</sup> 226.0783; found 226.0790.

L-3: To a degassed solution of 2-(4-bromophenyl)pyridine (414.0 mg, 1.77 mmol), [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (74.0 mg, 0.106 mmol) and PPh<sub>3</sub> (56.0 mg, 0.21 mmol) in diisopropylanmine (50 mL) was added the solution of ethynylpyrene (400.0 mg, 1.77 mmol) in THF (10 mL). Then CuI (20.0 mg, 0.106 mmol) was added and the reaction mixture was heated at 90 °C for 4 h. The mixture was poured into water (20 mL) and extracted with  $CH_2Cl_2$  (3 × 30 mL). Then the combined organic fractions were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvents evaporated to dryness. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:6, v/v). A yellow solid was obtained; yield 263.2 mg, 39.2%. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.72 (d, J = 4.4 Hz, 1 H), 8.67 (d, J = 8.8 Hz, 1 H), 8.23–8.18 (m, 4 H), 8.13–8.00 (m, 6 H), 7.81 (d, J = 7.6 Hz, 2 H), 7.76 (d, J = 3.6 Hz, 2 H), 7.26–7.25 (m, 1 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 132.3, 132.1, 131.5, 131.3, 129.9, 128.6, 128.4, 127.4, 127.1, 126.4, 125.9, 125.8, 125.7, 124.7, 124.5, 124.4, 95.3, 90.2 ppm. HRMS (EI): calcd. for C<sub>29</sub>H<sub>17</sub>N [M]<sup>-</sup> 379.1361; found 379.1367.

Pt-3: A mixture of L-3 (200.0 mg, 0.53 mmol) and [K<sub>2</sub>PtCl<sub>4</sub>] (109.0 mg, 0.26 mmol) in ethoxyethanol (6 mL) and water (2 mL) was heated at 80 °C for 20 h. After cooling to room temperature, the mixture was poured into water (10 mL) and the precipitate was collected and washed with water  $(2 \times 10 \text{ mL})$ . The crude product was dried under vacuum in a drying oven at 50 °C for 5 h. The precipitate was treated with Hacac (79.1 mg, 0.79 mmol) in the presence of Na<sub>2</sub>CO<sub>3</sub> (279.0 mg, 2.63 mmol) in 2-ethoxyethanol (6 mL) at 100 °C for 20 h. Water (10 mL) was added and the precipitate was collected and washed with water  $(2 \times 10 \text{ mL})$ . After drying in vacuo in an oven, the crude product was purified by column chromatography (silica gel,  $CH_2Cl_2$ /hexane = 1:1, v/v). A yellow solid was obtained; yield 20.0 mg, 5.6%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.03$  (d, J = 5.2 Hz, 1 H), 8.74 (d, J = 9.2 Hz, 1 H), 8.23–7.99 (m, 8 H), 7.93 (s, 1 H), 7.83 (t, J = 8.0 Hz, 1 H), 7.65 (d, J = 7.6 Hz, 1 H), 7.49–7.46 (m, 2 H), 7.15 (t, J = 6.0 Hz, 1 H), 5.50 (s, 1 H), 2.22 (s, 3 H), 2.08 (s, 3 H) ppm. FTIR (KBr):  $\tilde{v}$  = 3435, 2923, 2852, 1631, 1608, 1578, 1561, 1517, 1479, 1427, 1390, 1312, 1262, 1095, 1025, 852, 825, 780, 755, 716 cm<sup>-1</sup>. MS (MALDI-TOF): calcd. for C<sub>34</sub>H<sub>23</sub>NO<sub>2</sub>Pt [M]<sup>+</sup> 672.1377; found 672.1414. C<sub>34</sub>H<sub>23</sub>NO<sub>2</sub>Pt·H<sub>2</sub>O (690.65): calcd. C 59.13, H 3.65, N 2.03; found C 59.40, H 3.39, N 1.90.

**2-(4-Biphenylyl)pyridine** (L-4): 2-(4-Bromophenyl)pyridine (405.4 mg, 2.00 mmol), phenylboronic acid (244.0 mg, 2.00 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (85.0 mg, 0.073 mmol), aqueous Na<sub>2</sub>CO<sub>3</sub> (4.24 g, 2.0 M, 20 mL) and toluene (40 mL) were mixed in a flask. The mixture was degassed with argon and heated at reflux for 20 h. After being cooled, the solvent was evaporated under vacuum. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and then evaporated to dryness. The crude product was purified by column chromatography (silica gel,

CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 2:1, v/v). A white solid was obtained; yield 0.25 g, 54.8%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.71 (d, *J* = 4.4 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 2 H), 7.78–7.76 (m, 2 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.25–7.23 (m, 1 H) ppm. MS (EI): calcd. for C<sub>17</sub>H<sub>13</sub>N [M]<sup>+</sup> 231.1048; found 231.1051.

Pt-4: A mixture of 2-(4-biphenylyl)pyridine (115.6 mg, 0.50 mmol), [K<sub>2</sub>PtCl<sub>4</sub>] (103.8 mg, 0.25 mmol) in ethoxyethanol (6 mL) and water (2 mL) was heated at 80 °C for 20 h. After cooling to room temperature, the mixture was poured into water (20 mL) and the precipitate was collected and washed with water ( $2 \times 10 \text{ mL}$ ). The crude product was dried under vacuum at 50 °C for 5 h. Reaction of the precipitate with Hacac (75.0 mg, 0.75 mmol) in the presence of Na<sub>2</sub>CO<sub>3</sub> (265.0 mg, 2.50 mmol) in 2-ethoxyethanol (6 mL) at 100 °C for 20 h. After cooling to room temperature, water (10 mL) was added and the precipitate was collected and washed with water  $(2 \times 10 \text{ mL})$ . The crude product was dried in vacuo in an oven and then purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 1:1, v/v). A yellow solid was obtained; yield 94.0 mg, 97.8%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.00 (d, J = 5.2 Hz, 1 H), 7.84 (s, 1 H), 7.79 (t, J = 7.2 Hz, 1 H), 7.70 (d, J = 7.6 Hz, 2 H), 7.61 (d, J = 8.0 Hz, 1 H), 7.50–7.43 (m, 3 H), 7.10 (t, J =6.0 Hz, 1 H), 5.48 (s, 1 H), 2.01 (s, 6 H) ppm. <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ ):  $\delta = 185.7, 184.2, 168.0, 147.3, 143.9, 141.9, 141.8, 139.1,$ 138.1, 129.0, 128.6, 127.4, 127.2, 123.3, 122.8, 121.1, 118.4, 102.5, 28.3, 27.2 ppm. MS (MALDI-TOF): calcd. for  $C_{22}H_{19}NO_2Pt$ [M]<sup>+</sup> 524.1064; found 524.1099. C<sub>22</sub>H<sub>19</sub>NO<sub>2</sub>Pt (524.47): calcd. C 50.38, H 3.65, N 2.67; found C 50.53, H 3.57, N 2.38.

**DFT/TDDFT Calculations:** The structures of the complexes were optimized by using density functional theory (DFT) with the B3LYP functional and 6-31G(d)/LanL2DZ basis set. The related calculations in the excited state were carried out with time-dependent DFT (TDDFT) with the ground-state geometries. The 6-31G(d) basis set was employed for the C, H, N and O atoms, and the LanL2DZ basis set was used for Pt<sup>II</sup>. There are no imaginary frequencies for any of the optimized structures. All the calculations were performed with Gaussian 09.<sup>[40]</sup>

**Supporting Information** (see also the footnote on the first page of this article): Characterization and calculation of the compounds.

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