$[(C^N^N)Pt(C\equiv C)_n R]$ (HC^N^N = 6-aryl-2,2'-bipyridine, n = 1-4, R = aryl, SiMe₃) as a new class of light-emitting materials and their applications in electrophosphorescent devices[†]

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Tridentate cyclometalated platinum(II) complexes bearing σ -alkynyl ligands exhibit tunable photoluminescence and enhanced stability during vacuum deposition; OLEDs based on these materials display orange to red electrophosphorescence with low turn-on voltages (~4 V), maximum luminance approaching 10000 cd m⁻² and efficiency up to 4.2 cd A⁻¹.

Light-emitting metal-organic compounds have numerous potential applications in chemosensing and optoelectronic devices.¹ In this regard, we have focused our attention upon organometallic compounds with medium-sensitive phosphorescent properties. Recent studies have highlighted the employment of luminescent cyclometalated platinum(II) complexes in OLEDs² and as luminescent probes for biomolecules.³ In particular, the diverse photoluminescent properties of $[Pt(C^N^N)L]^+$ (L = phosphine, pyridine, isocyanide or Fischer carbene ligands) have been reported.⁴ We envisaged that incorporation of acetylide into cyclometalated Pt(II) complexes would destabilize non-radiative d-d transitions and maintain strict stereochemical integrity, while the Pt-C=CR interaction may facilitate tuning of the ³MLCT energies by variation of the R substituent.⁵ We now report the new acetylide derivatives 1-13 (Chart 1). These neutral organometallic $[(C^N^N)Pt(C\equiv C)_n R]$ complexes are sufficiently stable with respect to sublimation and thus are suitable for vacuum deposition in OLED fabrication.

Complexes 1–13 were prepared by treatment of the corresponding Cl-ligated precursor with $R(C\equiv C)_nH$ or $R(C\equiv C)_nCu$ in a dichloromethane/amine (10/1, v/v) solution in the presence of CuI. As established by thermogravimetric analysis, 1, 2, 12 and 13 are thermally stable up to 400 °C and decompose to give metallic platinum only at temperatures above 420 °C. The molecular structures of 2 and 7 were confirmed by X-ray crystallography (Fig. 1).‡The tolylacetylide phenyl ring and the Pt(C^N^N) unit in 2 are virtually coplanar; this implies that π



† Electronic supplementary information (ESI) available: General experimental procedure, analytical and spectral characterizations, OLED fabrication and performance. See http://www.rsc.org/suppdata/cc/b1/b108793b/



Fig. 1 ORTEP plots of 2 (right) and 7 (left) (30% probability ellipsoids).

orbitals across the Pt–tolylacetylide fragment can engage in favorable overlap in the crystal lattice. The alternating length of the butadiynyl moiety in 7 is consistent with poor Pt \rightarrow alkynyl back-bonding. Dimeric π – π stacking interactions of around 3.5 Å are observed in the crystal lattices of 2 and 7. We contend that the conjugation based on a σ – π interaction between the Pt(π) and arylacetylide moieties confers stability and rigidity to this system.

The electronic absorption spectra of 1–13 in CH₂Cl₂ solution at 298 K show an intense and broad band at λ_{max} 430–470 nm ($\varepsilon \sim 5 \times 10^3$ dm³ mol⁻¹ cm⁻¹), which tails beyond 500 nm. Excitation of complexes 1–13 in fluid solution at room temperature results in orange to red luminescence (Fig. 2). The emission energies are red-shifted from related [Pt(C^N^N)L]⁺ derivatives.⁴ This is in accordance with the strong σ -donating strength of the alkynyl ligand, which destabilizes the d π (Pt) HOMO to yield relatively low-energy MLCT 5d(Pt) $\rightarrow \pi^*$ (C^N^N) transitions. The emission maxima in dichloromethane at 298 K can be modified from 630 nm for **3** to 560 nm for **6** (range 1980 cm⁻¹). This illustrates the tunability of the emission energies, depending on the nature of (a) the 4-arylacetylide substituent (*i.e.* electron-withdrawing groups stabilize the Pt-based HOMO to yield blue-shifted emissions), and (b)



Fig. 2 Normalized photoluminescence spectra for selected complexes in CH_2Cl_2 solution at 298 K, illustrating tunability of emission energies.

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the tridentate ligand (*i.e.* lower π^* levels afford red-shifted emissions). Extension of the alkynyl conjugation length in [(C^N^N)Pt(C=C)_nR] results in slight deviations of the emission energy; a tendency to blue-shift is generally recognized [*i.e.* for R = Ph, **1** (n = 1, 17180 cm⁻¹) < **7** (n = 2, 17510 cm⁻¹); for R = SiMe₃, **8** (n = 1, 17540 cm⁻¹) < **9** (n = 2, 17730 cm⁻¹) < **10** (n = 3, 17890 cm⁻¹)]. For complex **11** (n = 4), a highly structured emission at λ_{max} 589 nm with a sharp vibronic progression of ~ 2100 cm⁻¹ is observed. This clearly demonstrates that the nature of the excited state is different and involves the acetylenic unit. All derivatives in the present study undergo self-quenching at room temperature in CH₂Cl₂. Except for **3**, the luminescent quantum yields of these complexes in CH₂Cl₂ compare well with those of classical [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) salts.

The intense tunable orange-red phosphorescence of these Pt(II) σ -alkynyl materials, plus their thermal stability and neutrality, render them good candidates as emitters in highefficiency OLEDs. The devices in the present study (top of Fig. 3: inset) were fabricated on indium-tin oxide (ITO) glass using the vacuum deposition method. NPB (N,N'-di-1-naphthyl-N,N'diphenylbenzidine) and Alq₃ [tris(8-quinolinonato)aluminium] were used as the hole- and electron-transporting layers, respectively. BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, bathocuproine) was used to confine excitons within the luminescent zone. Magnesium silver alloy was applied as the cathode. The [(C^N^N)Pt(C=C)_nR] materials were doped into the conductive host material CBP (4,4'-(N,N'-dicarbazole)biphenyl) with mass ratios of 2, 4 or 6%. The performances and optimal conditions of the devices using 1, 2, 12 and 13 as emitters are listed in the ESI.[†] Upon stimulation of positive bias voltage for devices with emitter ratios of 4 and 6%, intense orange to red electrophosphorescence is observed while blue fluorescence from the host and hole-transporting layers is negligible,⁶ thus implying that energy transfer from singlet to triplet excitons is complete.7 Notably low turn-on voltages in the 3.6–4.5 V range are observed. The emission maxima are independent of the doping level and applied voltage (for current density up to 600 mÅ cm⁻²). As shown in Fig. 3 (top), the EL



Fig. 3 Top: normalized electroluminescence spectra for 1, 2 and 13 at 4% doping level (inset: multi-layer configuration of OLED). Bottom: current density, voltage and luminance characteristics (inset: luminescent efficiency *vs*. current density) for OLED using 1 as emitter at 4% doping level.

red shift from 1 and 2 to 13 is in agreement with that observed for the solution photoluminescence. A maximum luminance of 7800 cd m⁻² at 11 V and a maximum efficiency of 2.4 cd A^{-1} at 30 mA cm⁻² is obtained for an orange OLED (λ_{max} 564 nm) using 1 at 4% doping level (bottom of Fig. 3). For the red OLED $(\lambda_{\text{max}} 612 \text{ (max)}), 656 \text{ nm}; \text{ CIE coordinates } x = 0.594, v =$ 0.341), a maximum luminance of 3100 cd m⁻² at 12 V and a maximum efficiency of 1.0 cd A⁻¹ at 30 mA cm⁻² is observed using 13 (4%) in CBP. These values are comparable with the best red-light OLEDs in the literature^{1,2,7} and demonstrate the great potential of platinum(II)-alkynyl complexes as electrophosphorescent emitters. It is important to note that luminescent metal-alkynyl complexes have been attracting substantial interest in recent years, yet practical applications have still to be realized. We have previously reported that OLEDs based on related platinum- and copper-arylacetylide complexes have relatively low luminances and/or are unstable during vacuum deposition.8

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Notes and references

‡ *Crystal data* for **2**: C₂₅H₁₈N₂Pt, *M* = 541.50, hexagonal, *R*3, *a* = *b* = 34.132(3), *c* = 8.6940(10) Å, *α* = *β* = 90, *γ* = 120°, *V* = 8771.6(15) Å³, *Z* = 18, *D_c* = 1.845 g cm⁻³, μ(Mo-Kα) = 7.221 mm⁻¹, *F*(000) = 4680, *T* = 300(2) K, 2*θ*_{max} = 51°, 3260 independent reflections, 253 variable parameters, *R*₁ = 0.0356 (*I* > 2*σ*(*I*)), *wR*₂ = 0.0950, GOF(*F*²) = 1.08. *Crystal data* for 7: C₂₆H₁₆N₂Pt, *M* = 551.50, monoclinic, *P*2₁/*c*, *a* = 15.268(3), *b* = 12.626(3), *c* = 10.929(2) Å, *β* = 107.33(3)°, *V* = 2011.2(7) Å³, *Z* = 4, *D_c* = 1.821 g cm⁻³, μ(Mo-Kα) = 6.991 mm⁻¹, *F*(000) = 1056, *T* = 300(2) K, 2*θ*_{max} = 51°, 3584 independent reflections, 262 variable parameters, *R*₁ = 0.0340, *wR*₂ = 0.0825, GOF(*F*²) = 0.956. CCDC reference numbers 172097 and 161089. See http://www.rsc.org/suppdata/cc/b1/b108793b/ for crystallographic data in CIF or other electronic format.

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