Highly luminescent phosphine oxide-containing bipolar alkynylgold(III) complexes for solution-processable organic light-emitting devices with small efficiency roll-offs†

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We report the synthesis of alkynylgold(III) complexes with an electron-transporting phosphine oxide moiety in the tridentate ligand and hole-transporting triarylamine moieties as auxiliary ligands to generate a new class of phosphine oxide-containing bipolar gold(III) complexes for the first time. Such gold(III) complexes feature high photoluminescence quantum yields of over 70% in 1,3-bis(N-carbazolyl)benzene thin films with relatively short excited-state lifetimes of less than 3.9 μs at a 20 wt% dopant concentration. Highly efficient solution-processable organic light-emitting devices have been prepared with superior current efficiencies of up to 51.6 cd A−1 and external quantum efficiencies of up to 15.3%. Notably, triplet–triplet annihilation has been significantly reduced, as exemplified by a very small efficiency roll-off of ~1% at a practical brightness of 500 cd m−2.

Introduction

Phosphorescent materials are superior in performance to fluorescent materials because of their capability to harvest all excitons for achieving an internal quantum efficiency of up to its theoretical value of 100%. One of the major challenges for commercialization of full-color all-triplet phosphorescent organic light-emitting devices (OLEDs) is the severe efficiency roll-offs at high brightness, i.e. 1000 cd m−2 and 5000 cd m−2, or even at a practical brightness of around 500–600 cd m−2 for full-color display, limiting their practical applicability in displays and solid-state lighting systems. Such severe efficiency roll-off mostly arises from the imbalance of carrier transporting characteristics in hole- and electron-transporting materials, resulting in a narrow recombination zone for excitons.1 Together with the relatively longer lifetimes of triplet excitons, high density of triplet excitons will be accumulated within the emissive layer,1 which significantly increases the chance of triplet–triplet annihilation (TTA). This in turn will inevitably dissipate energy via a non-radiative pathway, reducing device efficiencies at high current densities.1 Various approaches have been employed to alleviate these limitations, including the use of a graded or mixed emissive layer through doping hole- or electron-transporting materials into host materials to improve the carrier-transporting properties of the emissive layer as well as to broaden the exciton recombination zone,2 and the integration of hole-transporting moieties (such as triphenylamine and carbazole groups) and/or electron-transporting moieties (such as triazine and phosphine oxide groups) into single-molecule hosts to give ambipolar host materials in order to maximize charge balance and a reduced TTA.3–5

Among various carrier-transporting moieties, phosphine oxide has received immense attention owing to its excellent electron-transporting properties.4 Phosphine oxide derivatives are well known to be electron-deficient owing to the presence of a strong electron-withdrawing P=O moiety.4 Unlike the general approach of introducing electronegative atoms into the aromatic ring for enhancing electron-transporting properties,5 the incorporation of phosphine oxide not only can maintain the high triplet energy of host materials, as the tetrahedral phosphorus center in phosphine oxide can break the conjugation to keep the triplet energy of the molecule the same, but also improve the electron-transporting properties of the molecule.6–8 This distinct geometry of the phosphine oxide moiety also gives rise to the amorphous nature, which is a prerequisite for forming a uniform thin film.6 In addition, triarylphosphine oxide moieties are well known to have high chemical and oxidative stabilities.7 All these are prerequisite and crucial properties of solution-processable materials suitable for OLED applications.

In 2014, Yam and co-workers first reported a series of bipolar gold(III) complexes by incorporating electron-transporting benzimidazole moieties and hole-transporting triphenylamine...
in the alkynyl ligand. To allow them to function independently, the electronic communication between these two moieties should be reduced by methyl substitutions on the biphenyl linkage to introduce twisting between the moieties. Alternatively, manipulating the charge transporting properties of the metal complexes via separating the charge transporting groups on the alkynyl ligand and the cyclometalating ligand can overcome the limitation of the conventional method; however, the occurrence of charge transfer emission arising from donor and acceptor moieties being in close proximity may complicate colour tuning. In this work, bipolar gold(III) complexes bearing the phosphine oxide moiety on the cyclometalating ligand and hole-transporting triarylamine moieties on the arylethynyl ligands have been synthesized (Fig. 1), representing the first example to attach simultaneously electron-transporting and hole-transporting groups onto the gold(III) complexes but using the gold metal center to modulate the electronic coupling. These combine both the advantages of excellent electron-transporting properties of the phosphine oxide and the simple molecular design of bipolar alkynylgold(III) complexes. In particular, all of them are thermally stable with decomposition temperatures of >370 °C, as revealed in thermogravimetric analysis (TGA) traces (Fig. S1†). Notably, this class of gold(III) compounds demonstrates high photoluminescence quantum yields (PLQYs) of >70% in solid-state 1,3-bis(N-carbazolyl) benzene (MCP) thin films, almost double that of the structurally related analogue without phosphine oxide. Efficient solution-processable OLEDs with superior current efficiencies (CE) of up to 51.6 cd A⁻¹ and power efficiencies (PE) of up to 35.9 lm W⁻¹ are recorded, which are also double those of the previously reported bipolar gold(III) complexes. Remarkable external quantum efficiencies (EQEs) of up to 15.3% as well as very small efficiency roll-offs of ~1% have also been recorded at a practical brightness of 500 cd m⁻².

**Synthesis and characterization**

The phosphine oxide-containing cyclometalating ligand (4BuC≡N(C₆H₄Br)P(OPh)₂)₃C²Bu) was synthesized by palladium catalyzed C-P bond formation between 4BuC≡N(C₆H₄Br)C²Bu and diphenylphosphine oxide. The resulting cyclometalating ligand was then mercurated and transmetalated to gold(III) metal center to afford cyclometalated chlorogold(III) precursors. Incorporation of alkynes to the cyclometalated chlorogold(III) precursors by means of stirring in the presence of CuI and triethylamine in dichloromethane solution gave rise to a new class of phosphine oxide-containing alkynylgold(III) complexes upon purification. These compounds have been well characterized by ¹H, ¹³C(¹H) and ³¹P(¹H) nuclear magnetic resonance (NMR) spectroscopy, electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI) mass spectrometry, elemental analysis as well as infra-red (IR) spectroscopy. The ³¹P signals of the complexes are in the range of 23.61–26.82 ppm, and the presence of IR stretches in the range of 1118–1121 cm⁻¹ confirms the successful incorporation of the phosphine oxide moiety into the alkynylgold(III) compounds.

**Photophysical studies**

The UV-visible spectra of complexes 1–4 in dichloromethane solution display highly intense absorption bands at ca. 270–350 nm, which could be attributed to the intraligand (IL) π → π* transitions of phosphine oxide, triphenylamine and carbazole moieties, whereas the less intense absorption bands at ca. 380–450 nm are attributed to the metal-perturbed IL π → π* transitions of the cyclometalating ligands, with mixing of some intraligand charge transfer (ILCT) character from the phenyl ring to the pyridine ring (Fig. S2†). Additional Gaussian-shaped absorption bands at ca. 350–400 nm for complexes 3 and 4 are also observed, which could be assigned to IL π → π* transitions of the fluorene/triarylamine hybrids. With the exception of complex 1, all the complexes show absorption tails beyond 450 nm, which can be attributed to the ligand-to-ligand charge transfer (LLCT) π[alkynyl ligand] → π*[BuC≡N(C₆H₄P(OPh)₂)C²Bu] transition. With the extension of the conjugation length of the alkynyl ligands from the triphenylamine moiety to the heterocyclic fused fluorene/triarylamine hybrid, such absorption tail is found to be redshifted from complex 2 to 3 and 4. Similar assignments have
been made on a related cyclometalated alkylnylgold(III) system.4,10
Emission studies of complexes 2–4 have also been carried out in
degassed toluene solution (Fig. S3†). Upon excitation with λ ≥ 380 nm, all these complexes exhibit Gaussian-shaped emission
bands with peak maxima at ca. 566–580 nm. With the introduc-
tion of peripheral carbazole moieties in the alkynyl ligand of
complex 4, a slight blue shift of emission wavelength is observed
when compared with complex 3. Such a hypsochromic shift is
probably due to the electron-withdrawing nature of the nitrogen
atoms of the carbazole moieties that could stabilize the highest
occupied molecular orbital (HOMO). In addition, the PLQYs of
this series of complexes in toluene solution are in the range of 22–
48%, very close to those of the tetradeutate gold(μ) C’N’C’C’
complexes that were recently reported by Yam and co-workers,
representing one of the highest values in the reported litera-
ture.11 To further investigate the nature of the excited state of this
class of complexes, solvent-dependent emission studies have also
been conducted on complex 2 (Fig. S4†). The emission peak
maximum is found to exhibit a red shift of ~3120 cm⁻¹ in
response to an increase in solvent polarity from p-xylene (0 D) to
dichloromethane (1.6 D). This, together with the fitting of the
Lippert–Mataga plot (Fig. S5†), confirms the change transfer
nature of the excited state. Moreover, a significant solvent effect on
the PLQYs of complex 2 has been noted. In general, the PLQYs
determined in halogenated solvents are significantly lower than
that in non-halogenated solvents. However, the PLQY does not
decrease with the increasing ease of reduction of the aryl halide
solvent (i.e. chlorobenzene (−2.78 V vs. the saturated calomel
electrode (SCE)) and 1,2,4-trichlorobenzene (−2.00 V vs. SCE))22
nor with the strength of the C–X bond. The excited state reduction
potential of 2 (E₂(0/1)) based on E₀,0 energy and electrochemical
data,13 was found to be at ca. −1.68 V vs. SCE, which excludes the
possibility of the photo-induced electron transfer from the excited
species of 2 to aryl halide as the reduction potential of the aryl
halide has to be at least less negative than −1.68 V. On the other
hand, the drop in the PLQYs correlates with the red-shifting of the
emission in various solvents. This, together with the good agree-
ment of the fit to the plot of ln kᵣ versus Eₑₑₘ, where kᵣ is the non-
radiative decay rate constant and Eₑₑₘ is the emission energy,
based on the energy gap law (Fig. S6†), suggests that the cause of
the PLQY drop could be ascribed to an increase of the non-
radiative decay rate upon shifting the emission to lower energy,
in accordance with the energy gap law.14 Photophysical properties
of the solid-state thin films have also been investigated for
complexes 2–4. When doped into MCPP–TCTA mixed host films
doped with 5 wt% complexes 2–4 at 298 K.

![Graph showing emission spectra of thin MCPP–TCTA mixed host films doped with 5 wt% complexes 2–4.](Image)

**Fig. 2** Emission spectra of thin MCPP–TCTA mixed host films doped with 5 wt% complexes 2–4 at 298 K.

**Electrochemical studies**

To estimate the energy levels of their HOMO and lowest unoc-
cupied molecular orbitals (LUMO), cyclic voltammetric studies
have been carried out for complexes 2–4 and their cyclic vol-
tammograms and electrochemical data have been shown and
summarized in Fig. S8 and Table S2, respectively, in the ESI†. All
the complexes show one quasi-reversible reduction couple at
−1.35 V vs. SCE and one irreversible reduction wave at −1.81 V
vs. SCE. All these reduction couples are found to be indepen-
dent of the nature of the alkynyl ligands and hence they are
attributed to the reduction of the cyclometalating ligands. In
the oxidative scan, all the complexes show a first quasi-
reversible oxidation couple at +0.75 V to +0.92 V vs. SCE. This
oxidation couple can be attributed to the alkynyl ligand-
centered oxidation. The attachment of the fluorene moieties
at the peripheral of −C≡C–C₆H₄–N(C₆H₄)₂– in complexes 3 and
4 further extends the conjugation length, resulting in the de-
stabilization of HOMO levels, yielding less positive potentials
for the first oxidation of 3 and 4 (both occur at +0.75 V vs. SCE)
than that of 2 (+0.92 V vs. SCE). In addition, oxidation couples at
higher potentials (+1.15 V and +1.25 V vs. SCE) are observed for
complex 4 bearing carbazole moieties at the periphery. These
multiple quasi-reversible oxidation couples can be attributed to
carbazole-centered oxidation.
Electroluminescence studies

Taking advantage of their excellent solubility in a variety of common organic solvents and high PLQYs, solution-processable OLEDs based on these bipolar gold(III) complexes 2–4 as phosphorescent dopants have been made. In good agreement with the emission studies, the electroluminescence (EL) spectra of the devices are identical to the photoluminescence measured in solid-state thin films (Fig. S9†). A plot of EQEs of the OLEDs doped with 20 wt% of complexes 2–4 at different luminances is shown in Fig. 3. In addition, superior device performance has been realized with extraordinarily high CE and EQE. Notably, the optimized device doped with complex 2 (i.e. 20 wt%) gives a maximum CE of 51.6 cd A⁻¹ and EQE of 15.3% at a current density of 0.45 mA cm⁻². Surprisingly, the introduction of fluorene and carbazole moieties to generate higher generation complexes (i.e. 3 and 4, respectively) does not cause a severe degradation of the device performance. High CEs of up to 33.6 cd A⁻¹ (corresponding to an EQE of 10.6%) and 32.0 cd A⁻¹ (corresponding to an EQE of 9.8%) can be achieved for the devices based on 20 wt% of 3 and 4. In addition, the device based on 3 exhibits a higher PE (i.e. 39.0 lm W⁻¹), double that of the device based on 2 (i.e. 19.1 lm W⁻¹). Such a high PE can be ascribed to the HOMO destabilization in complex 3 that can greatly improve the hole injection from the hole-transporting layer into the emissive layer (particularly directly into the guest molecules), as shown in the electrochemical studies. More importantly, a small efficiency roll-off has been observed for the optimized device based on 2. Notably, the EQE has only dropped by ~1% and ~8% at a practical brightness of 500 cd m⁻² and 1000 cd m⁻², respectively. This is not the case for most other iridium(III) complexes.37 Such small efficiency roll-offs can be attributed to the presence of phosphine oxide moieties that balance charge carrier transport, as well as the relatively short excited-state lifetime of <3.9 μs in the 20 wt% MCP doped solid-state thin film. Further introduction of hole-transporting fluorene moieties in 3 and carbazole moieties in 4 could also demonstrate such bipolar properties, as exemplified in the 20 wt% devices. Table S3† summarizes the key parameters for devices based on 2–4. Nevertheless, such high CEs and EQEs are close to the highest values for both vacuum-deposited and solution-processable OLEDs based on gold(III) complexes.38

Conclusion

In conclusion, a novel class of cyclometalated alkynylgold(III) complexes displaying high PLQYs of up to 70% in solid-state thin films has been designed and synthesized. Notably, this is the first successful demonstration of direct incorporation of an electron-transporting phosphine oxide moiety into luminescent alkynylgold(III) complexes. The 3-D property of phosphine oxide moieties not only provides steric hindrance to reduce chromophoric quenching, doubling the PLQY than those of the structurally related analogues, but also improves the charge carrier balance. Superior device performance with maximum CEs of up to 51.6 cd A⁻¹ and EQEs of up to 15.3% can be realized for solution-processable OLEDs based on these alkynylgold(III) complexes. Together with the relatively short emission lifetimes in thin films, the degree of TTA has been significantly reduced as exemplified by the small efficiency roll-offs of ~1% and ~8% at a practical brightness of 500 and 1000 cd m⁻², respectively. These excellent device performances are by virtue of the distinct electron-transporting and geometric properties of the phosphine oxide moiety. These findings have provided insights into the design of new types of phosphorescent emitters that are capable of suppressing efficiency roll-offs to enhance the OLED performance.

Conflicts of interest

There are no conflicts to declare.

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