

# High-efficiency red electrophosphorescence based on neutral bis(pyrrole)-diimine platinum(II) complex†

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Efficient red electroluminescence from the excimer or oligomer of neutral phosphorescent bis(pyrrole)-diimine Pt(II) complex has been achieved with maximum external quantum efficiency, luminous efficiency, power efficiency and brightness of 6.5%, 9.0 cd A<sup>-1</sup>, 4.0 lm W<sup>-1</sup> and 11 100 cd m<sup>-2</sup>, respectively.

In recent years, highly-efficient phosphorescent organic light-emitting devices (OLEDs) have been an area of topical interest in material science and display technology.<sup>1</sup> At present, reports of red electrophosphorescent materials include Eu(III) chelates,<sup>2</sup> Pt(II) porphyrins,<sup>1,3</sup> cyclometalated Pt(II) acetylides,<sup>4</sup> Os(II) diimine,<sup>5</sup> and Ir(III) complexes.<sup>6</sup> The best performances of red electrophosphorescence are based on Ir(III) phosphors.<sup>6</sup> The red electrophosphorescence from Pt(II) porphyrin complexes shows a modest external quantum efficiency ( $\eta_{\text{ext}}$ ) of ~5% at low current with a brightness of 1–10 cd m<sup>-2</sup>, and the efficiency was found to sharply decrease at high current due to saturation of emissive sites, which is caused by the long decay lifetime of triplet excitations (> 50  $\mu$ s).<sup>1</sup> We recently discovered that tetradentate Pt(II) Schiff base complexes were found to be efficient yellow emitters for OLEDs.<sup>7</sup> Forrest and coworkers previously demonstrated efficient white OLEDs based on excimer or oligomer of Pt(II) phosphors.<sup>8</sup> In this work, we describe efficient red electroluminescence (EL) from the excimer or oligomer of neutral phosphorescent bis(pyrrole)-diimine Pt(II) complex. The present work highlights neutral Pt(II) complexes containing simple tetradentate N-donor as a new class of molecular phosphorescent materials with potential applications in organic optoelectronics.

The Pt(II) complexes, **PtPren**, **PtPrtmn**, and **PtPrdmphen** were synthesized by treating the N-donor ligand and sodium acetate in DMF with K<sub>2</sub>PtCl<sub>4</sub> at moderate temperature,<sup>9</sup> (see ESI†) and their chemical structures and absorption and photoluminescent (PL) spectra in degassed CH<sub>3</sub>CN are shown in Fig. 1. Due to the emission decay lifetime in the microsecond time region and the large Stokes shift between the absorption and emission band, the PL emission of the Pt(II) complexes is attributed to triplet excited states. Among the three Pt(II) complexes, the PL emission of **PtPrdmphen** occurs at the lowest energy, presumably due to its extended  $\pi$ -conjugated ligand system. **PtPren** shows a yellow emission with a peak maximum at 566 nm and a shoulder at 613 nm in CH<sub>3</sub>CN at 298 K. The concentration-dependent emissive behavior of **PtPren** in frozen CH<sub>3</sub>CN at 77 K has been

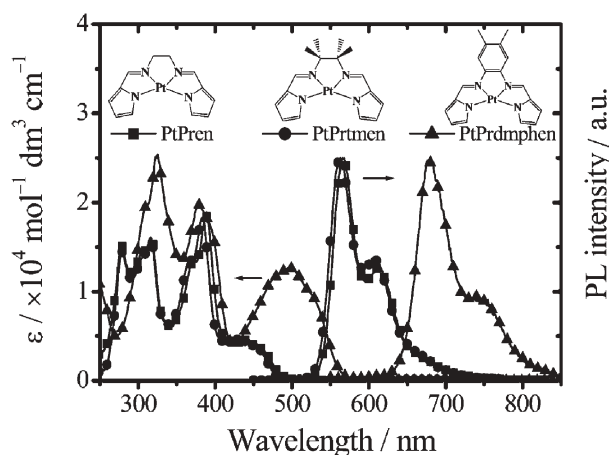


Fig. 1 Chemical structure of Pt(II) complexes and their absorption and PL emission spectra in CH<sub>3</sub>CN at 298 K.

investigated (Fig. 2). At a concentration of  $1.0 \times 10^{-6}$  mol dm<sup>-3</sup>, a vibronic yellow emission with peak maxima at 560 and 611 nm (vibrational progression 1510 cm<sup>-1</sup>) and a shoulder at 650 nm was observed. Increasing the concentration gave a red shift emission. Indeed, at complex concentrations >  $10^{-3}$  mol dm<sup>-3</sup>, the higher-energy yellow emission is almost replaced by the lower-energy red emission. A similar red shift in emission energy is also evident for

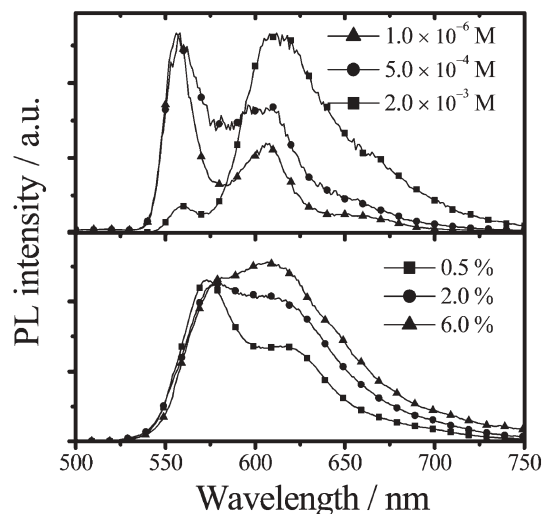


Fig. 2 PL spectra of **PtPren** in frozen CH<sub>3</sub>CN at 77 K (top) and **PtPren**-doped-CBP (bottom) thin films at 298 K.

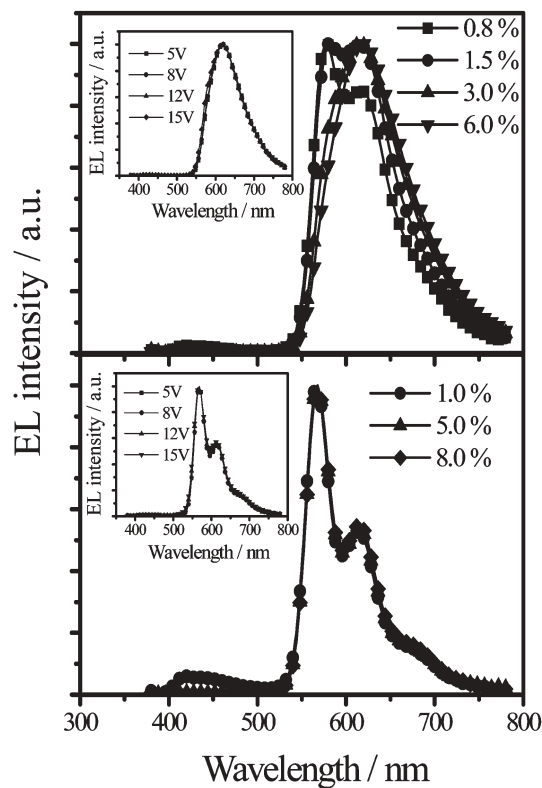
† Electronic supplementary information (ESI) available: General experimental procedure, syntheses, and electroluminescent properties of the reported Pt(II) complexes. See <http://www.rsc.org/suppdata/cc/b4/b415711g/>

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high dopant concentrations of **PtPren**-doped-4,4'-*N,N'*-dicarbazole-biphenyl (CBP) thin films (Fig. 2), where the "shoulder" dominates and the emission  $\lambda_{\text{max}}$  appears at 610 nm. We attribute this red shift with broader full width half maximum to the formation of excimer or oligomer at high concentrations, which is a commonly encountered phenomenon in solid state or solution Pt(II) complexes.<sup>8,10</sup> For **PtPrtmn**, no excimer or oligomer emission was observed, presumably the methylethylene moiety of **PtPrtmn** disfavors close intermolecular contacts.<sup>7</sup>

Compared with Pt(II) porphyrins, **PtPren** and **PtPrtmn** exhibit shorter PL lifetimes (4.2 and 3.6  $\mu\text{s}$  in  $\text{CH}_3\text{CN}$  at 298 K, respectively) and reasonable quantum efficiencies (9.7 and 10.5% upon excitation at 459 and 431 nm in  $1 \times 10^{-6}$  mol  $\text{dm}^{-3}$   $\text{CH}_3\text{CN}$ , respectively). The **PtPren** and **PtPrtmn** materials also show good thermal stability [decomposition temperature (TGA) = 288 and 320  $^\circ\text{C}$ , respectively]. **PtPrdmphen** is less suitable for OLED applications since its emission energy is close to the IR region with low quantum efficiency (0.10% upon excitation at 498 nm in  $1 \times 10^{-6}$  mol  $\text{dm}^{-3}$   $\text{CH}_3\text{CN}$ ). Ru(bpy)<sub>3</sub>Cl<sub>2</sub> is employed as a reference standard for all quantum efficiency calculations.

Fig. 3 shows the EL spectra of **PtPren** and **PtPrtmn** in the host of CBP, respectively. At a low dopant concentration of 0.8 wt%, the **PtPren**-based OLED gives orange-red emission with a peak maximum at 580 nm and a shoulder at 620 nm. At a high dopant



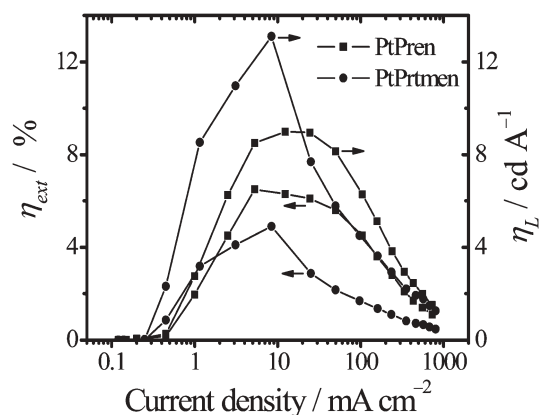
**Fig. 3** EL spectra of **PtPren**-top) and **PtPrtmn**-based (bottom) OLEDs with different dopant concentrations at applied voltage of 8 V. Inset: EL emission spectra of 6.0% **PtPren**-top) and 5.0% **PtPrtmn**-bottom) doped OLEDs at different applied voltages. The configuration of OLEDs is ITO/NPB (40 nm)/CBP : Pt(II) complex (*x* wt%, 30 nm)/BCP (10 nm)/Alq<sub>3</sub> (30 nm)/LiF (0.5 nm)/Al (150 nm).

concentration of 6.0%, the EL of **PtPren** shifts to red light with a peak maximum at 620 nm, which corresponds to the 1931 Commission Internationale de l'Éclairage (CIE\_1931) coordinates of (0.62, 0.38), comparable to pure red light at (0.65, 0.35). This red emission is attributed to the formation of **PtPren** excimer or oligomer. The maximum  $\eta_{\text{ext}}$ , luminous efficiency ( $\eta_{\text{L}}$ ), power efficiency ( $\eta_{\text{P}}$ ), and brightness for the 6.0% **PtPren**-doped OLEDs are 6.5%, 9.0  $\text{cd A}^{-1}$ , 4.0  $\text{lm W}^{-1}$ , and 11 100  $\text{cd m}^{-2}$ , respectively, while good efficiencies are still observed even at the high brightness of 5 000  $\text{cd m}^{-2}$  ( $\eta_{\text{ext}}$ ,  $\eta_{\text{L}}$ , and  $\eta_{\text{P}}$  are 5.2%, 7.7  $\text{cd A}^{-1}$ , and 2.4  $\text{lm W}^{-1}$ , respectively). The EL spectra of 6.0% **PtPren**-doped OLED exhibit negligible change for input voltages from 4 V to 16 V, as shown in Fig. 3. The performance of the **PtPren**-based OLEDs is substantially superior to previous reported results for red OLEDs derived from Pt(II) emitters.<sup>1,3,4</sup>

The **PtPrtmn**-based OLEDs give an orange emission with the CIE\_1931 coordinates of (0.51, 0.47) and do not exhibit red-shifted electroluminescence at high dopant concentrations (Fig. 3). Nevertheless, 5.0% **PtPrtmn**-doped OLEDs display good performance with maximum  $\eta_{\text{ext}}$ ,  $\eta_{\text{L}}$ ,  $\eta_{\text{P}}$ , and brightness of 4.9%, 13.1  $\text{cd A}^{-1}$ , 5.9  $\text{lm W}^{-1}$ , and 10 120  $\text{cd m}^{-2}$ , respectively. Fig. 4 shows that the EL efficiencies of **PtPren** and **PtPrtmn** decrease with increasing input current densities due to triplet-triplet annihilation, but it is noteworthy that the diminution in EL efficiency for the OLED based on **PtPren** is less dramatic.

In conclusion, high-efficiency red-triplet electroluminescent devices have been achieved through the employment of neutral N-chelating platinum(II) emitter, which is proposed to emit from excimer or oligomer species at high dopant concentrations. The combination of a short decay lifetime and reasonable quantum efficiency allows the 6.0% **PtPren**-doped OLED to achieve excellent brightness and efficiencies. These platinum(II) complexes represent good candidates for development toward high-performance OLED materials, particularly because of their ease in chemical and structural modification. It also provides alternative way to achieve efficient red electroluminescence.

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**Fig. 4**  $\eta_{\text{ext}}$  and  $\eta_{\text{L}}$  of 6.0% **PtPren**- and 5.0% **PtPrtmn**-doped OLEDs at different current densities.

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## Notes and references

- 1 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151; C. Adachi, M. A. Baldo, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, 2000, **77**, 904; C. Adachi, M. A. Baldo, M. E. Thompson and S. R. Forrest, *J. Appl. Phys.*, 2001, **90**, 5048.
- 2 M. D. McGehee, T. Bergstedt, C. Zhang, A. P. Saab, M. B. O'Regan, G. C. Bazan, V. I. Srdanov and A. J. Heeger, *Adv. Mater.*, 1999, **11**, 1349; Z. R. Hong, C. S. Lee, S. T. Lee, W. L. Li and S. Y. Liu, *Appl. Phys. Lett.*, 2003, **82**, 2218.
- 3 R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest and M. E. Thompson, *Chem. Mater.*, 1999, **11**, 3709.
- 4 W. Lu, B. X. Mi, M. C. W. Chan, Z. Hui, N. Y. Zhu, S. T. Lee and C. M. Che, *Chem. Commun.*, 2002, 206; W. Lu, B. X. Mi, M. C. W. Chan, Z. Hui, C. M. Che, N. Y. Zhu and S. T. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 4958.
- 5 Y. G. Ma, H. Y. Zhang, J. C. Shen and C. M. Che, *Synth. Met.*, 1998, **94**, 245; X. Z. Jiang, A. K. Y. Jen, B. Carlson and L. R. Dalton, *Appl. Phys. Lett.*, 2002, **81**, 3125.
- 6 L. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304; Y. J. Su, H. L. Huang, C. L. Li, C. H. Chien, Y. T. Tao, P. T. Chou, S. Datta and R. S. Liu, *Adv. Mater.*, 2003, **15**, 884; J. P. Duan, P. P. Sun and C. H. Cheng, *Adv. Mater.*, 2003, **15**, 224.
- 7 C. M. Che, S. C. Chan, H. F. Xiang, M. C. W. Chan, Y. Liu and Y. Wang, *Chem. Commun.*, 2004, 1484.
- 8 B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Thompson and S. R. Forrest, *Adv. Mater.*, 2002, **14**, 1032; V. Adamovich, J. Brooks, A. Tamayo, A. M. Alexander, P. I. Djurovich, B. W. D'Andrade, C. Adachi, S. R. Forrest and M. E. Thompson, *New J. Chem.*, 2002, **26**, 1171.
- 9 M. Riederer, E. Urban and W. Sawodny, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 860.
- 10 S. W. Lai, M. C. W. Chan, T. C. Cheung, S. M. Peng and C. M. Che, *Inorg. Chem.*, 1999, **38**, 4046; S. W. Lai, M. C. W. Chan, K. K. Cheung and C. M. Che, *Inorg. Chem.*, 1999, **38**, 4262.