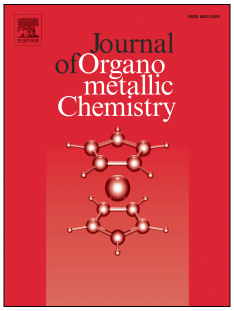

Synthesis of Alkynylgold(III) complexes with Bis-cyclometalating Ligand Derived from Ethyl 2,6-Diphenylisonicotinate and their Structural, Electrochemical, Photo- and Electroluminescence Studies

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PII: S0022-328X(15)00115-1

DOI: 10.1016/j.jorganchem.2015.02.037

Reference: JOM 18938

To appear in: *Journal of Organometallic Chemistry*

Received Date: 21 January 2015

Revised Date: 18 February 2015

Accepted Date: 24 February 2015

Please cite this article as: V.K.-M. Au, D.P.-K. Tsang, Y.-C. Wong, M.-Y. Chan, V.W.-W. Yam, Synthesis of Alkynylgold(III) complexes with Bis-cyclometalating Ligand Derived from Ethyl 2,6-Diphenylisonicotinate and their Structural, Electrochemical, Photo- and Electroluminescence Studies, *Journal of Organometallic Chemistry* (2015), doi: 10.1016/j.jorganchem.2015.02.037.

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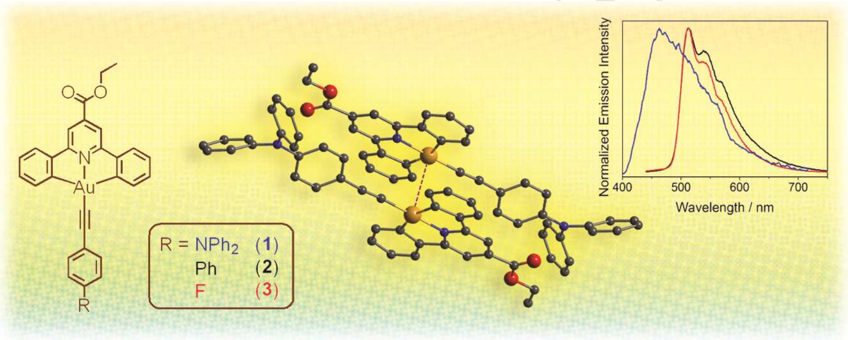
Dedicated to Prof. D. M. P. Mingos on the occasion of his 70th Birthday

Graphical Abstract



Synopsis

A series of alkynylgold(III) complexes has been synthesized and their electrochemical and photophysical properties have been studied. The crystal structure of one of the complexes revealed a short Au(III)···Au(III) distance of 3.44 Å. One of the complexes has also been utilized as the light-emitting layer in the fabrication of OLEDs.

Synthesis of Alkynylgold(III) complexes with Bis-cyclometalating Ligand Derived from Ethyl 2,6-Diphenylisonicotinate and their Structural, Electrochemical, Photo- and Electroluminescence Studies

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Dedicated to Prof. D. M. P. Mingos on the occasion of his 70th Birthday

Abstract

A series of alkynylgold(III) complexes with bis-cyclometalating ligand derived from ethyl 2,6-diphenylisonicotinate has been synthesized. The single crystal structure of one of the complexes revealed an unprecedentedly short Au(III)···Au(III) distance of 3.44 Å. These complexes were found to exhibit rich electrochemistry. Upon photoexcitation, the alkynylgold(III) complexes were found to show rich emission properties in various states at both ambient and low temperatures. One of the complexes have also been utilized as the light-emitting layer in the fabrication of organic light-emitting diodes, demonstrating the potentials and versatility of alkynylgold(III) complexes.

Keywords: Gold, photoluminescence, electroluminescence, electrochemistry

1. Introduction

Despite a long history of the chemistry of luminescent gold(I) complexes,[1] increasing attention has only been directed towards gold(III) luminescence in the recent years.[2] This is mainly attributed to the difficulty to observe luminescence in gold(III) complexes due to the electrophilicity of the gold(III) metal center and the presence of low-lying d-d ligand field states which would quench the luminescent excited states of gold(III) complexes.[1d,2]

After the successful attempt by the group of Yam to prepare room temperature luminescent gold(III) complexes through the incorporation of strong σ-donating ligands in 1993 [3] and the subsequent preparation of highly luminescent alkynylgold(III) complexes by the same group in the last decade,[4] there has been a continuing increase in interest in the exploration of light-emitting gold(III) complexes.[5–7] In particular, the rich photo- and electroluminescence properties of the alkynylgold(III) system has rendered them good candidates as light-emitting materials in organic light-emitting devices (OLEDs).[4a,5] The versatility of gold(III) complexes in supramolecular assemblies could also be exemplified by the formation of metallogels,[8ab] supramolecular polymers[8b] and nanostructures,[8c] as well as the rare observation of short Au(III)···Au(III) distances in some cationic gold(III) complexes.[7] Herein, a series of bis-cyclometalated alkynylgold(III) complexes, [Au{C^N(COOEt)^C}(C≡C-C_6H_4-R-*p*)] (R = $N(C_6H_5)_2$ (**1**), C_6H_5 (**2**), F (**3**)), has been synthesized and characterized, and the structures of two of the complexes were crystallographically studied. The electrochemical and photophysical properties of the complexes are also reported. The electroluminescence properites of one of the complexes have also been explored.

2. Experimental

2.1 Materials and reagents

The tridentate ligand, ethyl 2,6-diphenylisonicotinate, was prepared by standard acid-catalyzed esterification reaction between 2,6-diphenylisonicotinic acid and ethanol. The chlorogold(III) precursor, [Au{C^N(COOEt)^C}Cl] was synthesized according to a literature procedure of related bis-cyclometalated complexes.[4] Potassium tetrachloroaurate(III) was purchased from ChemPur, copper(I) iodide was from Lancaster, while 2,6-diphenylisonicotinic acid and triethylamine were from Aldrich. 4-Ethynyltriphenylamine was synthesized according to a literature procedure,[9] whereas 1-ethynyl-4-phenylbenzene and 1-ethynyl-4-fluorobenzene were from Maybridge. All other reagents were of analytical grade and used as received.

Other solvents were purified and distilled using standard procedures before use. All reactions were performed under anaerobic and anhydrous conditions using standard Schlenk techniques under an inert atmosphere of nitrogen unless otherwise specified.

2.2 Synthesis

2.2.1 [Au{C^N(COOEt)^C}(C≡C–C_6H_4–N(C_6H_5)$_2$-*p*)] (1)

(HC^N(COOEt)^CH = ethyl 2,6-diphenylisonicotinate)

The alkynylgold(III) complex was prepared according to a literature procedure.[4,5] To a mixture of [Au{C^N(COOEt)^C}Cl] (267 mg, 0.50 mmol), 4-ethynyltriphenylamine (202 mg, 0.75 mmol) and a catalytic amount of copper(I) iodide (10 mg, 0.05 mmol) was added dichloromethane (35 mL). Triethylamine (2 mL) was added to the resulting suspension. After stirring under an inert atmosphere at room temperature for 3 h, the solvent was removed *in vacuo*. The resulting residue was purified by column chromatography on silica gel with dichloromethane. The complex was then recrystallized by slowly diffusing diethyl ether vapor into the concentrated dichloromethane solution to give orange-yellow crystals. Yield: 172 mg (45 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K)/ppm: δ 1.46 (t, 3H, J = 7.1 Hz, $-CH_3$), 4.51 (q, 2H, $-OCH_2-$), 7.01 (d, 4H, J = 6.2 Hz, $-C{\equiv}CC_6H_4-$), 7.12 (m, 4H, $-N(C_6H_5)_2$), 7.29 (m, 6H, $-N(C_6H_5)_2$), 7.39 (t, 2H, J = 7.4 Hz, phenyl of C^N^C), 7.49 (d, 2H, J = 7.4 Hz, phenyl of C^N^C), 7.63 (d, 2H, J = 7.4 Hz, phenyl of C^N^C), 7.98 (s, 2H, pyridine of C^N^C), 8.07 (d, 2H, J = 7.4 Hz, phenyl of C^N^C). Positive FAB-MS: *m/z* 767 $[M]^+$. IR (KBr): 2147 cm^{-1} (ν(C≡C)). Elemental analyses calcd for $C_{40}H_{29}AuN_2O_2$•½CH_2Cl_2 (found): C, 60.12 (59.75); H, 3.74 (3.64); N, 3.46 (3.45).

2.2.2 [Au{C^N(COOEt)^C}(C≡C–C_6H_4–C_6H_5-*p*)] (2)

This was synthesized according to the synthetic procedure of **1** except that 1-ethynyl-4-phenylbenzene (134 mg, 0.75 mmol) was used in place of 4-ethynyltriphenylamine. The target complex **2** was obtained as yellow crystals. Yield: 122 mg (36 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K)/ppm: δ 1.49 (t, 3H, J = 7.2 Hz,

$-CH_3$), 4.53 (q, 2H, $-OCH_2-$), 7.31 (2H, m, biphenyl), 7.37 (1H, d, *J* = 8.7 Hz, biphenyl), 7.42–7.49 (m, 4H, biphenyl), 7.58-7.71 (m, 8H, biphenyl and phenyl of C^N^C), 8.01 (s, 2H, pyridine of C^N^C), 8.11 (d, 2H, *J* = 7.3 Hz, phenyl of C^N^C). Positive FAB-MS: *m/z* 675 $[M]^+$. Elemental analyses calcd for $C_{34}H_{24}AuNO_2$ (found): C, 60.45 (60.49); H, 3.58 (3.55); N 2.07 (2.02).

2.2.3 [Au{C^N(COOEt)^C}(C≡C–C_6H_4–F-*p*)] (**3**)

This was synthesized according to the synthetic procedure of **1** except that 1-ethynyl-4-fluorobenzene (90 mg, 0.75 mmol) was used in place of 4-ethynyltriphenylamine. The target complex **3** was obtained as yellow crystals. Yield: 71 mg (23 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K)/ppm: δ 1.48 (t, 3H, *J* = 7.2 Hz, $-CH_3$), 4.50 (q, 2H, $-OCH_2-$), 7.03 (t, 2H, *J* = 8.7 Hz, $-C_6H_4-$), 7.29 (t, 2H, *J* = 8.7 Hz, $-C_6H_4-$), 7.43 (t, 2H, *J* = 7.2 Hz, phenyl of C^N^C), 7.58 (m, 2H, phenyl of C^N^C), 7.65 (d, 2H, *J* = 7.2 Hz, phenyl of C^N^C), 7.99 (s, 2H, pyridine of C^N^C), 8.06 (d, 2H, *J* = 7.2 Hz, phenyl of C^N^C). Positive FAB-MS: *m/z* 617 $[M]^+$. Elemental analyses calcd for $C_{28}H_{19}AuFNO_2 \bullet ½H_2O$ (found): C, 53.69 (53.84); H, 3.22 (3.10); N 2.24 (2.36).

2.3 Physical measurements and instrumentation

^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or Bruker DPX-400 (400 MHz) Fourier transform NMR spectrometer with chemical shifts recorded relative to tetramethylsilane (Me_4Si). Positive FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer or a Thermo Scientific DFS high-resolution magnetic sector mass spectrometer. IR spectra were obtained on KBr disks on a Shimadzu IR Affinity-1 FTIR spectrophometer (4000-400 cm^{-1}). Elemental analyses for the metal complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing. Electronic absorption spectra of **1** were obtained on a Hewlett-Packard 8452A diode array spectrophotometer while those of **2** and **3** were obtained on a Varian Cary 50 UV-vis spectrophotometer. Steady state excitation and emission spectra of **1** were recorded on a Spex Fluorolog-2 Model F111 fluorescence spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube, while those of **2** and **3** were recorded on a Spex Fluorolog-3 Model FL3-211 spectrofluorometer, equipped with an R2658P photomultiplier tube (PMT) detector. Unless specified otherwise, the emission spectra were corrected for PMT response. Photophysical measurements in low-temperature glass were carried out with the sample solution loaded in a quartz tube inside a quartz-walled Dewar flask. Liquid nitrogen was placed into the Dewar flask for low-temperature photophysical measurements at 77 K. Excited-state lifetimes of solution samples were measured using a conventional laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). All solution samples for photophysical studies were freshly prepared under a high vacuum in a 10-cm^3 round-bottomed flask equipped with a side arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze-pump-thaw cycles. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 600 A electrochemical analyzer. The electrolytic cell used was a conventional two-compartment cell. Electrochemical measurements were performed in dichloromethane solutions with 0.1 M $^{n}Bu_4NPF_6$ as supporting electrolyte at room temperature. The reference electrode was a Ag/$AgNO_3$ (0.1 M in acetonitrile) electrode (CH Instruments, Inc.), and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the counter electrode. The working electrode surface was first polished with a 1-μm alumina slurry (Linde), followed by a 0.3-μm alumina slurry, on a microcloth (Buehler Co.). The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference.[10] Luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.[11a] A degassed aqueous solution of quinine sulfate in 1.0 N sulfuric acid ($\Phi = 0.546$, excitation wavelength at 365 nm) was used as the reference and corrected for the refractive index of the solution.[11b] All solutions for electrochemical studies were deaerated with prepurified argon gas just before measurements. Luminescence quantum yields of thin films were measured on a Hamamatsu C9920-03 Absolute Photoluminescence Quantum Yield Measurement System.

2.4 Crystal structure determination

Single crystals of **1** and **2** suitable for X-ray diffraction studies were grown by vapor diffusion of diethyl ether into a concentrated dichloromethane solution of the complex. For complex **1**, the X-ray diffraction data were collected on a Bruker Smart CCD 1000 using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) in the Department of Chemistry, The University of Hong Kong. The X-ray diffraction data for complex **2** were collected using synchrotron radiation (λ = 0.85 Å) on beamline 3W1A at the Beijing Synchrotron Radiation Facilities (BSRF) in the Institute of High Energy Physics (IHEP), Chinese Academy of Sciences. The diffraction data reduction and integration were performed by the HKL2000 software. The structures of both complexes were solved by direct methods and refined using the SHELXS program.[12] Full-matrix least-squares refinement on F^2 was used in the structure refinement. The positions of hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times those of the associated carbon atoms and participated in the calculation of final *R*-indices. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically.

2.5 OLED fabrication and characterization

The OLEDs were fabricated on patterned indium-tin oxide (ITO)-coated glass substrates with a sheet resisstance of 30 Ω/sq. The substrates were cleaned with Decon 90, rinsed with deionized water, dried in an oven, and treated in an ultraviolet ozone chamber. A 70-nm thick α-naphthylphenylbiphenyldiamine (NPB) was used as the holetransporting layer, and a 5-nm thick 4,4’4,”-tris(carbazole-9-yl)-triphenylamine (TCTA) was used as the carrier confinement layer. A 30-nm thick emissive layer consisting of 2 %, 4 %, 6 %, and 8% selected complex was doped into the *N*,*N*’-dicarbazolyl-3,5-benzene (MCP) layer via thermal codeposition. A 30-nm thick bis(2-methyl-8-quinolinato)-4-phenylphenolate) aluminum(III) (BAlq) was used as the electron-transporting layer; while LiF/Al was used as metal cathode. All films were sequentially deposited at a rate of 0.1−0.2 nm s^{-1} without vacuum break. A shadow mask was used to define the cathode and to make four 0.1 cm^2 devices on each substrate. Current density−voltage−luminance (J−V−L) characteristics and EL spectra were measured simultaneously with a programmable Keithley 2420 power source and a Photoresearch PR-655 spectroradiometer.

3 Results and discussion

3.1 Synthesis and characterization

The alkynylgold(III) complexes were synthesized according to a literature procedure, in which the chlorogold(III) precursor, [Au{C^N(COOEt)^C}Cl], was allowed to react with the respective alkyne in dichloromethane in the presence of a catalytic amount of copper(I) iodide and triethylamine under an inert atmosphere.[4,5] The target complexes were purified by column chromatography on silica gel using dichloromethane as eluent, followed by recrystallization from slow diffusion of diethyl ether into the concentrated dichloromethane solution of the complex. Complex **1** was isolated as orange crystals while complexes **2** and **3** were collected as yellow crystals. All of the complexes were soluble in dichloromethane and exhibited good air- and thermal-stabilities. ^{1}H NMR spectroscopy, FAB-mass spectrometry and satisfactory elemental analyses were performed to confirm the identities of the gold(III) complexes.

3.2 X-ray crystal structure

Single crystals of **1** and **2** were obtained by diffusion of diethyl ether vapor into a concentrated dichloromethane solution of the respective complex. The crystal structures were determined by X-ray crystallography. Crystal structure determination data are summarized in Table 1 while the selected intermolecular parameters are shown in Table 2. Figure 1 depicted the perspective views of the crystal structures of **1** and **2**, and the crystal packing diagrams of the complexes are shown in Figure 2.

In the crystal structure, the complex molecules were found to align in a head-to-tail fashion with some degree of π-π stacking interactions between adjacent

[Au{C^N(COOEt)^C}] moieties, as revealed by the short interplanar distances of about 3.63 and 3.45 Å in complexes **1** and **2**, respectively. Both gold(III) complexes exhibited square planar geometries with slight distortions from the ideal arrangement in the crystal structures. The C–Au–N angles were in the range of 80.53(19)–81.6(2)°, resulting from the steric requirements of the tridentate bis-cyclometalating {C^N(COOEt)^C} ligands. Similar observations were also reported in the related cyclometalated gold(III) complexes.[4,5] The [Au{C^N(COOEt)^C}] motif was essentially coplanar, and the Au–C (2.064(5)–2.071(6) Å) and Au–N (1.988(4)–1.995(6) Å) bond distances were similar to those found in other related gold(III) complexes.[4,5] In these alkynylgold(III) complexes, the dihedral angles between the [Au{C^N(COOEt)^C}] plane and the plane of the phenyl ring of the aryl alkynyl ligand were found to be about 31.4° in **1** and 2.9° in **2**. The Au–C≡C and C≡C–C angles of 172.3(5)–174.3(6)° and 174.6(6)–177.7(6)° showed only a minor deviation from the ideal 180°, establishing a slightly distorted linear arrangement, with the Au–C (1.946(9)–1.952(5) Å) and C≡C bond distances (1.196(7)–1.222(12) Å) similar to those found in the related cyclometalated alkynylgold(III) systems.[4,5]

As in other related organogold(III) complexes,[4,5] the shortest Au···Au distances between adjacent molecules in complexes **2** (4.6284(9) Å) were found to be longer than the sum of van der Waals radii for two gold(III) centers, revealing that no significant aurophilic interactions occurred in the crystal lattices of the complex. Interestingly, complex **1** was found to display an unprecedentedly short intermolecular Au(III)···Au(III) distance of 3.4435(3) Å, which was smaller than the theoretical Au(III)···Au(III) distance of 3.7 Å for the possible occurrence of aurophilic interactions between the gold(III) metal centers as predicted by Pyykkö and co-workers.[13] In spite of the presence of extended π–π stacking interactions that would assist the alkynylgold(III) complexes to be arranged in close proximity, related bis-cyclometalated complexes in the literature have not been observed to show a Au(III)···Au(III) distance shorter than 3.7 Å.[7] Recent DFT calculations have supported the occurrence of weak intermolecular Au(III)···Au(III) interactions in the solid-state structure of a cationic alkynylgold(III) complex in the literature.[7a] To the best of our knowledge, the Au(III)···Au(III) distance of complex **1** in the present work is the first observation of such a short Au(III)···Au(III) distance in neutral alkynylgold(III) complexes.

3.3 Electrochemical studies

The electrochemical properties of the alkynylgold(III) complexes **1**–**3** have been studied by cyclic voltammetry in dichloromethane (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$). The complexes were found to show a quasi-reversible first reduction couple at −1.11 to −1.14 V *versus* saturated calomel electrode (SCE). An irreversible second reduction couple was also observed at −1.71 to −1.75 V *versus* SCE. In addition, the complexes were found to exhibit an irreversible to quasi-reversible couple at +0.88 to +1.52 V *versus* SCE. The electrochemical data of complexes **1**–**3** are collected in Table 3.

With reference to the electrochemical studies of related gold(III) complexes in the literature,[4,5] the first reduction couple could be assigned to the ligand-centered reduction of the C^N(COOEt)^C ligand. The reduction potential of complexes **1**–**3** were found to be essentially the same, with values lying between −1.11 and −1.14 V *versus* SCE. The reduction potentials were found to be less negative than those of analogous alkynylgold(III) complexes with the unsubstituted 2,6-diphenylpyridine (C^N^C) ligand.[4] This could be attributed to the presence of the electron-withdrawing ethyl ester group directly substituted on the pyridine moiety of the cyclometalating C^N(COOEt)^C ligand. The electron-deficient substituent would make the π^* orbital much more lower-lying in energy and would thus increase the ease of reduction for the complex.

The anodic waves of complexes **1**–**3**, which ranged from +0.88 to +1.52 V *versus* SCE, were found to be rather sensitive to the nature of the alkynyl ligand. In view of the electron-deficient nature and the unlikely redox activitiy of the gold(III) metal center, the oxidation wave was assigned to the alkynyl ligand-centered oxidation of the complexes. The anodic waves were found to show potentials in the order **1** < **2** < **3**, in line with the electron-donating ability of the alkynyl group: $C\equiv C–C_6H_4–N(C_6H_5)_2$ > $C\equiv C–C_6H_4–C_6H_5$-*p* > $C\equiv C–C_6H_4–F$-*p*. A better electron-donating ability of the alkynyl group would be associated with a less positive potential of the alkynyl ligand-centered oxidation. Such an assignment was also in agreement with those of related alkynylgold(III) complexes in the literature.[4,5]

3.4 Electronic absorption properties

In dichloromethane solutions at room temperature, the complexes were generally found to exhibit a high energy absorption band at 325–340 nm region, and a moderately intense vibronically structured absorption band at 405–430 nm region. The extinction coefficients (ε) of the absorption bands were on the order of 10^3–10^4 $dm^3mol^{-1}cm^{-1}$, which were in agreement with those of related alkynylgold(III) complexes reported in the literature.[4,5] The absorption spectra of complexes **1**–**3** are depicted in Figure 3, while the photophysical data of the complexes are summarized in Table 4. The higher energy band at 325–340 nm region was assigned to the intraligand π-π* transition of the alkynyl ligands. On the other hand, the lower-energy absorption band was found to be at essentially the same wavelengths at about 405–430 nm for complexes **1**–**3**. With reference to the observations as well as literature results, the lower-energy band was assigned to a metal-perturbed intraligand π-π* transition of the tridentate bis-cyclometalating C^N(COOEt)^C ligand, with some charge-transfer character from the phenyl moiety to the central ester-substituted pyridine moiety.[4,5] For complex **1** containing the electron-rich 4-ethynyltriphenylamine ligand, the absorption shoulder beyond 450 nm could be assigned to a ligand-to-ligand charge transfer (LLCT) [π(C≡C-R)→π*{C^N(COOEt)^C}] transition from the alkynyl moiety to the cyclometalating ligand.[4,5]

The presence of an ethyl ester group (–COOEt) on the central pyridine ring of the tridentate ligand was observed to result in a substantial red shift in the absorption energy (*ca*. 405–430 nm) when compared to the literature complexes that contained the unsubstituted 2,6-diphenylpyridine (C^N^C) ligand (*ca*. 360–410 nm).[4] This could be attributed to the fact that the presence of the electron-withdrawing ester group would lower the energy level of the pyridine-based LUMO π* orbital to a much larger extent than the phenyl-based HOMO π orbital. This greatly reduced the energy difference between the HOMO and LUMO, and thus the energy of the resulting IL

π-π*[C^N(COOEt)^C] absorption.

3.5 Photoluminescence properties

The complexes were observed to be emissive at both ambient and low temperatures in various media. Table 4 summarizes the photophysical properties of complexes **1**–**3** and the representative emission spectra in dichloromethane solution and in low-temperature glass are respectively shown in Figures 4 and 5.

Upon excitation at $\lambda \geq 350$ nm at 298 K, all complexes were found to exhibit photoluminescence in dichloromethane solution at 298 K. Complexes **2** and **3** were observed to exhibit a vibronic-structured emission band at 511–538 nm, and the emission energies were rather insensitive to the variation of the nature of the alkynyl ligand. This emission band could be assigned to a metal-perturbed triplet intraligand π-π*excited state of the C^N(COOEt)^C ligand, probably with some phenyl to ester-substituted pyridine character.

On the contrary, complex **1** was observed to show an unusual blue-shifted emission band at *ca*. 463 nm. With reference to the emission properties of related gold(III) complexes with the same 4-ethynyltriphenylamine ligand,[4,5] an assignment of the emission of **1** to an origin from an alkynyl-to-tridentate ligand LLCT excited state would be unlikely. It was because the presence of the electron-withdrawing ethyl ester group on the pyridine moiety should lower the energy of the pyridine-based π* orbital to result in a red-shifted emission band of lower energy. In view of the close resemblance of the emission energy of **1** to that of the free 4-ethynyltriphenylamine ligand, the emission of **1** was tentatively assigned to be originated from an alkynyl-centered intraligand excited state.

In alcoholic glass at 77 K, complexes **1**–**3** were all found to exhibit vibronic-structured emission bands at 494–575 nm, and the emission energies were observed to be insensitive to the nature of the alkynyl ligands. The vibrational progressional spacings of 1200–1400 cm^{-1} were characteristic of the stretching frequencies of the C=C and C=N bonds in the tridentate ligands, suggestive of the involvement of the tridentate ligand in the excited state. Such emission bands were similar to the solution emission bands of **2** and **3**. The glass emission of complexes **1**–**3** were assigned to a metal-perturbed IL $^3[\pi\rightarrow\pi^*\{C\text{^}N(COOEt)\text{^}C\}]$ excited state. The observation of such IL emission band in complex **1** at low temperature suggested that the emissive states of complex **1** were rather close-lying in energies. The solid-state emission of the crystal and powder forms of complex **1** were also measured. At 298 and 77 K, complex **1** was found to exhibit a structureless emission band at 578–615 nm in the solid state. With reference to literature reports of solid-state emissions of related gold(III) complexes,[4,5] as well as the close-packing of the complex molecules in the crystal structure of **1**, the solid-state emission of **1** could tentatively be assigned to an excimeric nature. Complexes **2** and **3** were also observed to show similar emission maxima in the solid state at 611–613 nm at room temperature.

3.6 Electroluminescence properties

Multilayer OLEDs with the structures of ITO/NPB (70 nm)/ TCTA (5 nm)/x% Au(III) complex:MCP (30 nm)/BAlq (30 nm)/LiF (0.8 nm)/Al had been prepared by thermal evaporation at different concentrations (x) of 2, 4, 6, and 8 %. NPB and BAlq were used as hole-transporting and electron-transporting layers, respectively; while TCTA was employed as carrier confinement layer. Figure 6a depicts the electroluminescence (EL) spectra of devices doped with **1** as phosphorescent dopant at a current density of 100 mA cm^{-2}. The devices exhibited a broad, structureless emission band, and the EL peak maxima were found to shift from 520 to 548 nm with increasing dopant concentration from 2 to 8 %. The concentration dependence might be ascribed to the excimeric emission resulting from π-stacking of the cyclometalated ligand and a better packing of molecules at higher concentrations, which is well documented in square-planar metal complexes. Devices doped with complexes **1** were found to exhibit current efficiencies of 7.9 cd A^{-1} and EQE of 2.8 %. The device performance of the devices doped with complex **1** is depicted in Figure 6b-d.

4 Conclusion

A series of alkynylgold(III) complexes with an ester-substituted bis-cyclometalating ligand has been synthesized. The single crystal structure of one of the complexes revealed an unprecedentedly short Au(III)···Au(III) distance of 3.44 Å. The complexes were found to exhibit quasi-reversible reduction couples originated from the tridentate ligand and oxidation couples originated from the alkynyl ligands. In addition, the complexes were found to exhibit rich photo- and electroluminescence, rendering them potential candidates for supramolecular assembly and functions.

Acknowledgements

V. W.-W. Y. acknowledges support from The University of Hong Kong under the URC Strategic Research Theme on New Materials. This work has been supported by the University Grants Committee Areas of Excellence Scheme (AoE/P-03/08) and a General Research Fund (GRF) Grant from the Research Grants Council of the Hong Kong Special Administrative Region, P. R. China (HKU 17305614). V. K.-M. A. acknowledges the receipt of a University Postdoctoral Fellowship. Prof. W.-T. Wong and Dr. L. Szeto are gratefully acknowledged for their technical assistance in the determination of the crystal structure of complex **1**, and Mr. L.-Y. Yao is gratefully acknowledged for his technical assistance in the collection of crystal diffraction data of complex **2**.

Appendix A. Supplementary material

CCDC 1036010 (**1**) and 1036011 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1 Crystal and structure determination data of complexes **1** and **2**

complex	**[Au{C^N(COOEt)^C}(C≡C-C_6H_4-N$(C_6H_5)_2$-*p*)] (1)**	**[Au{C^N(COOEt)^C}(C≡C-C_6H_4-C_6H_5-*p*] (2)**
empirical formula	$C_{40}H_{29}AuN_2O_2$	$C_{34}H_{24}AuNO_2$
formula weight	766.62	675.51
temp, K	301(2)	293(2)
wavelength, Å	0.71073	0.85
crystal system	monoclinic	monoclinic
space group	P 2_1/c	P 2_1/c
a, Å	9.8039(4)	12.748(3)
b, Å	9.9712(4)	8.5030(17)
c, Å	32.0807(14)	24.151(5)
α, deg	90	90
β, deg	92.2930(10)	98.44(3)
γ, deg	90	90
volume, cm^3	3133.6(2)	2589.5(9)
Z, $Å^3$	4	4
density (calcd), gcm^{-3}	1.625	1.733
crystal size	0.40 mm × 0.26 mm × 0.05 mm	0.05 mm × 0.10 mm × 0.20 mm
index ranges	$-12 \leq h \leq 13$ $-13 \leq k \leq 13$ $-42 \leq l \leq 38$	$-16 \leq h \leq 16$ $-11 \leq k \leq 11$ $-31 \leq l \leq 31$
reflections collected / unique	23234 / 7556	12086 / 4092
GOF on F^2	1.134	1.058
final R indices $[I > 2\sigma(I)]$	R_1 = 0.0435 wR_2 = 0.0860	R_1 = 0.0511 wR_2 = 0.1416
largest diff peak and hole, e $Å^{-3}$	1.313 and −1.180	1.458 and −2.626

Table 2 Selected bond lengths (Å) and angles (deg) for complexes **1** and **2** with estimated standard deviations (esd’s) given in parentheses

[Au{C^N(COOEt)^C}(C≡C-C_6H_4-N$(C_6H_5)_2$-*p*)] (**1**)		**[Au{C^N(COOEt)^C}(C≡C-C_6H_4-C_6H_5-*p*]** (**2**)	
Bond Lengths (Å)			
Au(1)–C(21)	2.065(5)	Au(1)–C(7)	2.069(6)
Au(1)–C(37)	2.064(5)	Au(1)–C(13)	2.071(6)
Au(1)–N(2)	1.988(4)	Au(1)–N(1)	1.995(6)
Au(1)–C(1)	1.952(5)	Au(1)–C(18)	1.946(9)
C(1)–C(2)	1.196(7)	C(18)–C(19)	1.222(12)
Bond Angles (deg)			
C(21)–Au(1)–C(37)	161.8(2)	C(7)–Au(1)–C(13)	162.4(2)
N(2)–Au(1)–C(1)	177.65(19)	N(1)–Au(1)–C(18)	177.9(2)
Au(1)–C(1)–C(2)	172.3(5)	Au(1)–C(18)–C(19)	174.3(6)
N(2)–Au(1)–C(21)	80.53(19)	N(1)–Au(1)–C(7)	81.6(2)
N(2)–Au(1)–C(37)	81.33(19)	N(1)–Au(1)–C(13)	80.8(2)
C(1)–C(2)–C(3)	174.6(6)	C(18)–C(19)–C(20)	177.7(6)

Table 3 Electrochemical data for **1–3**[a]

Complex	**Oxidation E_{pa} / V vs SCE[b]**	**Reduction $E_{½}$ / V vs SCE[b] (ΔE_p / mV) [E_{pc} / V vs SCE[b]]**
1	+0.88	–1.14 (63), [–1.75]
2	+1.41	–1.11 (55), [–1.72]
3	+1.52	–1.12 (56), [–1.71]

[a] In dichloromethane solution with 0.1 M $^n\mathrm{Bu_4NPF_6}$ as supporting electrolyte at room temperature; working electrode, glassy carbon; scan rate 100 mV s^{-1}.

[b] E_{pa} refers to the anodic peak potential for the irreversible oxidation waves, whereas E_{pc} referes to the cathodic peak potential for the irreversible reduction waves. $E_{½} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively. $\Delta E_p = |E_{pa} - E_{pc}|$.

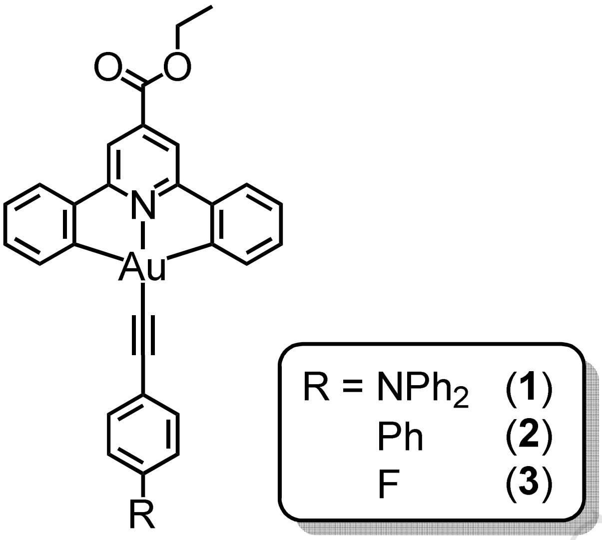
Table 4 Photophysical data for complexes **1–3**

	absorption[a]	**emission**		
complex	λ_{max}/nm (ε_{max} /dm^{3}mol^{-1}cm^{-1})	medium (T/K)	λ_{max}/nm (τ_0/μs)	Φ_{lum}[b]
1	328 (41610),	CH_2Cl_2 (298)	463 (0.6)	< 0.1 × 10^{-3}
	410 (7370),	Glass (77)[c]	494, 570 (95)	
	430 (7660)	Crystal (298)	615 (0.1)	
		Crystal (77)	605 (4.4)	
		Powder (298)	612 (0.1)	
		Powder (77)	578 (5.3)	
		Thin Film (298)		
		5% in MCP	557	0.30
2	339 (12330),	CH_2Cl_2 (298)	513, 538, 567 (1.2)	
	388sh (5620),	Glass (77)[c]	499, 537, 575 (80)	
	406 (5270),	Powder (298)	611, 655sh (4.2)	
	431 (3690)	Thin Film (298)		
		5% in MCP	514, 545sh	0.45
3	327 (11860),	CH_2Cl_2 (298)	511, 535, 570 (1.4)	
	388sh (3820),	Glass (77)[c]	499, 531, 566, 607sh (92)	
	408 (4390),	Powder (298)	613, 658 (6.0)	
	431 (3600)	Thin Film (298)		
		5% in MCP	513, 543sh	0.44

[a] In dichloromethane at 298 K.

[b] For CH_2Cl_2 solutions, the luminescence quantum yield, measured at 298 K using quinine sulfate as a standard; for thin films, the absolute photoluminescence quantum yield, measured under an excitation wavelength of 350 nm at 298 K.

[c] In EtOH–MeOH–CH_2Cl_2 (40:10:1 v/v).



Scheme 1 Structures of alkynylgold(III) complexes **1–3**

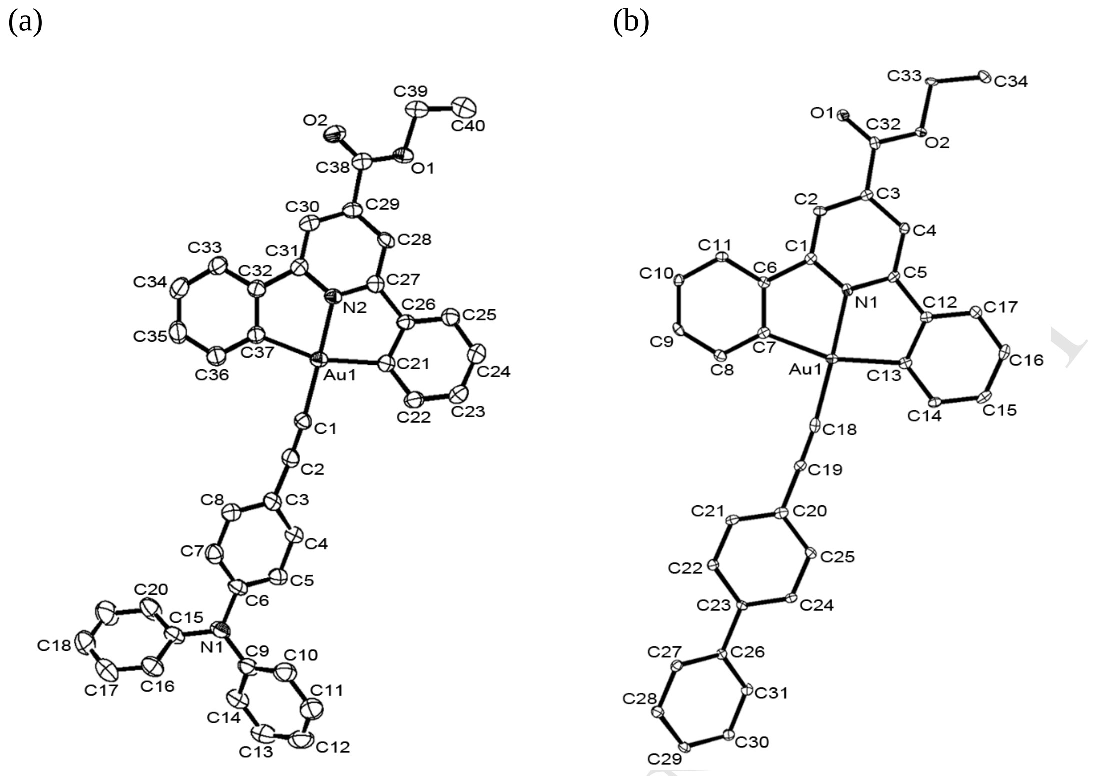
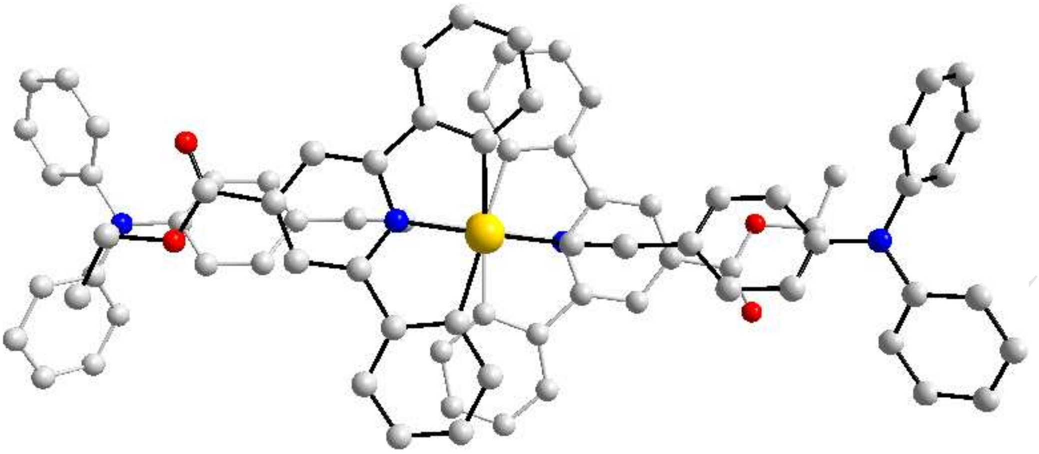
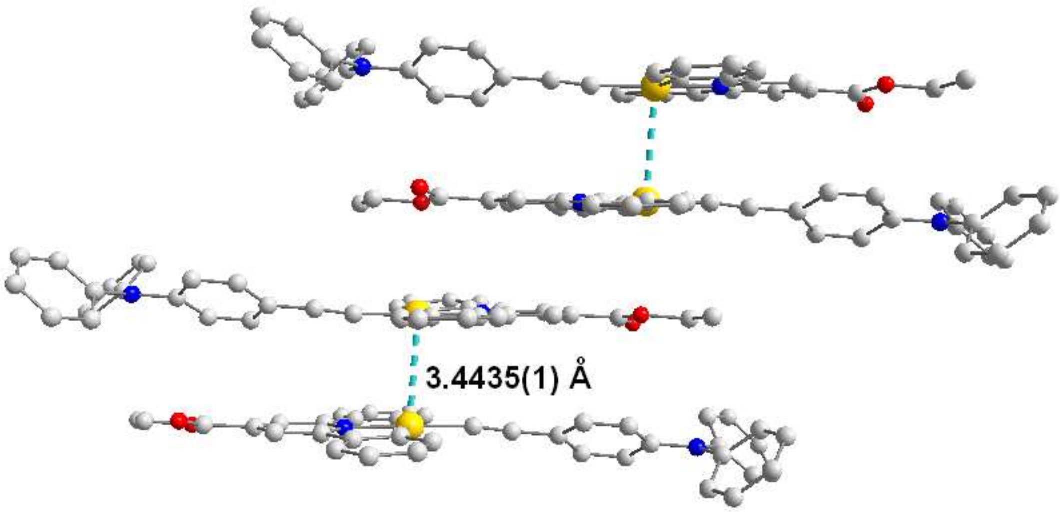


Figure 1 Perspective view of (a) **1** and (b) **2** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30 % probability level

(a)



(b)



(c)

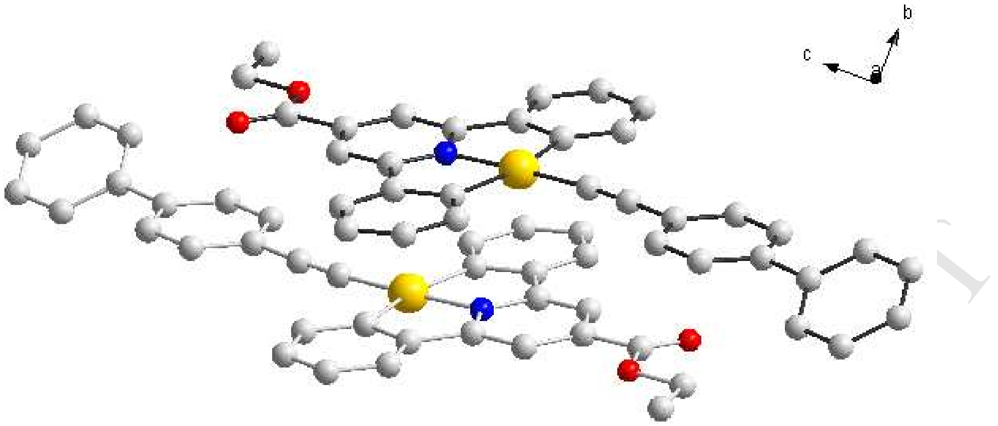


Figure 2 Crystal packing diagrams showing (a) the head-to-tail configuration of **1**, (b) the short gold-gold distances in **1** and (c) the head-to-tail configuration of **2**.

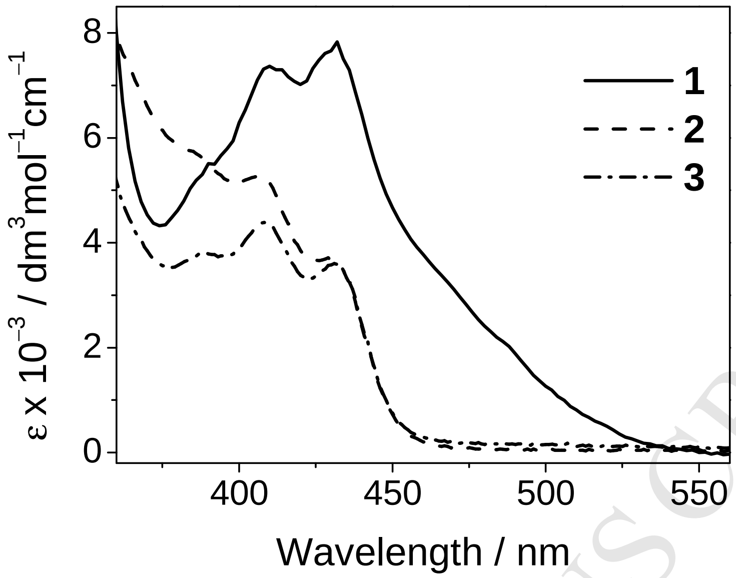


Figure 3 Electronic absorption spectra of complexes **1**–**3** in dichloromethane at 298 K

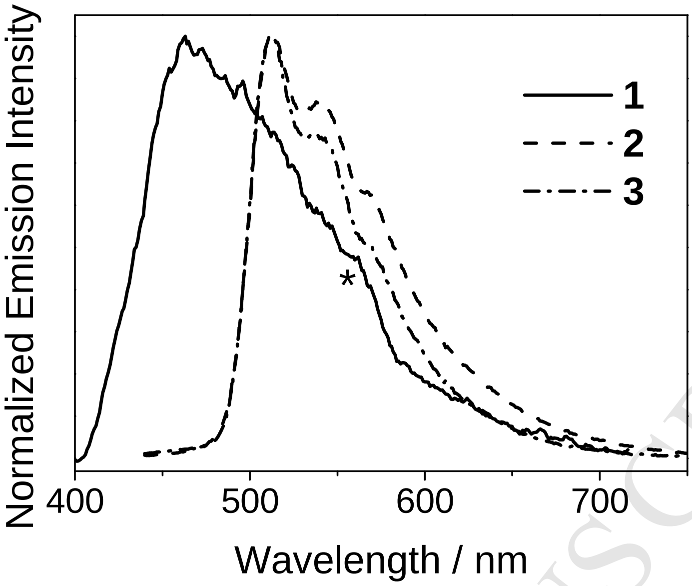


Figure 4 Normalized emission spectra of complexes **1**–**3** in dichloromethane at 298 K (Asterisk indicates the instrumental artifact)

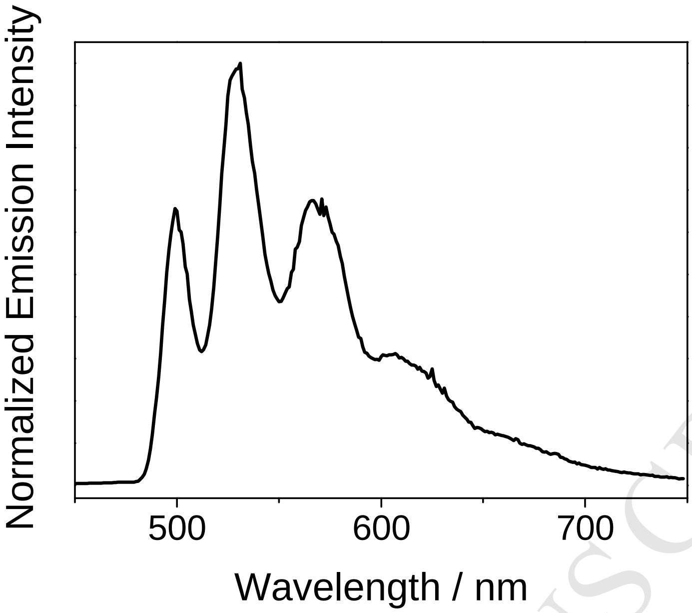
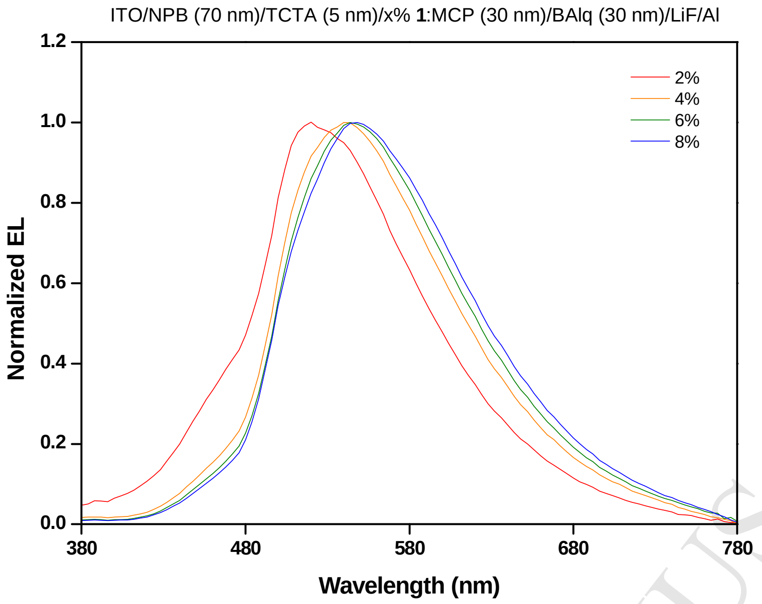
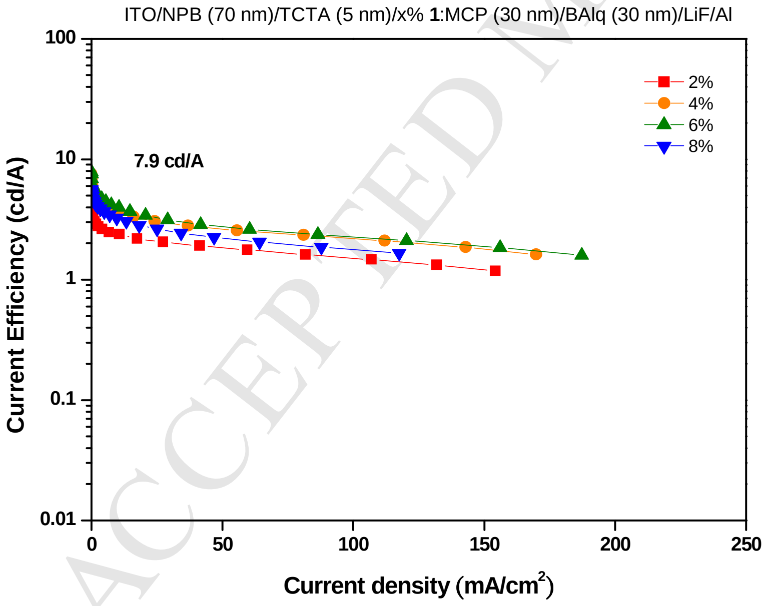


Figure 5 Emission spectrum of complex **3** in EtOH-MeOH-CH_2Cl_2 (40:10:1 v/v) glass at 77 K

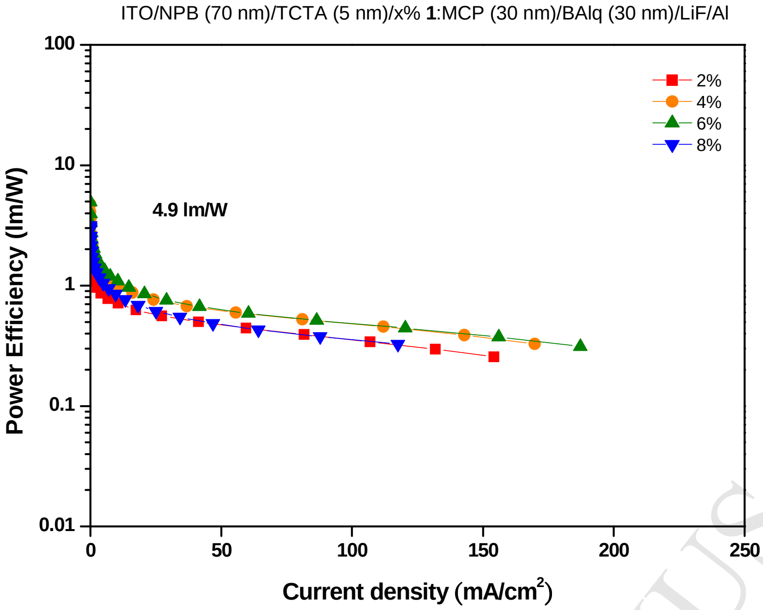
(a)


ITO/NPB (70 nm)/TCTA (5 nm)/x% **1**:MCP (30 nm)/BAlq (30 nm)/LiF/Al
Normalized EL
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
380
480
580
680
780
2%
4%
6%
8%

(b)


ITO/NPB (70 nm)/TCTA (5 nm)/x% **1**:MCP (30 nm)/BAlq (30 nm)/LiF/Al
Current Efficiency (cd/A)
Current density (mA/cm^2)
7.9 cd/A
0.01
0.1
1
10
100
0
50
100
150
200
250
2%
4%
6%
8%

(c)



(d)

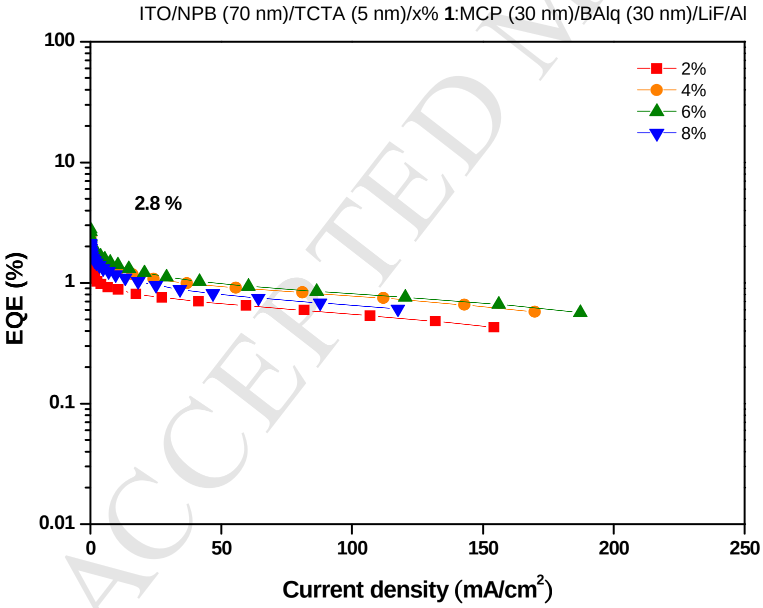


Figure 6 (a) Normalized EL spectra of devices doped with **1** as phosphorescent dopant at a current density of 100 mA cm^{-2}. (b) Current and (c) power efficiencies and (d) external quantum efficiencies (EQE) of the devices with different concentrations of **1** doped into the MCP layer as a function of current density.

Synthesis of Alkynylgold(III) complexes with Bis-cyclometalating Ligand Derived from Ethyl 2,6-Diphenylisonicotinate and their Structural, Electrochemical, Photo- and Electroluminescence Studies

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Dedicated to Prof. D. M. P. Mingos on the occasion of his 70th Birthday

Highlights

- A series of luminescent alkynylgold(III) complexes has been synthesized.
- The electrochemical and photophysical properties of the complexes were studied.
- The crystal structure of one of the complexes showed a short Au···Au distance.
- One of the complexes was used as the light-emitting layer to fabricate OLEDs.