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$[(C^\wedge N^\wedge N)Pt(C{\equiv}C)_nR]$ ($HC^\wedge N^\wedge N$ = 6-aryl-2,2′-bipyridine, n = 1–4, R = aryl, $SiMe_3$) as a new class of light-emitting materials and their applications in electrophosphorescent devices†

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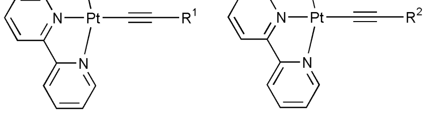
Tridentate cyclometalated platinum(II) complexes bearing σ-alkynyl ligands exhibit tunable photoluminescence and enhanced stability during vacuum deposition; OLEDs based on these materials display orange to red electrophosphorescence with low turn-on voltages (~4 V), maximum luminance approaching 10000 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 OLEDs[2] and as luminescent probes for biomolecules.[3] In particular, the diverse photoluminescent properties of $[Pt(C^\wedge N^\wedge N)L]^+$ (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 ^{3}MLCT energies by variation of the R substituent.[5] We now report the new acetylide derivatives **1–13** (Chart 1). These neutral organometallic $[(C^\wedge N^\wedge N)Pt(C{\equiv}C)_nR]$ 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 $Pt(C^\wedge N^\wedge N)$ unit in **2** are virtually coplanar; this implies that π 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 → 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(II) and arylacetylide moieties confers stability and rigidity to this system.



R^1 = C_6H_5 **1** 4-$MeOC_6H_4$ **3** 4-FC_6H_4 **5** C≡CPh **7** R^2 = C_6H_5 **12**
4-MeC_6H_4 **2** 4-ClC_6H_4 **4** 4-$NO_2C_6H_4$ **6** $SiMe_3$ **8** 4-MeC_6H_4 **13**
C≡C$SiMe_3$ **9** C≡C–C≡C$SiMe_3$ **10** C≡C–C≡C–C≡C$SiMe_3$ **11**

Chart 1

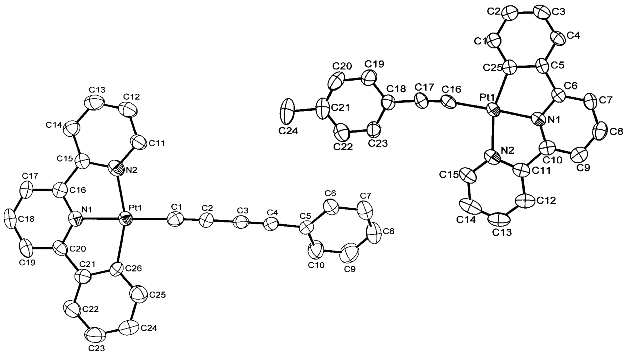


Fig. 1 ORTEP plots of **2** (right) and **7** (left) (30% probability ellipsoids).

The electronic absorption spectra of **1–13** in CH_2Cl_2 solution at 298 K show an intense and broad band at λ_{max} 430–470 nm (ε ~ 5 × 10^3 dm^3 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 $[Pt(C^\wedge N^\wedge N)L]^+$ derivatives.[4] This is in accordance with the strong σ-donating strength of the alkynyl ligand, which destabilizes the dπ(Pt) HOMO to yield relatively low-energy MLCT 5d(Pt) → π*($C^\wedge N^\wedge N$) 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)

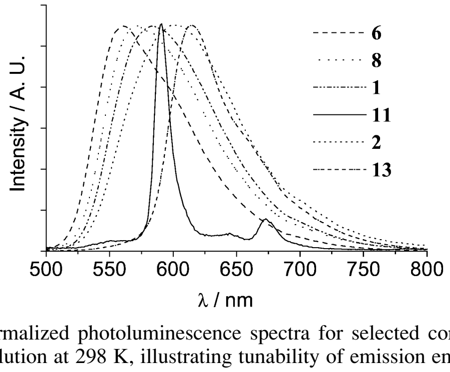


Fig. 2 Normalized photoluminescence spectra for selected complexes in CH_2Cl_2 solution at 298 K, illustrating tunability of emission energies.

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† 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/

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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)$_n$R] 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 = SiMe$_3$, **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 CH_2Cl_2. Except for **3**, the luminescent quantum yields of these complexes in CH_2Cl_2 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 high-efficiency 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 Alq$_3$ [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)$_n$R] 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 mA cm^{-2}). As shown in Fig. 3 (top), the EL 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 (λ_{max} 612 (max), 656 nm; CIE coordinates x = 0.594, y = 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]

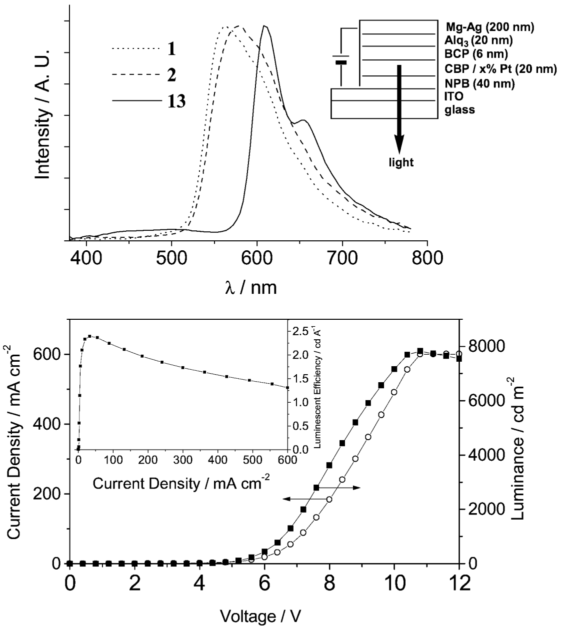

Fig. 3 Top: normalized electroluminescence spectra for **1**, **2** and **13** at 4% doping level (inset: multi-layer configuration of OLED). Bottom: current density, voltage and luminance characteristics (inset: luminescent efficiency *vs.* current density) for OLED using **1** as emitter at 4% doping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

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Notes and references

‡ *Crystal data* for **2**: $C_{25}H_{18}N_2Pt$, M = 541.50, hexagonal, $R\bar{3}$, a = b = 34.132(3), c = 8.6940(10) Å, α = β = 90, γ = 120°, V = 8771.6(15) Å^3, Z = 18, D_c = 1.845 g cm^{-3}, μ(Mo-Kα) = 7.221 mm^{-1}, F(000) = 4680, T = 300(2) K, $2\theta_{max}$ = 51°, 3260 independent reflections, 253 variable parameters, R_1 = 0.0356 ($I > 2\sigma(I)$), wR_2 = 0.0950, GOF(F^2) = 1.08. *Crystal data* for **7**: $C_{26}H_{16}N_2Pt$, M = 551.50, monoclinic, $P2_1/c$, a = 15.268(3), b = 12.626(3), c = 10.929(2) Å, β = 107.33(3)°, V = 2011.2(7) Å^3, Z = 4, D_c = 1.821 g cm^{-3}, μ(Mo-Kα) = 6.991 mm^{-1}, F(000) = 1056, T = 300(2) K, $2\theta_{max}$ = 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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