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# Tetradentate Schiff base platinum(II) complexes as new class of phosphorescent materials for high-efficiency and white-light electroluminescent devices†

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**The capabilities of readily prepared and sublimable Pt(II) Schiff base triplet emitters as OLED dopants have been examined; maximum luminous and power efficiencies and luminance of 31 cd A$^{-1}$, 14 lm W$^{-1}$, and 23,000 cd m$^{-2}$, respectively, and white EL (CIE: 0.33, 0.35) by simultaneous host/dopant emission, have been achieved.**

Schiff base ancillary ligands based on the parent *N,N′*-bis(salicylidene)-1,2-ethylenediamine ($H_2$salen) have impacted profoundly on a number of research areas for at least the last decade, with enantioselective organic oxidation being a notable example.[1] Nevertheless, application studies on metal–salen derivatives in material science remain sparse in the literature.[2,3] Hamada and coworkers pioneered the development of zinc(II) complexes bearing Schiff base ligands as blue to greenish-white emitters for employment in organic optoelectronics.[4] We now demonstrate that platinum(II) Schiff base compounds constitute an attractive class of phosphorescent materials that are easily synthesized, thermally stable, structurally diverse, and potentially important in materials applications.

Treatment of $K_2PtCl_4$ with the respective Schiff base in an aqueous KOH solution (1 M) under an argon atmosphere,[5] followed by appropriate purification steps, gave [Pt($L^{1-3}$)] (**1–3**, $H_2L^1$ = *N,N′*-bis(salicylidene)-1,2-ethylenediamine; $H_2L^2$ = *N,N′*-bis(salicylidene)-1,3-propanediamine; $H_2L^3$ = *N,N′*-bis(salicylidene)-1,1,2,2-tetramethylethylenediamine) as orange crystalline solids. Complexes **1–3** are stable in air, and no decomposition or ligand dissociation was observed in ethanol, 2-propanol, DMSO or acetonitrile under ambient conditions after several days. Thermogravimetric analysis (TGA) showed that all three complexes are stable under a nitrogen atmosphere up to 360 °C, and the decomposition temperatures of **1–3** are 406, 369 and 382 °C respectively.† In addition, **3** was observed to sublime before its decomposition temperature was reached, hence slow weight loss was detected from around 200 °C (to 95 wt%) before decomposition occurred.

The molecular structure of **3** was determined by X-ray crystallography‡ and is depicted in Fig. 1. In contrast to the reported structure for **1**, with a Pt···Pt distance of 3.277(1) Å,[6] there is no short (< 3.5 Å) intermolecular Pt···Pt or π–π interaction in the crystal lattice of **3** (shortest Pt···Pt distance = 5.922(9) Å).

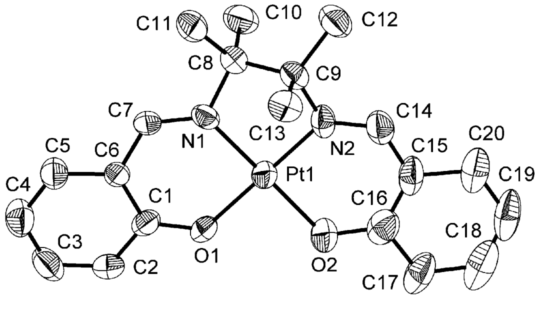

**Fig. 1** Perspective view of **3** (30 % thermal probability).

The absorption spectra of **1–3** in acetonitrile feature two intense absorption bands at around 340 ($\varepsilon \approx 1 \times 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$) and 420 ($\varepsilon \approx 0.5 \times 10^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$) nm, plus a weak low-energy absorption shoulder at around 500 nm ($\varepsilon \approx$ 60–80 mol$^{-1}$ dm$^3$ cm$^{-1}$; see Fig. 2 for **3**). Solvatochromic studies on **3** showed that the low-energy absorptions ($\lambda$ > 400 nm) undergo red shifts in low-polarity solvents (*e.g.* broad absorption at $\lambda_{max}$ 411 nm in MeOH becomes two distinct bands at $\lambda_{max}$ 433 and 455 nm in $C_6H_6$). We tentatively assign this absorption to a charge transfer transition involving the phenoxide lone pair (l) and the π* orbital of imine, *i.e.* $^1$[l(phenoxide) → π*(imine)], mixed with $^1$[Pt(5d) → π*(Schiff base)] MLCT character.

Complexes **1–3** exhibit intense phosphorescence in fluid solutions ($\lambda_{max}$ 537–592 nm; see Fig. 2 for **3** in acetonitrile) and in the solid state ($\lambda_{max}$ 548–598 nm) at room temperature (Table S1†). In acetonitrile at 298 K, **1**, **2** and **3** emit ($\tau$/μs; $\Phi_{em}$) at $\lambda_{max}$ 550 (3.5; 0.19), 592 (0.5; 0.09) and 541 (3.4; 0.18) nm, respectively. Compared to the absorption data, the emission of **3** displays smaller solvatochromic effects (*e.g.* $\lambda_{max}$ in MeOH at 537 nm is red-shifted by only *ca.* 300 cm$^{-1}$ to 546 nm in $C_6H_6$). The triplet emissive excited state of **3** in degassed acetonitrile is characterized by an absorption band at *ca.* 480 nm,† and the measured decay lifetime of 3.6 μs closely matches the emission lifetime in acetonitrile (3.4 μs). Complex **1** exhibits an irreversible anodic wave at 0.54 V *vs.* $Cp_2Fe^{+/0}$ in DMF. Based on the electrochemical data, the excited state of **1** is a powerful reductant with $E°(\mathbf{1}^+/\mathbf{1}^*) \leq -1.6$ V *vs.* SSCE. A comparable value of −1.75 V *vs.* SSCE was derived from quenching studies with pyridinium acceptors.†

The sublimability, relatively short emission lifetimes (*cf.* > 50 μs for PtOEP[7]) and high photoluminescent quantum efficiencies of complexes **1** and **3** render them suitable candidates as efficient electrophosphorescent dopants. OLEDs with emitting layers comprising the host material 4,4′-(*N,N′*-dicarbazole)biphenyl (CBP) plus **3** as dopant at different concentrations were fabricated

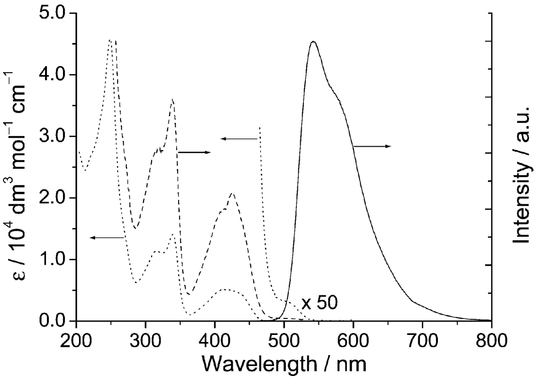

**Fig. 2** Absorption (dot), excitation (dash, $\lambda_{em}$ = 541 nm) and emission (solid line, $\lambda_{ex}$ = 413 nm) spectra of **3** in acetonitrile at 298 K.

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† Electronic supplementary information (ESI) available: synthesis and spectroscopic, thermal (TGA), photophysical, electrochemical and EL characterization; CIF. See http://www.rsc.org/suppdata/cc/b4/b402318h/

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(configuration: [ITO/NPB (400 Å)/CBP:**3** (300 Å)/BCP (200 Å)/ $Alq_3$ (300 Å)/LiF (5 Å)/Al (1500 Å)]).† These devices require low turn-on voltages of around 3 V. At 1.0 to 6.0 wt%, only EL from the dopant **3** at $\lambda_{max}$ 550 (sh 590) nm is observed, although a minor peak at $\lambda_{max}$ 420 nm from NPB is visible at 0.5 wt%.

At the optimized dopant concentration of 4.0 wt%, the maximum external quantum efficiency ($\eta_{ext}$), luminous efficiency ($\eta_L$), power efficiency ($\eta_P$), and luminance are (current density/mA $cm^{-2}$ in parentheses): 11% (8.5), 31 cd $A^{-1}$ (8.5), 14 lm $W^{-1}$ (8.5), and 23,000 cd $m^{-2}$ (683), respectively (Fig. 3). The performance of the **3**-doped OLED (4.0 wt%) at different current density is listed in Table 1. We note that (i) even at the high luminance of 10,000 cd $m^{-2}$, $\eta_{ext}$, $\eta_L$, and $\eta_P$ is 4.1%, 13 cd $A^{-1}$, and 4.0 lm $W^{-1}$, respectively, and (ii) reasonable $\eta_L$ is observed at very high current densities (*e.g.* 4.1 cd $A^{-1}$ at 500 mA $cm^{-2}$). The EL spectra for this OLED exhibit no significant change from 3 to 16 V, and the Commission Internationale de l'Eclairage (CIE) coordinates at 8 V are (0.48, 0.52), which correspond to orange light.

In order to realise the generation of white EL, devices comprising the host material bis(2(2′-hydroxyphenyl)pyridine)beryllium ($Bepp_2$) plus complex **1** as dopant at different concentrations were prepared (configuration: [ITO/NPB (500 Å)/$Bepp_2$:**1** (500 Å)/LiF (15 Å) /Al (1500 Å)], with devices A–D corresponding to 3.2, 7.7, 11.1 and 16.7 wt% of **1** respectively; Fig. 4).† All devices begin to glow at 4–5 V and exhibit two emission bands at $\lambda_{max}$ 448 and 552 nm in the EL spectra. Device A (3.2 wt% of **1**) gives a luminous efficiency of 0.79 lm $W^{-1}$ and luminance of 450 cd $m^{-2}$ at 20 mA $cm^{-1}$. The highest achieved luminance is 3045 cd $m^{-2}$ at 307 mA $cm^{-2}$. Importantly, the CIE coordinates of device A are (0.33, 0.35), which closely approaches that of white light (defined as 0.33, 0.33); the white emission is produced by the simultaneous EL of $Bepp_2$ and **1** in the device. Upon increasing the concentration of **1**, both the luminance and luminous efficiency are enhanced and the emission of **1** becomes more dominant in the EL spectra (especially in device C). However, the overall device efficiency diminishes at 16.7 wt% (device D); this is consistent with aggregation of dopant molecules at sufficiently high concentrations, which can lead to intermolecular quenching.

Saliently, the performance of OLEDs employing the Schiff base dopant **3** are substantially superior to previously reported results for platinum(II) emitters,[7,8] and the excellent brightness and efficiencies approach or are comparable to those obtained for the intensely studied bis- and tris-cyclometalated iridium(III) electrophosphorescent materials.[9] While most examples of white OLEDs require multilayer configurations,[8b,10] we note that pure white EL has been achieved in this work using a relatively simple device configuration.

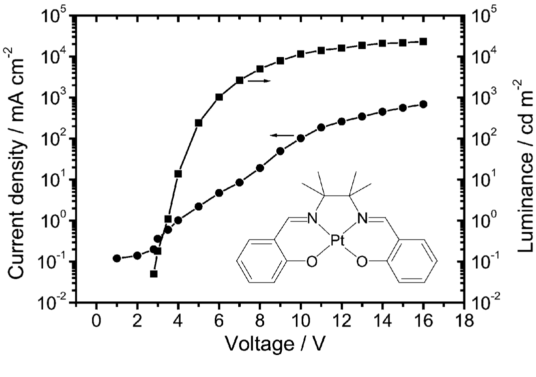

**Fig. 3** Current density and luminance curves of **3**-doped OLED (4.0 wt %) against applied voltage.

**Table 1** Performance of **3**-doped OLED (4.0 wt %) at different $I^a$

| Current density/ mA $cm^{-2}$ | *V*/V | *L*/ cd $m^{-2}$ | $\eta_{ext}$ (%) | $\eta_L$/ cd $A^{-1}$ | $\eta_P$/ lm $W^{-1}$ |
|---|---|---|---|---|---|
| 1 | 4.0 | 14 | 0.47 | 1.4 | 1.1 |
| 10 | 7.1 | 3 010 | 11 | 30 | 13 |
| 20 | 8.1 | 5 050 | 9.1 | 25 | 10 |
| 100 | 10.0 | 11 500 | 3.9 | 11 | 3.5 |
| 500 | 14.5 | 21 200 | 1.5 | 4.1 | 0.9 |

[a] Configuration: [ITO/NPB/CBP:**3**/BCP/$Alq_3$/LiF/Al].

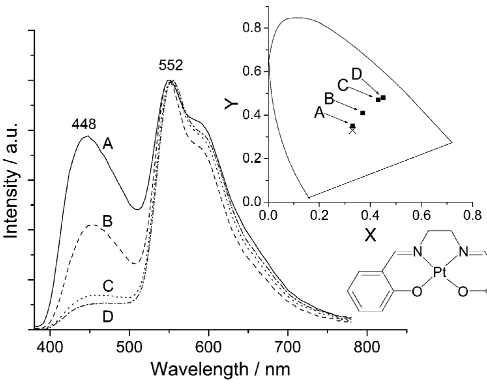

**Fig. 4** EL spectra of devices A–D (3.2, 7.7, 11.1 and 16.7 wt% of **1** respectively) and corresponding CIE coordinates (inset, cross indicates pure white emission).

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## Notes and references

‡ Crystal data for **3**: $C_{20}H_{22}N_2O_2Pt$, $M$ = 517.49, monoclinic, $P2_1/c$, $a$ = 22.384(5), $b$ = 20.718(4), $c$ = 12.077(2) Å, $\beta$ = 94.90(3)°, $V$ = 5580(2) $Å^3$, $T$ = 253(2) K, $Z$ = 12, $\mu$ = 7.558 $mm^{-1}$, $2\theta_{max}$ = 50.7°, 9009 independent reflections ($R_{int}$ = 0.069), 658 parameters, $R_1$ = 0.039 ($I > 2\sigma(I)$), $wR_2$ = 0.081. CCDC 217004. See http://www.rsc.org/suppdata/cc/b4/b402318h/ for crystallographic data in .cif or other electronic format.

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