A novel class of phosphorescent gold(III) alkynyl-based organic light-emitting devices with tunable colour†

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A novel class of luminescent cyclometalated gold(III) alkynyl complexes has been demonstrated to possess EL properties and has been employed in the roles of electrophosphorescent emitters or dopants of organic light-emitting diodes (OLEDs) with high brightness and efficiency.

There have been significant improvements in OLED efficiencies by using phosphorescent materials to generate light emission from both singlet and triplet excitons. One approach, particularly for small molecule OLEDs, is to efficiently harvest triplet excitons through incorporation of heavy metal centres, which would increase spin–orbit coupling and hence intersystem crossing into the triplet state.[1–3] Apart from the emission efficiency issue, an exploration of possible methods to bring about a variation in the emission colour would be important. Most of the common approaches involve the use of different light-emitting materials or multi-component blended mixtures of light-emitting materials with different emission characteristics for colour tuning.[4,5] Recent reports have shown that the emission colours of OLEDs could be generated by using phosphorescent materials as dopants or non-doping emitters through a change in the dopant concentration or a variation of bias voltage.[6,7]

Despite recent interest in the exploration of electrophosphorescent materials, most of the works have been focused on those of iridium(III),[2,3,5] ruthenium(II)[7,8] and platinum(II),[6,9,10] with other metal centres relatively less extensively explored.[11–13] In contrast to the isoelectronic platinum(II) compounds which are known to show rich luminescence properties, very few examples of luminescent gold(III) compounds have been reported.[14] As an extension of our efforts on luminescent metal alkynyls,[15] our group has recently prepared a novel class of luminescent neutral cyclometalated gold(III) alkynyl complexes, [Au(C^N^C)(C≡C–R)], and demonstrated the idea that incorporation of a strong σ-donating alkynyl ligand into the [Au(C^N^C)] moiety would enrich the photoluminescence (PL) properties.[16] Taking the advantage that these cyclometalated gold(III) alkynyl complexes are neutral and are thermally stable, fabrication of OLEDs can be achieved by vacuum deposition of such luminescent compounds. Herein, we describe the use of a series of luminescent cyclometalated gold(III) alkynyl compounds, [Au(C^N^C)(C≡C–R)] [HC^N^CH = 2,6-diphenylpyridine, R = C_6H_5 (**1**) and $C_6H_4N(C_6H_5)_2$-*p* (**2**)] [Fig. 1 (left)], as a new class of electrophosphorescent materials, both in the role of emitters and dopants, of OLEDs to give electroluminescence (EL) with high brightness and efficiency.

Complex **2** was synthesized by modification of a method reported previously for **1**.[16] The molecular structure of **2** has been characterized by X-ray crystallography‡ and is shown in Fig. 1 (right), in which the Au(III) metal centre shows a distorted square-planar geometry with the coordination of a tridentate C^N^C chelator as well as the 4-ethynyl-*N*,*N*-diphenylbenzenamine ligand. The UV-vis absorption spectrum of **1** shows a moderately intense vibronic-structured absorption band at 364–402 nm in dichloromethane, which is tentatively assigned as a metal-perturbed intraligand (IL) π–π* transition of the C^N^C ligand, involving some charge transfer from the phenyl moiety to the pyridyl unit. In addition to the vibronic-structured absorption band, the concomitant appearance of an absorption tail at *ca.* 460 nm in the electronic absorption spectrum of **2** suggests the possibility of an admixture of an intraligand (IL) π–π*[C^N^C and C≡C–$C_6H_4N(C_6H_5)_2$-*p* and a ligand-to-ligand charge transfer (LLCT) π[C≡C–$C_6H_4N(C_6H_5)_2$-*p*] → π*(C^N^C) transition for the assignment of the low-energy absorption bands (Fig. 2).

In dichloromethane solution at room temperature, **1** exhibits a vibronic-structured emission band with band maximum at around 480 nm and is assigned as originated from a metal-perturbed intraligand ^{3}[π–π*] state of the tridentate C^N^C ligand, with charge transfer character from the phenyl ring to the pyridyl unit. On the other hand, dichloromethane solutions of **2** (in the range 4.5×10^{-6}–1.0×10^{-2} mol dm^{-3}) show a structureless emission band at 620 nm upon excitation at 460 nm. In view of the higher-lying π[C≡C–$C_6H_4N(C_6H_5)_2$-*p*] orbital energy due to the presence of the strongly electron-releasing amino substituent, the lower-energy emission band in **2** is tentatively assigned as derived from an LLCT ^{3}{π[C≡C–$C_6H_4N(C_6H_5)_2$-*p*] → π*(C^N^C)} excited

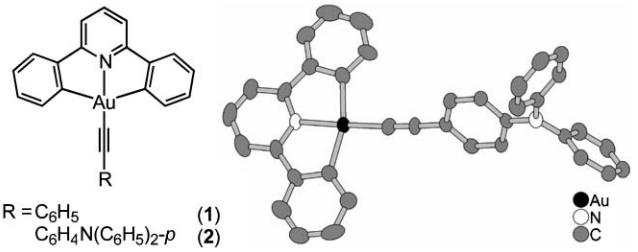

Fig. 1 Molecular structures of **1** and **2** (left) and perspective drawing of **2** (right). Hydrogen atoms and a solvent molecule are omitted for clarity.

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† Electronic supplementary information (ESI) available: crystal packing of **2**; EL spectra and current density and luminance *versus* voltage characteristics of device 2; plot of external quantum efficiency *versus* current density of device 5; characterization data of **2** and experimental details of OLEDs fabrication. See http://www.rsc.org/suppdata/cc/b5/b503315b/index.sht

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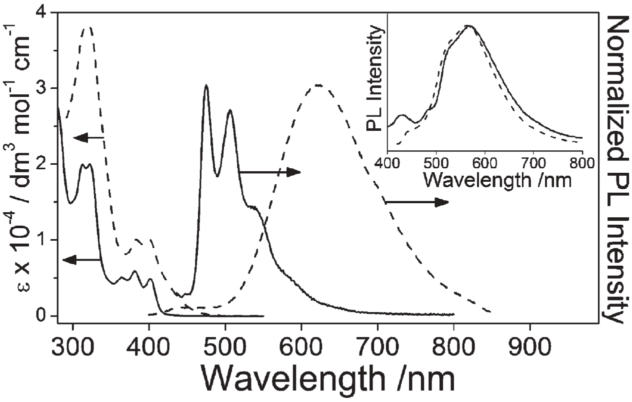

Fig. 2 UV-vis absorption and normalized PL spectra of compound **1** (—) and **2** (---) in dichloromethane at 298 K. Inset: solid state (thin film) PL spectra of compound **1** (—) and **2** (---) at 298 K. No correction was applied to correct for the instrumental response.

state (Fig. 2). In the solid-state thin film, both **1** and **2** display a low-energy structureless emission band at around 564–568 nm (Fig. 2 inset), assignable to the dimeric or excimeric emission arising from the π–π stacking of the C^N^C ligand. The observation of π–π stacking of the C^N^C ligand in the crystal packing of **2** may account for the occurrence of the dimeric/oligomeric or excimeric emission in the solid state.†

Apart from the well-studied systems of cyclometalated iridium(III) and platinum(II), other examples in the literature involving the use of d block transition metal-containing materials as the emitter in electrophosphorescent OLEDs are relatively rare.[12] Multilayer OLEDs (devices 1–5) are fabricated by employing **1** and **2** as electrophosphorescent emitters or dopants† and they exhibit intense electroluminescence upon applying a DC voltage. Fig. 3 shows the electroluminescence spectra of device 1 [ITO/4,4′-bis{*N*-(1-naphthyl)-*N*-phenyl-amino}biphenyl (NPB) (60 nm)/**1** (30 nm)/aluminium tris(8-hydroxyquinoline) (Alq_3) (10 nm)/LiF (1 nm)/Al (90 nm)] at different DC voltages applied. The EL spectra exhibit a blue vibronic-structured band at 452 nm and a red-orange band at about 585 nm, ascribed to the EL of NPB and **1**, respectively. At a lower DC voltage, the EL arising from **1** is more intense relative to that of NPB. Upon increasing the DC voltage, the relative EL intensity ratio of **1** : NPB decreases gradually. In view of this, the emission colour of device 1 can be tuned from orange to blue by applying different DC voltages. These results indicate that some holes are blocked by **1** leading to light emission from the NPB layer. With the increasing applied bias, more electrons can pass through layer **1** and recombine with holes in the NPB layer, which results in more light emission from NPB.

In order to verify that the high-energy EL band originated from NPB and to obtain a pure EL spectrum of **1**, *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-[1,19-biphenyl]-4,4′-diamine (TPD), which has a lower highest occupied molecular orbital (HOMO) level (5.5 eV)[17] than that of NPB (5.2 eV),[18] was used instead of NPB as the hole transporting material in device 2 [ITO/TPD (70 nm)/**1** (10 nm)/Alq_3 (40 nm)/LiF (0.6 nm)/Al (150 nm)]. The lower HOMO level of TPD can reduce the energy barrier for hole transport from the TPD layer to layer **1**, in other words, layer **1** cannot block the holes at the TPD/**1** interface so that the holes and electrons can only recombine in the region of layer **1**, resulting in light emission only from **1**. The EL spectrum of device 2 shows only one EL band at around 585 nm with a driving voltage of about 5 V.† The EL spectrum compares well with the photoluminescence (PL) spectrum of **1** (Fig. 2 inset), indicating that both EL and PL arise from the same excited state or the same type of exciton, *i.e.* from the dimeric/oligomeric or excimeric intraligand triplet excited state or exciton resulting from the π stacking of the C^N^C ligand. Similarly, the EL spectrum of device 3 [ITO/TPD (70 nm)/**2** (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (20 nm)/Alq_3 (10 nm)/LiF (1 nm)/Al (150 nm)], using **2** as the emitting material, shows only one band at around 580 nm with a driving voltage of about 6.5 V. The slightly higher driving voltage is due to the increase in emitting layer thickness (30 nm) and the introduction of an additional BCP hole blocking layer.

Apart from utilizing these cyclometalated gold(III) alkynyl compounds as an emitter layer of OLEDs, other devices have also been fabricated in which the present phosphorescent compounds were doped in the host material of 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) in the emitting layer. Fig. 4 displays the normalized EL

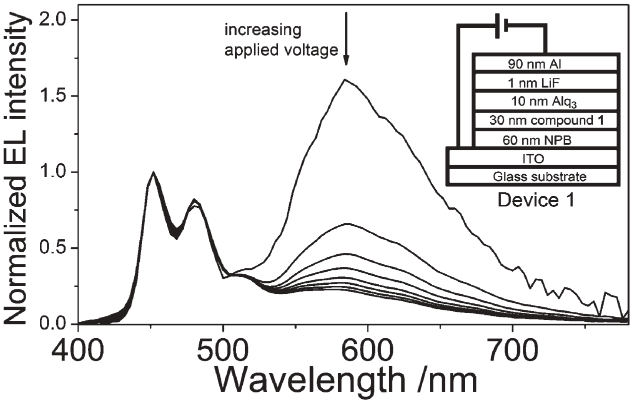

Fig. 3 Electroluminescence spectra of device 1 at different DC voltages applied (from top to bottom: 6, 8, 10, 12, 14, 16, 18, 20 V); the EL intensities are normalized in the range of 450–480 nm. Inset: schematic drawing showing the OLED structure of device 1.

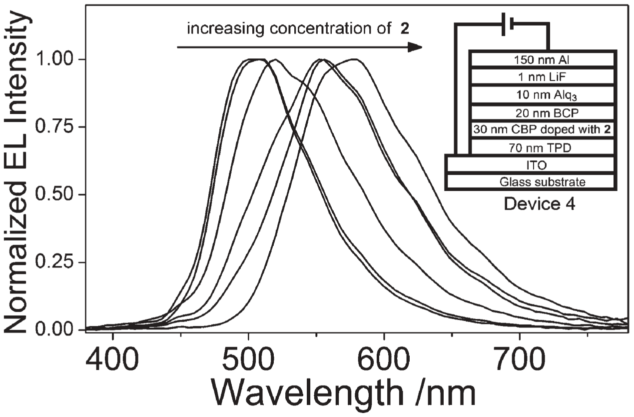

Fig. 4 Normalized electroluminescence spectra of devices 4a–f, with different concentrations of **2** (1, 3, 6, 12, 18 and 100 wt%) as dopant, upon applying 12 V DC voltage. Inset: schematic drawing showing the OLED structure of device 4.

spectra of devices 4a–f [ITO/TPD (70 nm)/CBP doped with **2** (30 nm)/BCP (20 nm)/Alq_3 (10 nm)/LiF (1 nm)/Al (150 nm)], with different concentrations of **2** (1, 3, 6, 12, 18 and 100 wt%, respectively) as dopant, upon applying 12 V DC voltage. The EL band maxima are found to red-shift from 500 nm to 580 nm upon increasing the dopant concentration. Since the emitting layer in device 4 is fabricated by the simultaneous vacuum deposition of **2** and the host, a higher dopant concentration of **2** may give rise to a higher order and better packing of the molecules, leading to a stronger π stacking of the C^N^C ligand, and hence a lower energy dimeric/oligomeric or excimeric intraligand EL is observed. As a consequence, the concentration-dependent colour tuning can be accomplished by making use of the relationship between the EL band position and the dopant concentration. Although the dependence of the EL colour on the dopant concentration of other square-planar metal complexes has been reported, in which the EL spectra exhibited both the monomeric and excimeric emissions with different relative intensities upon variation of dopant concentration,[6] the present study indicates the unusual observation of a shift of the EL band to the red upon increasing the concentration of **2** as the dopant rather than the commonly observed dual emissions reported in other related square-planar metal complex systems.

In order to improve the efficiency, BCP and Alq_3 were replaced by 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi), which has a higher electron mobility, as both the electron transport material and the hole block material in device 5 [ITO/TPD (70 nm)/CBP doped with 6 wt% **2** (30 nm)/TPBi (60 nm)/LiF (1 nm)/Al (150 nm)]. An intense EL band is observed at about 515 nm, comparable to the EL band in device 4c having the same dopant concentration. This device gave a peak with maximum external quantum efficiency η_{ext} of 5.5%, corresponding to a current efficiency of 17.6 cd A^{-1} and luminance power efficiency of 14.5 lm W^{-1} with the highest luminance of 10000 cd m^{-2} at 21.3 V.† Although there were two recent reports of a maximum external quantum efficiency of 15.4 and 19% on the cyclometalated iridium(III) phenylpyridine [$Ir(ppy)_3$] and [$Ir(ppy)_2(acac)$], respectively, in an OLED,[3] the high brightness and external quantum efficiency values in the present study are comparable to the values of most other electrophosphorescent OLEDs reported.[13]

In conclusion, a novel class of luminescent cyclometalated gold(III) alkynyl complexes has been demonstrated to possess EL properties and has been employed in the roles of electrophosphorescent emitters or dopants of OLEDs with high brightness and efficiency. The colour of the EL has been shown to be capable of tuning by a variation in the applied DC voltage as well as the dopant concentration. A maximum external quantum efficiency of 5.5%, corresponding to a current efficiency of 17.6 cd A^{-1} and luminance power efficiency of 14.5 lm W^{-1}, has been obtained in one of the multilayer OLEDs.

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Notes and references

‡ Crystal data of **2**: $C_{38}H_{27}AuCl_2N_2$, $M = 779.48$, triclinic, $a = 10.052(2)$, $b = 10.463(2)$, $c = 16.117(3)$ Å, $\alpha = 82.04(3)$, $\beta = 84.82(3)$, $\gamma = 66.02(3)^\circ$, $U = 1532.8(5)$ Å^3, $T = 301$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 5.004 mm^{-1}, 7423 reflections measured, 4772 unique ($R_{\text{int}} = 0.0332$) which were used in all calculations. The final $wR(F^2)$ was 0.1086 (all data). CCDC 262037. See http://www.rsc.org/suppdata/cc/b5/b503315b/index.sht for crystallographic data in CIF or other electronic format.

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