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Synthesis, Luminescence, and Electrochemistry of Mix-Capped Trinuclear Copper(I) Acetylide Complexes. X-ray Crystal Structures of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OEt\text{-}p)]PF_6$ and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_2\text{-}\eta^1\text{-C}\equiv CC_6H_4NO_2\text{-}p)]PF_6$

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Two luminescent mix-capped trinuclear copper(I) acetylide complexes, $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OEt\text{-}p)]PF_6$ (**1**) and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_2\text{-}\eta^1\text{-C}\equiv CC_6H_4NO_2\text{-}p)]PF_6$ (**2**), have been synthesized and their photophysical and electrochemical properties studied. The X-ray crystal structures of **1** and **2** have also been determined.

Introduction

Transition-metal alkynyl complexes have been widely studied in view of the ability of the alkynyl group to bond to transition metals to form a large number of mono- and polynuclear complexes which display an unusual variety of bonding modes.[1] Recent interests also arose as a result of the increasing attention on metal-containing oligomeric and polymeric materials with polarizable moieties for the fabrication of electronic, liquid crystal, and nonlinear optical devices.[2−9] Conjugated organic polymer systems have been of interest in nonlinearity studies.[10] It was proposed that the presence of electron-donating and electron-accepting substituents would result in strong second-harmonic generation.[11] Incorporation of polarizable transition-metal ions into such push−pull donor−acceptor molecules helps create a delocalized charge-transfer state from the donor to the acceptor and may increase the hyperpolarizability.[2b,c,3,9] In view of the potential applications of alkynylmetal complexes and our recent efforts on the synthesis, photophysics, and spectroscopic studies of alkynyl-bridged polynuclear d^{10} metal complexes,[12] a program was launched to design donor−acceptor alkynyl complexes using the triangular d^{10} metal core as the basic building block. In this paper, we report the synthesis, luminescence, and electrochemistry of two mix-capped trinuclear copper(I) acetylide complexes, $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OEt\text{-}p)]PF_6$ (**1**) and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_2\text{-}\eta^1\text{-C}\equiv CC_6H_4NO_2\text{-}p)]PF_6$ (**2**). The crystal structures of these two complexes will also be described. Complex **2** with a donor acetylide on one end and an acceptor acetylide on the other end may exhibit

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interesting properties and may possess potential for generating NLO effects.

Experimental Section

Materials and Reagents. The ligand bis(diphenylphosphino)methane was obtained from Strem Chemicals Inc. 4-Ethoxyphenylacetylene and 4-methoxyphenylacetylene were obtained from Maybridge Chemical Co. Ltd. 4-Nitrophenylacetylene[13] and $[\mathrm{Cu_2}(\mu\text{-dppm})_2(\mathrm{MeCN})_2](\mathrm{PF_6})_2$[14] were prepared according to literature procedures. All other solvents were purified and distilled using standard procedures before use.[15] All other reagents were of analytical grade and used as received.

Synthesis of Copper(I) Acetylide Complexes. All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques.

$[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\mathrm{CC_6H_4OMe}\text{-}p)(\mu_3\text{-}\eta^1\text{-C}{\equiv}\mathrm{CC_6H_4}\text{-}\mathrm{OEt}\text{-}p)]\mathrm{PF_6}$ (1). This was prepared by modification of a method described in the literature.[12a,b,16] A solution of $[\mathrm{Cu_2}(\mu\text{-dppm})_2(\mathrm{MeCN})_2](\mathrm{PF_6})_2$ (0.38 g, 0.3 mmol) in acetone/methanol (15 mL/5 mL) was treated with $\mathrm{HC{\equiv}CC_6H_4OMe}$-$p$ (26.4 mg, 0.4 mmol), $\mathrm{HC{\equiv}CC_6H_4OEt}$-$p$ (29.2 mg, 0.4 mmol), and an excess of KOH. The mixture was stirred at room temperature for 24 h. After evaporating to dryness, the solid residue was extracted with acetone (20 mL). Subsequent successive recrystallization by diffusion of diethyl ether into the concentrated solution resulted in the formation of yellow crystals of **1**. Yield: 0.19 g (53%). UV−vis ($\mathrm{CH_2Cl_2}$), λ/nm ($\epsilon_{\max}$/dm^3 mol^{-1} cm^{-1}): 260 (54 350), 304 (42 080), 368sh (8350). IR (Nujol mull, KBr) ν/cm^{-1}: 840s [ν(P−F)]. Raman (solid) ν/cm^{-1}: 2020s [ν(C≡C)]. ^{1}H NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 1.5 (t, 3H, $-\mathrm{CH_3}$ of OEt, $J_{\mathrm{H-H}}$ 12.8 Hz), 3.3 (m, 6H, $-\mathrm{CH_2}-$ of dppm), 4.0 (s, 3H, −OMe), 4.3 (q, 2H, $-\mathrm{CH_2}-$ of OEt, $J_{\mathrm{H-H}}$ 12.8 Hz), 6.8−7.6 (m, 68H, −Ph). Positive FAB-MS: *m/z* 1619 {M$^+$}. Anal. Calcd for $\mathrm{C_{94}H_{82}O_2P_7F_6Cu_3 \cdot 2H_2O}$: C, 62.68; H, 4.78. Found: C, 62.86; H, 4.71.

$[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\mathrm{CC_6H_4OMe}\text{-}p)(\mu_2\text{-}\eta^1\text{-C}{\equiv}\mathrm{CC_6H_4}\text{-}\mathrm{NO_2}\text{-}p)]\mathrm{PF_6}$ (2). The procedure was similar to that of **1** except $\mathrm{HC{\equiv}CC_6H_4NO_2}$-$p$ (29.4 mg, 0.2 mmol) was used in place of $\mathrm{HC{\equiv}CC_6H_4OEt}$-$p$ to give red crystals of **2** after successive recrystallization. Yield: 0.14 g (40%). UV−vis ($\mathrm{CH_2Cl_2}$), λ/nm ($\epsilon_{\max}$/dm^3 mol^{-1} cm^{-1}): 256sh (59 100), 300sh (38 750), 402 (14 450). IR (Nujol mull, KBr) ν/cm^{-1}: 2019m [ν(C≡C)], 1334s [ν(N⋯O)], 834s [ν(P−F)]. Raman (solid) ν/cm^{-1}: 2019s [ν(C≡C)], 1330s [ν(N⋯O)]. ^{1}H NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 3.3 (m, 6H, $-\mathrm{CH_2}-$), 3.9 (s, 3H, −OMe), 6.7−7.5 (m, 64H, −Ph), 8.2 (d, 4H, aryl H *ortho* to $\mathrm{NO_2}$, $J_{\mathrm{H-H}}$ 8.9 Hz). Positive FAB-MS: *m/z* 1620 {M$^+$}. Anal. Calcd for $\mathrm{C_{92}H_{77}P_7F_6NO_3Cu_3 \cdot 3H_2O}$: C, 60.71; H, 4.56; N, 0.77. Found: C, 61.04; H, 4.39; N, 0.49.

Physical Measurements and Instrumentation. UV−vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra were obtained on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) Fourier transform NMR spectrometer. Positive-ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed by the Institute of Chemistry, Chinese Academy of Sciences. 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 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were recorded on a Tektronix model TDS-620A (500 MHz, 2GS/s) digital oscilloscope and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a 10-cm^3 round-bottom flask equipped with a sidearm 1-cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than 4 freeze−pump−thaw cycles. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc., model CHI 620 Electrochemical Analyzer interfaced to an IBM-compatible personal computer. The electrolytic cell used was a conventional two compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a Vycor glass. A Ag/AgNO$_3$ (0.1 mol dm^{-3} in $\mathrm{CH_3CN}$) reference electrode was used. The ferrocenium−ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 M $^n\mathrm{Bu_4NPF_6}$). The working electrode was a glassy-carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported elsewhere.[17]

Crystal Structure Determination. Crystal data for **1**: $\{[\mathrm{Cu_3P_6O_2C_{94}H_{82}}]^+\mathrm{PF_6}^-\}$; fw = 1765.13, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.563(3)$ Å, $b = 24.774(4)$ Å, $c = 24.668(4)$ Å, $\beta = 105.27(2)$°, $V = 9175(2)$ Å^3, $Z = 4$, $D_c = 1.278$ g cm^{-3}, μ(Mo Kα) = 8.68 cm^{-1}, $F(000) = 3632$, $T = 301$ K. A yellow crystal of dimensions 0.20 × 0.10 × 0.35 mm mounted on a glass fiber was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data collection was made with 3° oscillation (60 images) at a 120 mm distance and 300 s exposure. The images were interpreted and intensities integrated using program *DENZO*.[18a] There were 16 375 unique reflections obtained from a total of 63 181 measured reflections ($R_{\mathrm{int}} = 0.045$). There were 10 264 reflections with $I > 3\sigma(I)$ considered observed and used in the structural analysis. These reflections were in the range h 0−18; k 0−29; l −29 to 29 with $2\theta_{\max} = 51.2$°. The space group was determined uniquely by systematic absences, and the structure was solved by Patterson methods, expanded by Fourier methods (*PATTY*[18b]), and refined by full-matrix least-

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squares using the software package *TeXsan*[18c] on a Silicon Graphics Indy computer. A crystallographical asymmetric unit consists of one formula unit. In the least-squares refinement, all 112 atoms were refined anisotropically and 82 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 1009 variable parameters by least squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.040F_o^2)^2]$ for 10 264 reflections with $I > 3\sigma(I)$ was reached at $R = 0.053$ and $wR = 0.086$ with a goodness-of-fit of 2.69. $(\Delta/\sigma)_{max} = 0.05$, except for the F atoms which have a value of 0.34. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.33 and 0.47 e Å^{-3}, respectively.

Crystal data for **2**: $\{[Cu_3P_6O_3NC_{92}H_{77}]^+PF_6^-\cdot(CH_3)_2CO\}$; fw = 1824.15, monoclinic, space group $P2_1/n$ (No. 14), a = 18.06(1) Å, b = 22.929(8) Å, c = 21.268(7) Å, β = 99.36(4)°, V = 8692(6) Å^3, Z = 4, D_c = 1.394 g cm^{-3}, μ(Mo Kα) = 9.21 cm^{-1}, $F(000)$ = 3752, T = 301 K. An orange crystal of dimensions 0.20 × 0.15 × 0.35 mm mounted on a glass fiber was used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) using $\omega-2\theta$ scans with ω-scan angle (0.58 + 0.35 tan θ)° at a scan speed of 16.0 deg min^{-1} (up to 6 scans for reflection $I < 15\sigma(I)$). Unit cell dimensions were determined based on 25 reflections in the 2θ range of 22.5−25.9°. Intensity data (in the range of $2\theta_{max}$ = 48.1°; h 0−20; k 0−25; l −24 to 24, and 3 standard reflections measured after every 300 reflections showed a decay of 3.54%) were corrected for decay and for Lorentz and polarization effects and empirical absorption corrections based on the Ψ-scan of four strong reflections (minimum and maximum transmission factors 0.931 and 1.000). There were 14 558 reflections measured, of which 14 066 were unique and R_{int} = 0.044. There were 7634 reflections with $I > 3\sigma(I)$ considered observed and used in the structural analysis. The space group was uniquely determined from systematic absences, and the structure was solved by direct methods (*SIR92*[18d]), expanded by Fourier method, and refined by full-matrix least-squares using the software package *TeXsan*[18c] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consists of one formula unit. In the least-squares refinement, the 3 Cu atoms, 7 P atoms, 3 O atoms, 1 N atom, and 92 C atoms were refined anisotropically, the 9 F atoms (having occupation numbers 1.0, 0.7, 1.0, 1.0, 0.7, 0.7, 0.3, 0.3, and 0.3, respectively) of the disordered PF_6^- anion and the 3 C atoms and 1 O atom of the acetone solvent molecule were refined isotropically, and 83 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 1007 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.040F_o^2)^2]$ for 7634 reflections with $I > 3\sigma(I)$ was reached at $R = 0.050$ and $wR = 0.067$ with a goodness-of-fit of 1.79. $(\Delta/\sigma)_{max}$ = 0.05 for atoms of the complex cation. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.66 and 0.50 e Å^{-3}, respectively. Crystal and structure determination data as well as the selected bond distances and bond angles for **1** and **2** are collected in Tables 1−4, respectively.

Results and Discussion

Reaction of 3 equiv of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](PF_6)_2$ in an acetone/methanol mixture with 2 equiv of each alkyne $HC{\equiv}CC_6H_4R$-p (R = OMe and OEt for **1**; R = OMe and NO_2 for **2**) in the presence of an excess of KOH followed by successive recrystallization gave yellow and red crystals of **1** and **2**, respectively. The mix-capped unsymmetric compounds **1** and **2** were found to be free of their respective symmetric bi-capped byproducts after several successive recrystallization processes. All newly synthesized complexes were characterized by elemental analyses, positive FAB-MS, and ^{1}H NMR, IR, and Raman spectroscopy. The crystal structures of **1** and **2** have been determined by X-ray crystallography.

Table 1. Crystal and Structure Determination Data for $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OMe\text{-}p)(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OEt\text{-}p)]PF_6$ (1)

formula	$\{[Cu_3C_{94}H_{82}O_2P_6]^+PF_6^-\}$
fw	1765.13
T, K	301
a, Å	15.563(3)
b, Å	24.774(4)
c, Å	24.668(4)
β, deg	105.27(2)
V, Å^3	9175(2)
cryst color and shape	yellow prism
cryst system	monoclinic
space group	$P2_1/c$ (No. 14)
Z	4
$F(000)$	3632
D_c, g cm^{-3}	1.278
cryst dimens, mm	0.20 × 0.10 × 0.35
λ, Å (graphite-monochromated Mo Kα)	0.710 73
μ, cm^{-1}	8.68
collection range	$2\theta_{max}$ = 51.2° (h 0−18; k 0−29; l −29 to 29)
oscillation, deg	3
no. of images collect	60
distance, mm	120
exposure time, s	300
no. of data collect	63 181
no. of unique data	16 375
no. of data used in refinement, m	10 264
no. of parameters refined, p	1009
R^a	0.053
wR^a	0.086
goodness-of-fit, S	2.69
max shift, $(\Delta/\sigma)_{max}$	0.05
residual extrema in final difference map, e Å^{-3}	+1.33, −0.47

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.040F_o^2)^2]$ with $I > 3\sigma(I)$.

Table 2. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OMe\text{-}p)(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OEt\text{-}p)]PF_6$ (1)

Bond Lengths (Å)			
Cu(1)⋯Cu(2)	2.621(1)	C(1)−C(2)	1.182(8)
Cu(2)⋯Cu(3)	2.6087(9)	C(11)−Cu(1)	2.188(7)
Cu(1)⋯Cu(3)	2.574(1)	C(11)−Cu(2)	2.350(7)
C(1)−Cu(3)	2.224(6)	C(11)−Cu(3)	2.142(7)
C(1)−Cu(2)	2.098(6)	C(11)−C(12)	1.210(8)
C(1)−Cu(1)	2.191(6)		

Bond Angles (deg)			
Cu(1)−Cu(3)−Cu(2)	60.75(3)	Cu(2)−C(1)−Cu(3)	74.2(2)
Cu(1)−Cu(2)−Cu(3)	58.96(3)	Cu(1)−C(11)−Cu(3)	72.9(2)
Cu(2)−Cu(1)−Cu(3)	60.28(3)	Cu(2)−C(11)−Cu(3)	70.8(2)
Cu(1)−C(1)−Cu(2)	75.3(2)	Cu(1)−C(11)−Cu(2)	70.4(2)
Cu(1)−C(1)−C(2)	134.0(5)	Cu(1)−C(11)−C(12)	137.3(5)
Cu(2)−C(1)−C(2)	142.9(5)	Cu(2)−C(11)−C(12)	132.7(5)
Cu(3)−C(1)−C(2)	130.5(5)	Cu(3)−C(11)−C(12)	142.2(6)
Cu(1)−C(1)−Cu(3)	71.3(2)		

The perspective drawings of the crystal structures of **1** and **2** with atomic numbering are depicted in Figures 1 and 2, respectively. The structure determinations show that each complex cation consists of an isosceles triangle of copper atoms with a dppm ligand bridging each edge to form a roughly planar $[Cu_3P_6]$ core. The

Table 3. Crystal and Structure Determination Data for $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_2\text{-}\eta^1\text{-C}\equiv CC_6H_4NO_2\text{-}p)]PF_6$ (2)

formula	$\{[Cu_3C_{92}H_{77}NO_3P_6]^+PF_6^-\cdot(CH_3)_2CO\}$
fw	1824.15
T, K	301
a, Å	18.06(1)
b, Å	22.929(8)
c, Å	21.268(7)
β, deg	99.36(4)
V, Å^3	8692(6)
cryst color and shape	orange prism
cryst system	monoclinic
space group	$P2_1/n$ (No.14)
Z	4
$F(000)$	3752
D_c, g cm^{-3}	1.394
cryst dimens, mm	0.20 × 0.15 × 0.35
λ, Å (graphite-monochromated Mo Kα)	0.710 73
μ, cm^{-1}	9.21
collection range	$2\theta_{max} = 48.1°$ (h 0−20; k 0−25; l −24 to 24)
scan mode and scan speed, deg min^{-1}	$\omega-2\theta$, 16.0
scan width, deg	$0.58 + 0.35 \tan\theta$
no. of data collect	14 558
no. of unique data	14 066
no. of data used in refinement, m	7634
no. of parameters refined, p	1007
R^a	0.050
wR^a	0.067
goodness-of-fit, S	1.79
max shift, $(\Delta/\sigma)_{max}$	0.05
residual extrema in final difference map, e Å^{-3}	+0.66, −0.50

[a] $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.040F_o^2)^2]$ with $I > 3\sigma(I)$.

Table 4. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_2\text{-}\eta^1\text{-C}\equiv CC_6H_4NO_2\text{-}p)]PF_6$ (2)

Bond Lengths (Å)			
Cu(1)···Cu(2)	2.707(1)	C(1)−Cu(1)	2.011(7)
Cu(2)···Cu(3)	2.557(1)	C(1)−C(2)	1.214(9)
Cu(1)···Cu(3)	2.758(1)	C(10)−Cu(2)	2.077(7)
C(1)−Cu(3)	2.211(7)	C(10)−Cu(3)	2.074(7)
C(1)−Cu(2)	2.321(7)	C(10)−C(11)	1.208(9)

Bond Angles (deg)			
Cu(1)−Cu(3)−Cu(2)	61.08(3)	Cu(1)−C(1)−Cu(3)	81.4(3)
Cu(1)−Cu(2)−Cu(3)	63.13(3)	Cu(2)−C(1)−Cu(3)	68.7(2)
Cu(2)−Cu(1)−Cu(3)	55.80(3)	Cu(1)−C(10)−Cu(3)	65.3(2)
Cu(1)−C(1)−Cu(2)	77.0(2)	Cu(2)−C(10)−Cu(3)	76.1(2)
Cu(1)−C(1)−C(2)	139.0(6)	Cu(1)−C(10)−Cu(2)	63.8(2)
Cu(2)−C(1)−C(2)	131.7(6)	Cu(2)−C(10)−C(11)	135.6(6)
Cu(3)−C(1)−C(2)	132.0(6)	Cu(3)−C(10)−C(11)	144.8(6)

bridging mode of the alkynyl group is asymmetric, with the Cu−C bond distances in **1** and **2** in the range 2.098(6)−2.224(6) Å and 2.011(7)−2.321(7) Å, respectively. The bond angles between the alkynyl group and each copper atom are in the range of 130.5(5)−142.9(5)° for **1** and 131.7(6)−144.8(6)° for **2**. The distances of the C≡C bond in **1** and **2** are 1.182(8)−1.210(8) Å and 1.208(9)−1.214(9) Å, characteristic of typical metal acetylide σ bonding.[1] A similar bonding mode has been found in analogous complexes.[12a,c,i−k,16] The Cu···Cu distances are in the range of 2.574(1)−2.621(1) Å for **1** and 2.557(1)−2.758(1) Å for **2**, which are smaller than the sum of van der Waals radii for copper (2.8 Å),[19] suggesting that there may be the presence of some weak metal−metal interactions in these complexes.

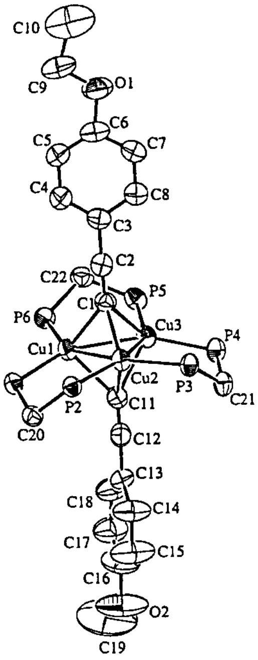

Figure 1. Perspective drawing of the complex cation of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OEt\text{-}p)]PF_6$ (**1**) with atomic-numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

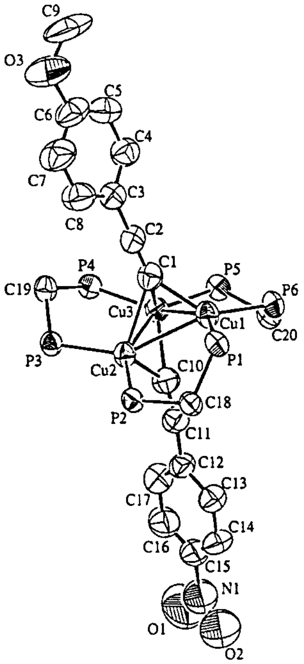

Figure 2. Perspective drawing of the complex cation of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv CC_6H_4OMe\text{-}p)(\mu_2\text{-}\eta^1\text{-C}\equiv CC_6H_4NO_2\text{-}p)]PF_6$ (**2**) with atomic-numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

The electronic absorption spectra for complexes **1** and **2** in dichloromethane are characterized by absorption bands at ca. 260 and 300 nm. The high-energy absorption band at ca. 260 nm is likely to arise from a

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(19) Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.

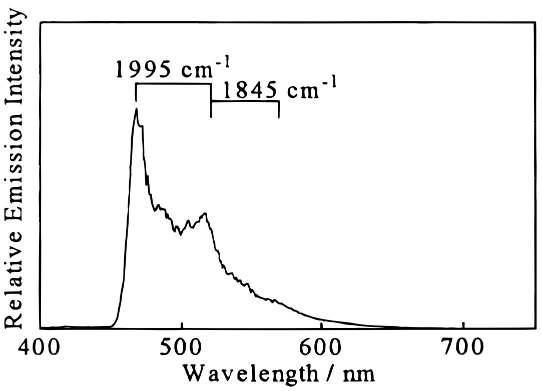

Figure 3. Solid-state emission spectrum of **1** at 77 K.

Table 5. Photophysical Data for Complexes 1 and 2

complex	medium (*T*/K)	absorption λ/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1})	emission λ_{em}/nm(τ_o/μs)
1	CH_2Cl_2 (298)	260 (54 350), 304 (42 080), 368sh (8350)	
	acetone (298)		479 (5.6)
	solid (298)		475, 502 (17.6)
	solid (77)		467, 515, 569
	EtOH/MeOH (4:1 v/v) (77)		456, 498
2	CH_2Cl_2 (298)	256sh (59 100), 300sh (38 750), 402 (14 450)	
	acetone (298)		489 (3.6)
	solid (298)		671 (0.2)
	solid (77)		697
	EtOH/MeOH (4:1 v/v) (77)		464, 509, 568sh

phosphine ligand-centered ($\pi \rightarrow \pi^*$) transition since their corresponding free ligand, dppm, also absorbs strongly in this region. The lower energy band at ca. 300 nm is tentatively assigned as an acetylide ligand-centered absorption in view of its absorption energy being similar to those of the free aryl acetylenes. In addition, a low-lying absorption band at ca. 368 and 402 nm is observed in **1** and **2**, respectively. It is noted that complex **2** shows a lower energy absorption than **1**, which is in line with the energy of the π^* orbital, i.e., 4-methoxyphenylacetylide > 4-nitrophenylacetylide. It is likely that this absorption band involves a metal-perturbed [$\pi \rightarrow \pi^*(RC{\equiv}C^-)$] IL or [$d\sigma^*(Cu) \rightarrow \pi^*(RC{\equiv}C^-)$] MLCT transition.

Excitations of solid samples and fluid solutions of complexes **1** and **2** at $\lambda > 350$ nm produce long-lived, intense luminescence. Their photophysical data are collected in Table 5. It is interesting to note that complexes **1** and **2** show vibronically structured bands in the solid state and/or in fluid solutions. Vibronically structured bands with vibrational progressional spacings of ca. 1840−2040 cm^{-1} characteristic of ν(C≡C) stretching modes of the acetylide in the ground state are observed, which are suggestive of the involvement of the aryl acetylide in the excited state. The emission spectrum of **1** in the solid state at 77 K is shown in Figure 3.

With reference to previous studies on trinuclear copper(I) acetylide complexes,[12a,c,h,j] the lowest lying emissive state of complex **1** is tentatively assigned as derived from an acetylide-to-metal ligand-to-metal charge-transfer transition (LMCT), owing to the good σ-donating properties of 4-methoxy- and ethoxyphenylacetylide, mixed with a metal-centered $3d^94s^1$ excited-state modified by metal−metal interactions in view of the short Cu···Cu distances observed. It is interesting to note that complex **2** emits at a much lower energy than **1** in the solid state. It is likely that this emission originates from the ligand-centered 4-nitrophenylacetylide unit, as a similar low-energy emission band also appears in the free 4-nitrophenylacetylene ligand at 77 K in MeOH/EtOH glass. Similar assignment has also been reported for other related systems.[12h] Thus, it is likely that for the very electron deficient acetylides, such as 4-nitrophenylacetylide, the lowest lying excited states are no longer LMCT in nature, instead they are dominated by an intraligand $\pi \rightarrow \pi^*(RC{\equiv}C^-)$ character.

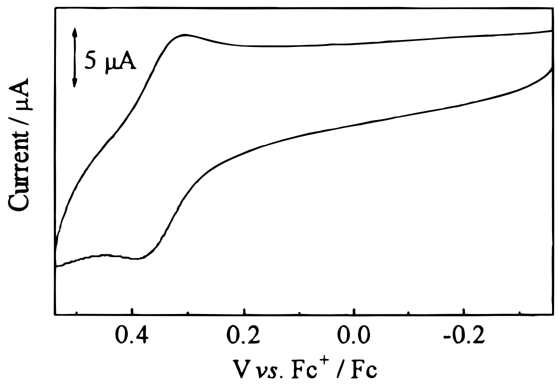

Figure 4. Cyclic voltammogram of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OMe\text{-}p)(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OEt\text{-}p)]PF_6$ (**1**) in acetonitrile (0.1 M $^nBu_4NPF_6$) showing the quasi-reversible oxidation couple. Scan rate: 100 mV/s.

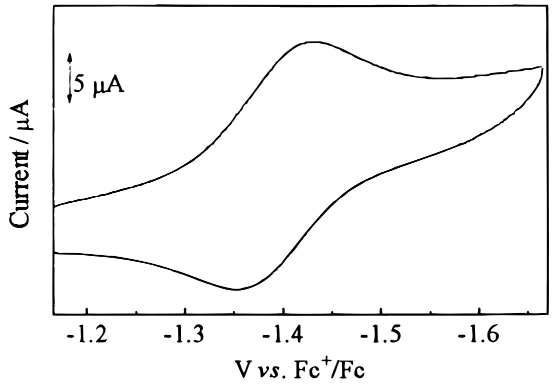

Figure 5. Cyclic voltammogram of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OMe\text{-}p)(\mu_2\text{-}\eta^1\text{-}C{\equiv}CC_6H_4NO_2\text{-}p)]PF_6$ (**2**) in acetonitrile (0.1 M $^nBu_4NPF_6$) showing the quasi-reversible reduction couple. Scan rate: 100 mV/s.

The cyclic voltammogram of complex **1** in MeCN (0.1 M $^nBuNPF_6$) shows a quasi-reversible oxidation couple at ca. +0.33 V vs Fc$^+$/Fc (Figure 4), which is assignable to a metal-centered Cu(I) → Cu(II) oxidation.[12a,c,h] An irreversible electrode process upon oxidation is observed in complex **2** which contains 4-nitrophenylacetylide. It is likely that the large electron-withdrawing nature of the nitro group renders the one-electron-oxidized form of this complex highly unstable and would undergo decomposition. In addition, cyclic voltammetric studies of complex **2** showed the presence of a quasi-reversible reduction couple of ca. −1.39 V vs Fc$^+$/Fc (Figure 5), which coincides with the value found for the reduction of 4-nitrophenylacetylene. It is likely that the reduction couple observed in **2** is derived from a one-electron acetylide ligand-centered reduction.

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Supporting Information Available: Tables giving fractional coordinates and thermal parameters, general displacement parameter expressions (*U*), and all bond distances and bond angles for complexes **1** and **2** (66 pages). Ordering information is given on any current masthead page.

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