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# Synthesis, characterization, photophysics and electrochemistry of polynuclear copper(I) and gold(I) alkynyl phosphine complexes

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## ABSTRACT

A series of polynuclear copper(I) and gold(I) alkynyl complexes, [Cu$_3$($\mu$-dppm)$_3$($\mu_3$-$\eta^1$-C$\equiv$C-Np)$_2$]BF$_4$ (**1**), [Cu$_3$($\mu$-dppm)$_3$($\mu_3$-$\eta^1$-C$\equiv$CC$_6$H$_4$CN-4)$_2$]BF$_4$ (**2**) and [{AuP(Tol-*p*)$_3$(C$\equiv$C)}$_2$Np-1,5] (**3**), have been synthesized and shown to exhibit rich photoluminescence at ambient and low temperatures. The electrochemistry of the complexes has also been studied in detail by cyclic voltammetry.

## 1. Introduction

The field of metal alkynyl chemistry has been developing rapidly [1–7] since the early report describing the preparation of metal alkynyl complexes in 1953 [8]. In part, this is because of their interesting physical properties, which include non-linear optical effects, luminescence capability, liquid crystallinity, conductivity and electronic communications, which have led to a range of possible applications in electronic and optoelectronic devices and in the rapidly evolving field of solution fabricated nano-materials [5–7,9–18]. In addition, the existence of unsaturated *sp*-hybridized orbitals on the carbon atoms of the alkynyl moieties is crucial to make alkynyl units promising building blocks in the construction of metal alkynyl complexes through $\sigma$-bonding and/or $\pi$-coordination, giving rise to the formation of a number of mono- and polynuclear complexes that display unusual structural diversity. All these have made metal alkynyl complexes an attractive family of compounds for extensive study for many years.

Among all the metal alkynyl complexes, the luminescent d$^{10}$ metal-containing complexes represent an interesting class. The presence of highly flexible bonding modes in that the alkynyl functionalities can coordinate to the d$^{10}$ metal centers in different fashions [19–24], together with the existence of weak metal···metal contacts that originate from relativistic and correlation effects [25,26], are believed to play a determining role in governing the interesting excited state properties. In this work, attempts have been made to explore the work on multinuclear coinage metal complexes with various acene-containing alkynyl ligands through the synthesis of polynuclear copper(I) complexes, namely [Cu$_3$($\mu$-dppm)$_3$($\mu_3$-$\eta^1$-C$\equiv$C-Np)$_2$]BF$_4$ (**1**) and [Cu$_3$($\mu$-dppm)$_3$($\mu_3$-$\eta^1$-C$\equiv$CC$_6$H$_4$CN-4)$_2$]BF$_4$ (**2**), and the dinuclear gold(I) complex, [{AuP(Tol-*p*)$_3$(C$\equiv$C)}$_2$Np-1,5] (**3**). Through a systematic comparison study between complexes having different metal centers and alkynyl ligands, these complexes are believed not only to provide insights into the spectroscopic origins of d$^{10}$ metal alkynyl complexes, but also to possess a promising potential to serve as ideal and versatile building blocks in the construction and assembly of luminescent organometallic oligomers and metal-based functional materials.

## 2. Experimental

### 2.1. Materials and reagents

Bis(diphenylphosphine)methane (dppm) and triethylamine were obtained from Lancaster Synthesis Ltd. Copper(I) iodide,

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1-ethynylnaphthalene and potassium fluoride were purchased from Aldrich. (Trimethylsilyl)acetylene (98%) was purchased from GFS Chemicals Inc. 4-Ethynylbenzonitrile [27], $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$ [28] and $[Au\{P(Tol)_3\}Cl]$ [29] were prepared according to literature procedures. Tetra-*n*-butyl-ammonium hexafluorophate (Aldrich, 98%) was recrystallized for no less than three times from hot absolute ethanol and then dried under vacuum for 12 h prior to use. All amines were distilled over potassium hydroxide prior to use. Acetone (Merck, GR) for photophysical and photochemical measurements was used as received. Acetonitrile (Lab Scan, HPLC) and dichloromethane (Lab Scan, AR) were purified and distilled using standard procedures before use. All other reagents were of analytical grade and were used as received.

### 2.2. Physical measurements and instrumentation

$^1H$ NMR and $^{31}P\{^1H\}$ spectra were recorded on a Bruker AVANCE 400 (400 MHz) FT-NMR spectrometer. Chemical shifts ($\delta$, ppm) were reported relative to tetramethylsilane ($Me_4Si$) for $^1H$ NMR and 85% phosphoric acid ($H_3PO_4$) for $^{31}P\{^1H\}$ NMR spectroscopy. Positive ion fast atom bombardment (FAB) and positive ion electrospray ionization (ESI) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer and a Finnigan LCQ mass spectrometer, respectively. Infrared spectra were obtained as KBr disc on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer ($4000-400\ cm^{-1}$). Elemental analyses of all metal complexes were performed on a Flash EA 1112 elemental analyzer by the Institute of Chemistry at the Chinese Academy of Sciences in Beijing. UV–Vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra at room temperature and at 77 K were obtained on a Spex Fluorolog-2 Model F111 fluorescence spectrophotometer equipped with a Hamamatsu R928 PMT detector. Low-temperature solid state emission and excitation spectra were recorded with solid samples loaded in a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen. Room temperature spectra were recorded similarly but without liquid nitrogen inside the Dewar flask. Low-temperature emission and excitation of the samples in frozen glass were recorded with the same setup as for the solid state samples. For solution emission and excitation spectra, samples were degassed on a high vacuum line in a two-compartment cell consisting of a 10-mL Pyrex bulb and a 1-cm path length quartz cuvette, and sealed from the atmosphere by a Bibby Rotaflo HP6 teflon stopper. The solutions were subjected to at least four freeze-pump-thaw cycles. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. Luminescence decay signals were detected by a Hamamatsu R928 PMT and recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope, and analyzed using a program for exponential fits. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 600A electrochemical analyzer. The electrolytic cell used was a conventional two-compartment cell. Electrochemical measurements were performed in acetonitrile solutions with $0.1\ mol\ dm^{-3}$ $^nBu_4NPF_6$ as supporting electrolyte at room temperature. The reference electrode was a $Ag/AgNO_3$ (0.1 M in acetonitrile) electrode, 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. All solutions for electrochemical studies were deaerated with prepurified argon gas just before measurements.

### 2.3. Crystal structure determination

Single crystals of **3** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether vapor into an acetonitrile solution of **3**. The crystal structure was determined on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods employing the SHELXL-97 program [30]. Gold, phosphorus and many non-hydrogen atoms were located according to the direct methods and the successive least-squares Fourier cycles. The positions of other non-hydrogen atoms were found after successful refinement by full-matrix least squares using program SHELXL-97 [30]. One crystallographic asymmetric unit consisted of one formula unit. In the final stage of least-squares refinement, disordered atoms were refined isotropically, other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated by SHELXL-97 program [30]. The positions of hydrogen atoms were calculated based on 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.

### 2.4. Synthesis of polynuclear $d^{10}$ metal alkynyl complexes

#### 2.4.1. $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}Np)_2]BF_4$ (**1**)

This was synthesized according to modification of a procedure reported previously for trinuclear copper(I) alkynyl phosphine complexes [31–37]. A mixture of $[Cu_2\text{-}(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$ (100 mg, 0.08 mmol) and 1-ethynylnaphthalene (17 mg, 0.12 mmol) with an excess of triethylamine (0.03 mL, 0.22 mmol) in acetone solution was stirred at room temperature for 24 h. The reaction mixture was filtered and evaporated to dryness. The solid residue was then washed with diethyl ether. Recrystallization by layering of *n*-hexane onto a dichloromethane solution of the product afforded complex **1** as yellow crystals. Yield: 60 mg, 62%. $^1H$ NMR (400 MHz, acetone-$d_6$, 298 K, relative to $Me_4Si$): $\delta$ 3.33–3.39 (m, 6H, $-CH_2-$), 6.68–7.16 (m, 60H, $-C_6H_5$), 7.56 (t, 2H, $J = 8.0$ Hz, Np), 7.60 (d, 2H, $J = 8.0$ Hz, Np), 7.63 (dd, 2H, $J = 7.0$ and 8.0 Hz, Np), 7.75 (dd, 2H, $J = 7.0$ and 8.0 Hz, Np), 8.09 (d, 2H, $J = 8.0$ Hz, Np), 8.16 (d, 2H, $J = 8.0$ Hz, Np), 8.70 (d, 2H, $J = 8.0$ Hz, Np). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-$d_6$, 298 K, relative to 85% $H_3PO_4$)/ppm: $\delta$ −6.23 (s). Positive FAB-MS: *m*/*z* 1647 $[M-BF4]^+$. IR (KBr disc, $\nu/cm^{-1}$): 2001 (m), $\nu(C{\equiv}C)$. Elemental analyses. Found: C, 68.87; H, 4.68. Calc. for **1**: C, 68.61; H, 4.65%.

#### 2.4.2. $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4CN\text{-}4)_2]BF_4$ (**2**)

This was prepared by a method similar to that of complex **1** except 4-ethynylbenzonitrile (27 mg, 0.12 mmol) was used in place of 1-ethynylnaphthalene. Recrystallization by vapor diffusion of diethyl ether into the acetone solution of the complex yielded yellow crystals of complex **2**. Yield: 61 mg, 55%. $^1H$ NMR (400 MHz, acetone-$d_6$, 298 K, relative to $Me_4Si$): $\delta$ 3.32–3.38 (m, 6H, $-CH_2-$), 6.86–7.22 (m, 60 H, $-C_6H_5$), 7.40 (d, 4H, $J = 8.3$ Hz, $-C_6H_4-$), 7.81 (d, 4H, $J = 8.3$ Hz, $-C_6H_4-$). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-$d_6$, 298 K, relative to 85% $H_3PO_4$)/ppm: $\delta$ −5.10 (s). Positive FAB-MS: *m*/*z* 1596 $[M-BF4]^+$. IR (KBr disc, $\nu/cm^{-1}$): 1993 (m), $\nu(C{\equiv}C)$; 2222 (m), $\nu(C{\equiv}N)$. Elemental analyses. Found: C, 66.28; H, 4.59; N, 1.59. Calc. for **2**: C, 66.37; H, 4.43; N, 1.66%.

#### 2.4.3. $[\{AuP(Tol\text{-}p)_3(C{\equiv}C)\}_2Np\text{-}1,5]$ (**3**)

This was synthesized according to modification of a procedure reported previously for alkynylgold(I) phosphine complexes [38]. A mixture of $[Au\{P(Tol)_3\}Cl]$ (100 mg, 0.19 mmol) and 1,5-bis(trimethylsilylethynyl)naphthalene (30 mg, 0.09 mmol) in the presence of an excess of potassium fluoride (16 mg, 0.28 mmol) in dichloromethane-methanol (15:1 v/v, 32 mL) was stirred at room