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Robust phosphorescent platinum(II) complexes with tetradentate O^N^C^N ligands: high efficiency OLEDs with excellent efficiency stability†

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The Pt(II) complexes (1–3) bearing tetradentate O^N^C^N ligands display high emission quantum yields (0.76–0.90) and good thermal stability (T_d > 400 °C). Complex 3 is an excellent green phosphorescence dopant for OLEDs with excellent efficiency and low efficiency roll-off (η_L, η_{Ext}(max) = 66.7 cd A^{-1}, 18.2%; η_L, η_{Ext} (1000 cd m^{-2}) = 65.1 cd A^{-1}, 17.7%).

Square planar platinum(II) complexes containing *N*-donor and/or cyclometalated ligands have emerged to be important classes of phosphorescent materials[1–6] with useful practical applications in molecular and bio-molecular sensing[2] and in organic electronics.[3–6] Our interest in this area is to develop robust phosphorescent Pt(II) complexes supported by tetradentate ligands. Platinum(II) complexes bearing symmetric bis(2′-phenol)bipyridines (N_2O_2),[7] Schiff base (Salphen),[8] bis(pyrrole)diimine (Prtmen),[9] *N*,*N*-di(2-phenylpyrid-6-yl)-aniline (C^N*N^C)[10] and tetradentate bis(*N*-heterocyclic carbene) (tetra-NHC)[11] ligands have been reported with their emission energy ranging from blue to red color (Chart 1). We have also reported that the OLED fabricated with [Pt(salphen)] (salphen = *N*,*N*′-bis(salycilidene)-1,2-phenylene-diamine) achieved a long device lifetime.[8] This may be attributed to the stability of Pt(II) emitter endowed by the dianionic tetradentate ligand so that the OLED device lifetime could be greatly improved.

Recently, we reported a series of cyclometalated platinum(II) complexes supported by a new tetradentate ^{Ind}O^N^C^N ligand (^{Ind}O^N^C^N = 5,5-dibutyl-2-(3-(pyridin-2-yl)-4,6-difluoro-phenyl)-5H-indeno[1,2-b]pyridin-9-olate; Chart 1).[12] This Pt(II) complex shows both high energy monomer emission (∼480–520 nm) and low energy excimer emission (>600 nm) enabling the fabrication of high-efficiency WOLEDs by using it as a single emissive dopant. However, excimer emission is not desirable in achieving high performance red, green and blue OLEDs. Herein, we report a new class of Pt(II) complexes supported by the rigid tetradentate O^N^C^N ligands (O^N^C^N = 2-(4-(3,5-di-*tert*-butylphenyl)-6-(3-(pyridin-2-yl)phenyl)-pyridin-2-yl)phenolate and its derivatives; Chart 1). Complexes **1–3** display high emission quantum yields (ϕ) up to 90%, are thermally stable (T_d > 400 °C), and could be obtained in high purity by sublimation at ∼290 °C under 4 × 10^{-5} torr. Importantly, **3** shows minimal intermolecular aggregation or excimer formation thereby minimizing the device efficiency roll-off at high luminance.

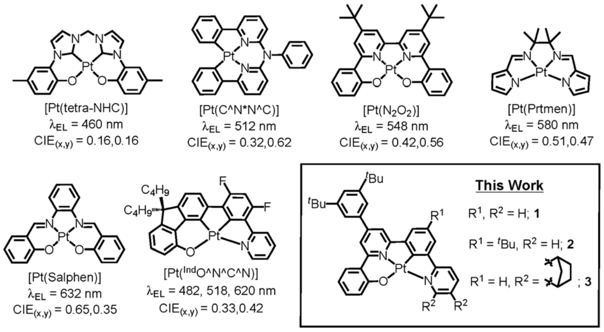

Chart 1 The literature electrophosphorescent Pt(II) complexes with tetradentate ligands and chemical structure of complexes **1–3**.

The preparation of **1–3** involves a one-step reaction with high product yields (up to 80%). They were prepared by the reaction of H–O^N^C^N ligands with K_2PtCl_4 in a refluxing CH_3COOH and $CHCl_3$ mixture (9 : 1). The ^{1}H-NMR spectra of **1–3** and molecular packing diagrams and crystallographic data of **2** and **3** are given in the ESI.† Perspective views of **2** and **3** are depicted in Fig. 1. The [(O^N^C^N)Pt] motif in each case is virtually planar with the torsion angles O1–N1–C13–N2 in the range of 0.11° to 2.55°. Two molecules of **2** or **3** are aligned in a head-to-head orientation with a Pt···Pt distance of 3.218 Å and 3.396 Å, respectively. There are intermolecular π···π interactions (∼3.5 Å) between each pair of molecules of **2** or **3**.

The spectroscopic and photophysical data of **1–3** are presented in Table 1. As depicted in Fig. 2, these complexes in CH_2Cl_2 display intense absorption bands at wavelengths below 300 nm (ε > 3.8–4.5 × 10^4 mol^{-1} dm^3 cm^{-1}), which are assigned to $^1\pi$–π* transitions of the O^N^C^N ligands, and moderate intense absorption bands at 421–438 nm ($\varepsilon \approx$ 6580–9440 mol^{-1} dm^3 cm^{-1}) with

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† Electronic supplementary information (ESI) available: Experimental procedures, X-ray structures of **2** and **3**, device performance. CCDC 830685 and 907730. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37862k

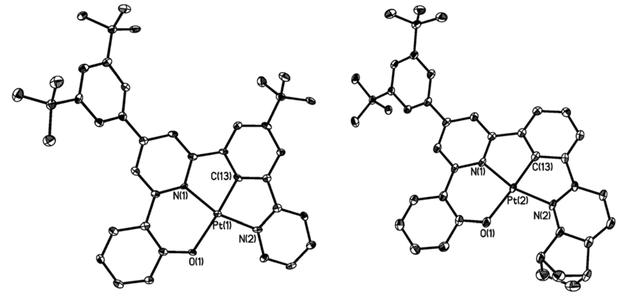

Fig. 1 Perspective view of **2** (left) and **3** (right) (all hydrogen atoms are omitted for clarity).

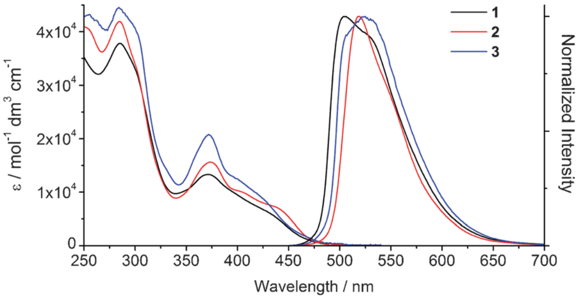

Fig. 2 UV absorption spectra and emission spectra of **1–3** in CH_2Cl_2 (2.0×10^{-5} mol dm^{-3}).

weak absorption tails at >460 nm ($\varepsilon \approx$ 1600–2600 mol^{-1} dm^3 cm^{-1}). The absorption bands of all complexes follow Beer's law with the complex concentrations ranging from 10^{-4} to 10^{-5} mol dm^{-3}. Solvatochromic effect has been observed. With **1** as an example, the absorptions at $\lambda > 400$ nm red shift in energy in low-polarity solvents (*e.g.* complex **1**, the broad absorption at λ_{max} 420 nm in MeCN is red-shifted to 444 nm in C_6H_6). We tentatively assign the absorptions at > 400 nm to charge transfer transition with mixed phenoxide lone pair (l) to π* orbital of N^C^N, *i.e.* ^{3}[l → π*(N^C^N)] and ^{1}[Pt(5d) → π*(O^N^C^N)] MLCT characters.

In degassed CH_2Cl_2, complexes **1–3** are strongly emissive with emission quantum yields in the range of 0.76–0.90 and emission lifetimes (τ) in the microsecond time regime (~4–5 μs) (Table 1). Each of the complexes shows a structureless emission band with λ_{max} at 503, 518 and 522 nm for **1**, **2**, and **3**, respectively. Similar to the absorption data, the emission of **1** also displays a solvatochromic effect (*e.g.* λ_{max} of **1** in MeOH at 500 nm is red-shifted to 512 nm in C_6H_6). We tentatively assign the emissions of **1–3** to mixed ^{3}MLCT and ^{3}[l → π*(N^C^N)] (l = lone pair of phenoxide) excited states. Notably the self-quenching rate constant k_q of **3** (8.82×10^7 mol^{-1} dm^3 s^{-1}) is smaller than that of **1** and **2** ($1.78–2.08 \times 10^9$ mol^{-1} dm^3 s^{-1}) and is relatively smaller than the reported values (~10^8 to 10^9 mol^{-1} dm^3 s^{-1}) of the other reported luminescent Pt(II) complexes. This reveals that the bulky norbornane group on the pyridine moiety can block intermolecular interactions thus disfavouring excimer formation in solutions.

As complex **3** has a high phosphorescence quantum yield, a reasonably short radiative lifetime (τ_r = 5.4 μs) and ineffective self-quenching at high complex concentrations, this complex is a good candidate for PHOLED since the triplet–triplet annihilation and concentration quenching effect arising from the intermolecular interactions can be minimized even at high dopant concentration.[13]

Multi-layer devices by thermal deposition have been fabricated using **1** or **3** as emitting material and with a device structure of ITO/di-[4-(*N*,*N*-ditolyl-amino)-phenyl]cyclohexane (TaPc, 70 nm)/mCP: **1** or **3** (*x*%, 30 nm)/1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB, 40 nm)/LiF (0.5 nm)/Al (100 nm). TaPc and TmPyPB were chosen as hole-transporting material and electron-transporting material respectively; this combination has been known to give a good device efficiency for phosphorescent green emitters. On the other hand, in the case of the commonly used host material, 4,4′-bis(carbazol-9-yl)-biphenyl (CBP), the LUMO (−3.0 eV) cannot cover the LUMOs of **1** and **3**, therefore a wider band-gap derivative, 1,3-bis(carbazol-9-yl)-benzene (mCP), was used as host material. The device performance was optimized by varying the doping concentration of the complex. A maximum current efficiency of 30.2 cd A^{-1} was obtained at 1% dopant concentration of **1** (device A) while a maximum current efficiency of 66.7 cd A^{-1} was achieved at 13% of **3** (device B); the performance data are depicted in Table 2. As depicted in Fig. 3, the EL spectra of devices A and B have not been affected by the operation voltage. As the position and shape of the EL spectra are similar to the solution PL spectra, the EL of both devices are assigned to come from the platinum(II) complexes. A blue emitting component at around 450 nm, which is attributed to the emission of the host material, has been observed in the EL spectra of device A. This is a sign of incomplete energy transfer from the host material to **1**. Presumably this is due to the low dopant concentration of 1%. The blue emitting component vanished when the dopant concentration increased to 2% (Fig. S15, ESI†). Nevertheless, at the same time, another emitting component at >600 nm

Table 1 Physical, spectroscopic and photophysical data of **1–3**

Complex	UV-vis absorption[a] λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})	Emission[a] Solution[a] λ_{max}/nm (τ_p; τ_r/μs)[b]	Quantum[c] yield (ϕ_p)	k_q[d]/ mol^{-1}dm^3 s^{-1}	HOMO[e] [eV]	LUMO[e] [eV]	Electrochemical bandgap [eV]	T_d [°C]
1	284 (38 070), 371 (13 240), 426 (6580)	503 (4.7; 6.4)	0.73	2.08×10^9	−4.93	−2.69	2.24	518
2	285 (42 520), 374 (15 720), 404 (10 090), 438 (7170)	518 (3.7; 4.5)	0.82	1.79×10^9	−4.93	−2.64	2.29	430
3	284 (44 730), 371 (20 950), 421 (9440)	522 (4.9; 5.4)	0.90	8.82×10^7	−5.16	−2.65	2.51	405

[a] Determined in a degassed dichloromethane solution (2×10^{-5} mol dm^{-3}). [b] τ_p = room temperature lifetime; τ_r = radiative lifetime of the triplet state deduced from $\tau_r = \tau_p/\phi_p$. [c] Emission quantum yield was measured in a degassed dichloromethane solution (2×10^{-5} mol dm^{-3}) by the optical dilute method with 9,10-bis(phenylethynyl)anthracene (BPEA) in degassed benzene as the standard (ϕ_r = 0.85). [d] Self-quenching constant. [e] The HOMO and LUMO levels were estimated from onset potentials using $Cp_2Fe^{0/+}$ values of 4.8 eV below the vacuum level.

Table 2 Device performance for device A and device B

		Efficiency (η_L[b]/cd A^{-1}; η_p[c]/lm W^{-1}; η_{Ext}[d]/%)			CIE coordinates (*x*, *y*)[e]		
Device[a]	Conc.	Max.	@ 1000 cd m^{-2}	@ 10 000 cd m^{-2}	Max.	@ 1000 cd m^{-2}	@ 10 000 cd m^{-2}
A	1%	30.2; 14.6; 8.6	29.8; 13.8; 8.5	17.1; 5.0; 4.9	(0.234, 0.650)	(0.234, 0.650)	(0.238, 0.639)
B	13%	66.7; 34.1; 18.2	65.1; 30.7; 17.7	48.5; 17.2; 13.2	(0.282, 0.657)	(0.304, 0.647)	(0.296, 0.561)

[a] ITO/TaPc (70 nm)/mCP: **1** or **3** (*x*%, 30 nm)/TmPyPB (40 nm)/LiF (0.5 nm)/Al (100 nm). [b] Current efficiency. [c] Power efficiency. [d] External quantum efficiency. [e] Commission Internationale d'Eclairage chromaticity coordinates.

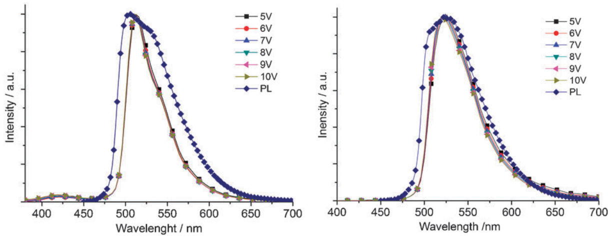

Fig. 3 Comparisons between PL and EL spectra (left – device A; right – device B).

developed and the CIE$_x$ increased. This is attributed to excimer emission from **1**. As a result, the color of the devices gradually shifted from green to greenish-yellow upon an increase in the dopant concentration of **1** and the maximum device efficiency dropped to 26.9 cd A^{-1} at 4% dopant concentration.

On the other hand, the maximum efficiency of the devices fabricated with **3** increased with dopant concentration up to a high dopant level of 13% (Fig. 4). No extra emitting component or significant shift in CIE was observed. These data show that excimer formation is successfully suppressed by the norbornane group. Green emission with CIE coordinates of (0.304, 0.647) has been obtained at 1000 cd m^{-2}. Besides device efficiency and color, the devices fabricated with **3** showed excellent performance in efficiency roll-off. Only 2.4% roll-off (65.1 cd A^{-1}) was observed at 1000 for the device B.

Phosphorescent platinum(II) complexes have been reported for white OLED (WOLED) fabricated with one single emitter. Excimer emission from Pt(II) complexes can be obtained even at a low dopant concentration of 3%.[4,12,14] Nevertheless, this characteristic feature of Pt(II) complexes could be detrimental to RGB panel application as the color purity, device efficiency and efficiency stability can also be affected at high dopant concentration. However, low dopant concentration is not desirable for industry/practical application. In this work, this dilemma has been resolved by incorporation of the norbornane group to the O^N^C^N ligand. To the best of our knowledge, device B is the best green-emitting OLED using platinum(II) emitting material, taking into account the maximum device efficiency (η_L: 66.7 cd A^{-1}; η_{Ext}: 18.2%), colour purity (CIE: 0.282, 0.657) and efficiency stability (2.4% roll-off@1000 cd m^{-2}).

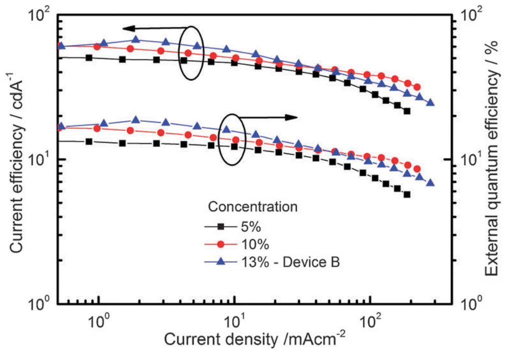

Fig. 4 Efficiency of the device fabricated with **3**.

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