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Luminescent Hepta- and Tetradecanuclear Complexes of 5,5′-Diethynyl-2,2′-bipyridine Capped with Triangular Trinuclear Cu_3/Ag_3 Cluster Units

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Heteroheptanuclear ReM_6 (M = Cu **2**, Ag **3**) complexes of 5,5-diethynyl-2,2′-bipyridine were prepared by the reaction of $[M_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ (dppm = bis(diphenylphosphino)methane) with the precursor compound $Re(Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3)(CO)_3Cl$ in the presence of potassium fluoride by fluoride-catalyzed desilylation. When $[Cu_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ reacts directly with $Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3$, a binuclear Cu^I complex $[Cu_2(\mu\text{-dppm})_2(SiMe_3C{\equiv}CbpyC{\equiv}CSiMe_3)_2]^{2+}$ (**4**) was isolated. Further addition of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ into a THF-MeOH (3:1, v/v) solution of **4** in the presence of potassium fluoride induced isolation of a tetradecanuclear Cu^I_{14} complex $[Cu_{14}(\mu\text{-dppm})_{14}(C{\equiv}CbpyC{\equiv}C)_2]^{10+}$, which is composed of a binuclear $Cu_2(\mu\text{-dppm})_2$ and four triangular trinuclear Cu_3 units. Both heteroheptanuclear $Re^IM^I_6$ and tetradecanuclear Cu^I_{14} complexes display luminescence in both solid states and dichloromethane solutions at room temperature with emissive lifetimes in the range of microseconds. The dual emissive feature for the ReM_6 and Cu^I_{14} complexes is ascribed tentatively to originate from both MLCT [d(Re/Cu) $\rightarrow \pi^*$ (bpy)] and LMCT (acetylide $\rightarrow M_3$) transitions.

Introduction

Recent interests in metal alkynyl complexes have been stimulated by their rich spectroscopic and luminescent properties and potential applications in molecular electronics.[1−7] In most cases, these compounds were prepared by direct reactions of alkynyls with simple metal ions or metal components,[1−9] and in some cases, they were derived from incorporation of a metal alkynyl unit with another metal component by self-assembly.[10−15]

To attain long-lived luminescent metal alkynyl materials with high quantum efficiency, one of the feasible approaches is to design multicomponent systems that incorporate two

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types of organometallic emitters.[2,16−22] It has been shown that diyne can serve as an excellent bridging ligand to fabricate heterometallic or multicomponent arrays by introducing two different luminophores in a stepwise manner.[23,24] Another possible route is to design bipyridyl- or terpyridyl-functionalized alkynyl ligands containing both alkynyl and bipyridyl/terpyridyl capable of associating with two types of organometallic chromophores or luminophores.[2,16−22,25]

It has been revealed that the triangular trinuclear M_3 cluster is one of the basic structural units in metal alkynyl complexes.[4,14b,26,27] Reaction of RC≡C with diphosphine-bridged binuclear complexes $[M_2(\mu\text{-}PPh_2XPPh_2)_2(MeCN)_2]^{2+}$ ($M = Cu^I$, Ag^I; $X = CH_2$, NH) usually helps to isolate trinuclear complexes $[M_3(\mu\text{-}PPh_2XPPh_2)_3(\mu_3\text{-}C{\equiv}C{-}R)_m]^{n+}$ ($m = 1$ or 2; $n = 2$ or 1) with triangular M_3 cluster structures capped with single or double bridging μ_3-C≡C−R.[28−32] It is demonstrated that these trinuclear alkynyl complexes usually emit intense photoluminescence in both solid states and solutions with LMCT emissive parentage, modified by M−M contacts.[4,32] Alternately, 2,2′-bipyridyl when bound to d^6, d^8, or d^{10} metal components is a well-known π-electron acceptor to afford emission originating from the MLCT excited state.[33,34] In view of the bifunctional character of bipyridiyl-functionalized alkynyl ligands,[25] it is anticipated that triangular trinuclear $M_3(\mu_3\text{-}C{\equiv}C)$ cluster and Re^I(bpy) or Cu^I(bpy) units are likely introduced via ethynyl and 2,2′-bipyridyl bonding, affording dual chromophores or emitters originating from LMCT and MLCT transitions, respectively. Aiming at designing heterometallic and multicomponent materials of 5,5′-diethynyl-2,2′-bipyridine with long-lived luminescence, our synthetic strategy is first to introduce Re^I or Cu^I organometallic chromophores via 2,2′-bipyridyl chelation and then to associate two triangular trinuclear M_3 cluster units with two ethynyl groups in a μ_3-bonding mode. We describe herein the preparation, characterization, and photophysical properties of a series of multinuclear complexes of 5,5′-diethynyl-2,2′-bipyridine capped with triangular trinuclear Cu_3/Ag_3 cluster units.

Experimental Procedures

Materials and Reagents. The operations were carried out under an argon atmosphere using vacuum-line and Schlenk techniques. The solvents were purified and distilled by standard procedures prior to use. The reagents rhenium(I) pentacarbonyl chloride ($Re(CO)_5Cl$), silver hexafluoroantimonate ($AgSbF_6$), and bis(diphenylphosphino)methane (dppm) were available commercially. The 5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine ($Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3$) was synthesized by the method described in the literature.[21,35] The precursor compounds $[M_2(dppm)_2(MeCN)_2]X_2$ ($M = Cu$, $X = ClO_4$; $M = Ag$, $X = SbF_6$) were prepared according to the literature procedures.[36,37] ***Caution:*** *Perchlorate salts are potentially explosive and should be handled carefully.*

Re($Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3$)($CO)_3$Cl (1). 5,5′-Bis(trimethylsilylethynyl)-2,2′-bipyridine (174.3 mg, 0.5 mmol) and rhenium pentacarbonyl chloride (180.8 mg, 0.5 mmol) were dissolved in toluene and heated at 60 °C for 5 h. The solvent was removed in vacuo to leave an orange residue that was dissolved to 5 mL of dichloromethane. The solution was layered with 30 mL of diethyl ether and placed in a fridge. The product was precipitated as orange needle crystals in a few hours. Yield: 96%. Anal. Calcd for $C_{23}H_{24}ClN_2O_3ReSi_2$: C, 42.22; H, 3.70; N, 4.28. Found: C, 42.56; H, 3.55; N, 4.35. ESI-MS (*m*/*z*): 654 $[M]^+$, 581 $[M\text{-}SiMe_3]^+$. IR (KBr, cm^{-1}): ν 2162 (w, C≡**C), 2023 (s, CO), 1933 (s, CO), 1913 (s, CO), 1251 (m, SiMe**$_3$). ^1H NMR ($CDCl_3$, ppm): δ 9.1 (s, 2H, *H*-6,6′), 8.0 (d, 2H, $J = 8.0$ Hz, *H*-4,4′), 7.3 (d, 2H, $J = 8.0$ Hz, *H*-3,3′), 0.32 (s, 18H, Si(CH_3)$_3$).

$[\{Cu_3(\mu\text{-}dppm)_3\}_2(C{\equiv}CbpyC{\equiv}C)\{Re(CO)_3Cl\}](ClO_4)_4$ (2). Potassium fluoride (23.2 mg, 0.40 mmol) and **1** (65.4 mg, 0.10 mmol) were added to 50 mL of dichloromethane−methanol (2:1, v:v) with stirring for 20 min. $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ (345.3 mg, 0.30 mmol) was then added to the solution that was stirred at

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room temperature for 2 days. The solvents were removed under reduced pressure, and the red residue was dissolved in 2 mL of dichloromethane that was chromatographed on a silica gel column. The product was collected as the second red band using dichloromethane−ethanol (10:1, v:v) as an eluent. Yield: 49%. Anal. Calcd for $C_{167}H_{138}Cl_5Cu_6N_2O_{19}P_{12}Re$: C, 55.82; H, 3.87; N, 0.78. Found: C, 56.01; H, 3.77; N, 0.91. ESI-MS (*m*/*z*): 799 $[M-(ClO_4)_4]^{4+}$. IR (KBr, cm^{-1}): ν 2018 (s, CO), 1913 (s, CO), 1893 (s, CO), 1095 cm^{-1} (s, ClO_4). ^1H NMR ($CDCl_3$, ppm): δ 9.1 (s, 2H, *H*-6,6′), 8.9 (d, 2H, $J = 8.0$ Hz, *H*-4,4′), 7.7 (d, 2H, $J = 8.0$ Hz, *H*-3,3′), 7.3−7.0 (m, 120H, C_6H_5), 3.2 (m, 12H, PCH_2P). ^{31}P NMR ($CDCl_3$, ppm): −7.4 (s).

$[\{Ag_3(\mu\text{-dppm})_3\}_2(C{\equiv}CbpyC{\equiv}C)\{Re(CO)_3Cl\}](SbF_6)_4$ (3). Potassium fluoride (11.6 mg, 0.20 mmol) and **1** (32.7 mg, 0.05 mmol) were added to 30 mL of dichloromethane−methanol (2:1, v/v) with stirring for 20 min. To the solution was added an acetonitrile (20 mL) solution of $[Ag_2(dppm)_2(MeCN)_2](SbF_6)_2$ (226.8 mg, 0.15 mmol), which was stirred at room temperature for 2 days. Diffusion of diethyl ether onto the concentrated orange−red solution in a few days afforded the product as orange−red crystals. Yield: 44%. Anal. Calcd for $C_{167}H_{138}Ag_6ClF_{24}N_2O_3P_{12}ReSb_4{\cdot}CH_2Cl_2{\cdot}2CH_3CN{\cdot}3H_2O$: C, 44.66; H, 3.31; N, 1.21. Found: C, 44.98; H, 3.47; N, 1.13. ESI-MS (*m*/*z*): 1232 $[\{Ag_3(\mu\text{-dppm})_3\}_2(C{\equiv}CbpyC{\equiv}C)Re(CO)_3Cl(SbF_6)]^{3+}$, 876 $[M-(SbF_6)_4+CH_3CN]^{4+}$. IR (KBr, cm^{-1}): ν 2020 (s, CO), 1914 (s, CO), 1894 (s, CO), 659 (s, SbF_6). ^1H NMR ($CDCl_3$, ppm): δ 8.9 (s, 2H, *H*-6,6′), 8.7 (d, 2H, $J = 8.0$ Hz, *H*-4,4′), 7.6 (d, 2H, $J = 8.0$ Hz, *H*-3,3′), 7.5−7.0 (m, 120H, C_6H_5), 3.6 (m, 12H, PCH_2P). ^{31}P NMR ($CDCl_3$, ppm): 5.2 (d, $J_{Ag\text{-}P} = 397$ Hz).

$[Cu_2(\mu\text{-dppm})_2(SiMe_3C{\equiv}CbpyC{\equiv}CSiMe_3)_2](ClO_4)_2$ (4). 5,5′-Bis(trimethylsilylethynyl)-2,2′-bipyridine (74.3 mg, 0.22 mmol) was added to a dichloromethane solution (20 mL) of $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ (115.0 mg, 0.10 mmol) with stirring at room temperature for 1 day to afford a clear orange solution. Diffusion of diethyl ether into the concentrated dichloromethane solution gave the product as orange crystals. Yield: 86%. Anal. Calcd for $C_{90}H_{92}Cl_2Cu_2N_4O_8P_4Si_4$: C, 60.32; H, 5.17; N, 3.13. Found: C, 59.92; H, 5.21; N, 3.14. ESI-MS (*m*/*z*): 796 $[M-(ClO_4)_2]^{2+}$. IR (KBr, cm^{-1}): ν 2163 (w, C≡**C**), 1250 (m, $SiMe_3$), 1095 (s, ClO_4). ^1H NMR ($CDCl_3$, ppm): δ 8.5 (s, 4H, *H*-6,6′), 8.2 (d, 4H, $J = 8.0$ Hz, *H*-4,4′), 7.8 (d, 4H, $J = 8.0$ Hz, *H*-3,3′), 7.4−7.0 (m, 40H, C_6H_5), 3.3 (s, 4H, PCH_2P), 0.39 (s, 36H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$, ppm): −9.6 (s).

$[Cu_{14}(\mu\text{-dppm})_{14}(C{\equiv}CbpyC{\equiv}C)_2](ClO_4)_{10}$ (5). Potassium fluoride (11.6 mg, 0.20 mmol) and **4** (44.8 mg, 0.025 mmol) were dissolved in 30 mL of THF-MeOH (3:1, v/v) with stirring for 20 min. To the solution was added $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ (172.5 mg, 0.15 mmol), which was stirred at room temperature for 3 days. The red solution was evaporated in vacuo, and the residue was dissolved in 3 mL of dichloromethane. Layering *n*-hexane onto the solution gave the product as red microcrystals. Yield: 46%. Anal. Calcd for $C_{378}H_{320}Cl_{10}Cu_{14}N_4O_{40}P_{28}$: C, 59.19; H, 4.21; N, 0.73. Found: C, 59.33; H, 4.11; N, 0.76. ESI-MS (*m*/*z*): 667.5 $[M-(ClO_4)_{10}]^{10+}$. IR (KBr, cm^{-1}): ν 1995 (w, C≡**C), 1095 (s, ClO**$_4$). ^1H NMR ($CDCl_3$, ppm): δ 7.7 (s, 4H, *H*-6,6′), 7.5 (m, 4H, *H*-4,4′), 7.4 (m, 4H, *H*-3,3′), 7.3−6.9 (m, 280H, C_6H_5), 3.6 (s, 4H, PCH_2P), 3.2 (s, 24H, PCH_2P). ^{31}P NMR ($CDCl_3$, ppm): −8.4 (s), −14.9 (s).

Crystal Structural Determination. Crystals coated with epoxy resin or sealed in capillaries with mother liquors were measured on a RIGAKU MERCURY CCD diffractometer. Reflection data were collected at 130 K by a ω scan technique using graphite-monochromated Mo− Kα ($\lambda = 0.71073$ Å) radiation. An absorption correction by multiscan was applied to the intensity data. The structures were solved by direct methods, and the heavy atoms were located from the E-map. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically with isotropic thermal parameters. The structures were refined on F^2 by full-matrix least-squares methods using the *SHELXTL-97* program package.[38] Crystallographic data for **1**, **3**, and **4** are summarized in Table 1.

Table 1. Crystallographic Data for Complexes $1{\cdot}1/2CH_2Cl_2$, $\mathbf{3}{\cdot}CH_2Cl_2{\cdot}2CH_3CN{\cdot}3H_2O$, and **4**

	$\mathbf{1}{\cdot}1/2CH_2Cl_2$	$\mathbf{3}{\cdot}CH_2Cl_2{\cdot}2CH_3CN{\cdot}3H_2O$	**4**
empirical formula	$C_{23.5}H_{25}Cl_2N_2O_3ReSi_2$	$C_{172}H_{152}Ag_6Cl_3F_{24}N_4O_6P_{12}ReSb_4$	$C_{90}H_{92}Cl_2Cu_2N_4O_8P_4Si_4$
fw	696.74	4625.39	1791.9
space group	*Pca*2(1)	$P\bar{1}$	$P\bar{1}$
a (Å)	17.319(1)	14.74(2)	12.907(3)
b (Å)	15.226(1)	16.47(3)	17.048(4)
c (Å)	21.5290(12)	19.92(4)	22.999(6)
α (deg)		86.46(11)	69.329(7)
β (deg)		83.96(10)	82.117(9)
γ (deg)		82.76(7)	78.799(9)
V (Å^3)	5677.1(3)	4767(15)	4632(2)
Z	8	1	2
ρ_{calcd} (g/cm^3)	1.630	1.611	1.285
μ (mm^{-1})	4.580	2.007	0.692
radiation (λ, Å)	0.71073	0.71073	0.71073
T (K)	130	130	130
R1[a] (F_o)	0.0299	0.0603	0.0496
wR2[b] (F_o^2)	0.0761	0.1651	0.1210
GOF	1.048	1.042	1.064

[a] $R1 = \Sigma|F_o - F_c|/\Sigma F_o$. [b] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^{1/2}$.

For **3**, the $Re(CO)_3Cl$ chromophore and one (labeled Sb3) of four hexafluoroantimonates (SbF_6^-) are disordered and located alternately at each side of the dipyridyl with the statistical occupancy factors of 0.50 for $Re(CO)_3Cl$ and SbF_6^- (labeled Sb3), respectively. When $Re(CO)_3Cl$ is located at one side of the dipyridyl, then hexafluoroantimonate (labeled Sb3) is oriented at the other side of the dipyridyl and vice versa. Furthermore, one of three carbonyls (CO) and chloride (Cl) in $Re(CO)_3Cl$ chromophores exhibits a statistical distribution with the occupancy factors of 0.23 for C3, O3, and Cl′ and 0.27 for C3′, O3′, and Cl, respectively. For the dipyridyl, a statistical distribution occurs between N1 and C15 and between N2 and C17. The locations or coordinates of N1 (N2) are the same as those of C15 (C17) with occupancy factors of 0.50, respectively.

For **4**, there exists two types of different oriented molecules in the crystal packing. One of the trimethylsilyl groups ($\text{-}Si(CH_3)_3$) is disordered with occupancy factors of 0.50 for Si4, Si4′, C37−C39, and C37′−C39′, respectively. Additionally, one of the perchlorates is located by a statistical distribution with the occupancy factors of 0.50 for O6−O8 and O6′−O8′, respectively.

Physical Measurements. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer model 240C automatic instrument. Electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane−methanol or acetonitrile−methanol as a mobile phase. UV−vis absorption spectra were measured on a Perkin-Elmer Lambda 25 UV−vis spectrometer. Infrared spectra were recorded on a Magna750 FT-IR spectrophotometer with a KBr pellet. ^1H and ^{31}P NMR spectra were measured on a Varian UNITY-500 spectrometer with $SiMe_4$

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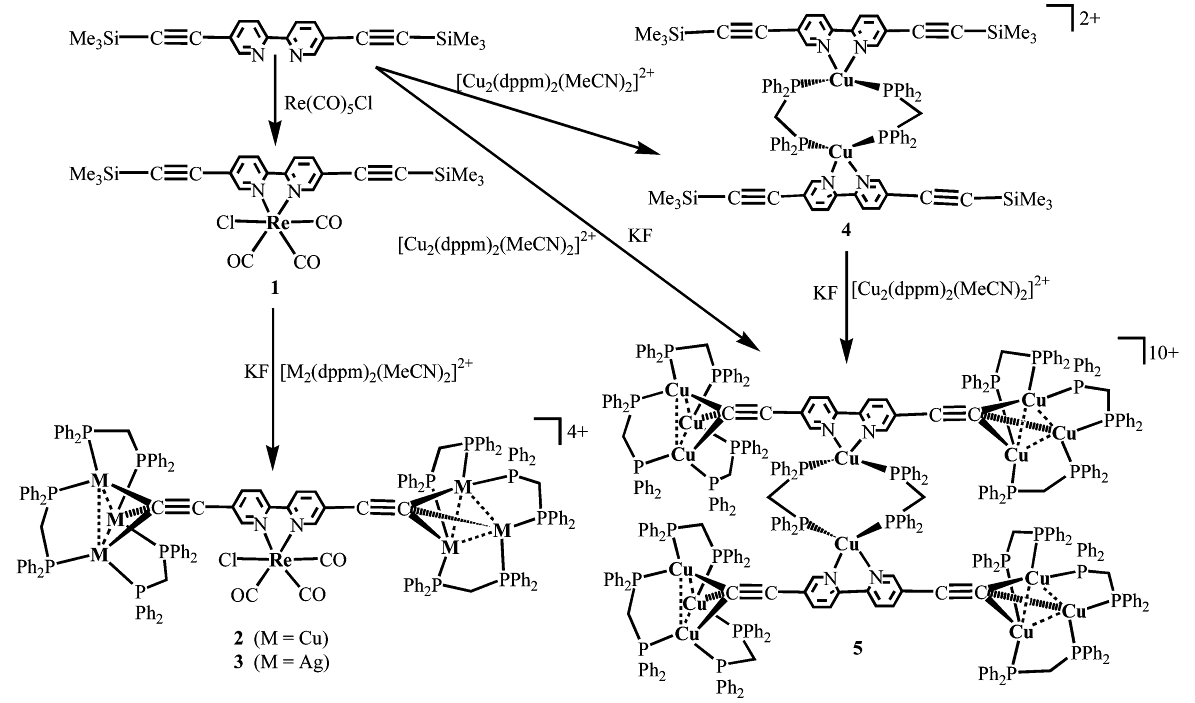
[38] Sheldrick, G. M. *SHELXL-97*, *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 1. Synthetic Routes to Compounds **1**−**5**



as the internal reference and 85% H_3PO_4 as external standard, respectively. Emission and excitation spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a red-sensitive photomultiplier type R928. Emission lifetimes in the solid states or degassed solutions were determined on an Edinburgh Analytical Instrument (F900 fluorescence spectrometer) using a LED laser at 397 nm excitation, and the resulting emission was detected by a thermoelectrically cooled Hamamatsu R3809 photomultiplier tube. The instrument response function at the excitation wavelength was deconvolved from the luminescence decay.

Results and Discussion

As indicated in Scheme 1, the reaction of $\mathrm{Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3}$ with $\mathrm{Re(CO)_5Cl}$ in toluene at 60 °C gave $\mathrm{Re(Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3)(CO)_3Cl}$ (**1**). When **1** reacted with $[\mathrm{M_2}(\mu\text{-dppm})_2(\mathrm{MeCN})_2]^{2+}$ in the presence of KF, heteroheptanuclear $\mathrm{ReM_6}$ complexes **2** (M = Cu) and **3** (M = Ag) were afforded. When $\mathrm{Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3}$ reacted with $[\mathrm{Cu_2}(\mu\text{-dppm})_2(\mathrm{MeCN})_2]^{2+}$ in the absence of KF, binuclear complex **4** was isolated in 86% yield. Further addition of $[\mathrm{Cu_2}(\mu\text{-dppm})_2(\mathrm{MeCN})_2]^{2+}$ to **4** in the presence of KF induced isolation of tetradecanuclear $\mathrm{Cu^I{}_{14}}$ complex **5** by fluoride-catalyzed desilylation of $\mathrm{Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3}$. Complex **5** is also accessible by reaction of 7 equiv of $[\mathrm{Cu_2}(\mu\text{-dppm})_2(\mathrm{MeCN})_2]^{2+}$ with 2 equiv of $\mathrm{Me_3SiC{\equiv}CbpyC{\equiv}CSiMe_3}$ in the presence of KF via a one step reaction.

Compounds **1**−**5** were characterized by microanalyses, ESI-MS spectrometry, and ^{1}H and ^{31}P NMR spectroscopy, and **1**, **3**, and **4** were characterized by X-ray crystallography. The ESI-MS revealed that the molecular ion fragments $[\mathbf{1}]^+$, $[\mathbf{2} - (\mathrm{ClO_4})_4]^{4+}$, $[\mathbf{3} - (\mathrm{SbF_6})_4]^{4+}$, and $[\mathbf{4} - (\mathrm{ClO_4})_2]^{2+}$ occur as the base peaks or the principal peaks with high abundance ratios. For **5**, the complex cation fragment $[\mathbf{5} - (\mathrm{ClO_4})_{10}]^{10+}$ (*m/z*: 667.5) with perfect isotropic distribution was observed in the ESI-MS (Figure S1, Supporting Information). The ^{31}P NMR spectra show one signal at −7.4 (s), 5.2 (d, $J_{\mathrm{Ag-P}}$ = 397 Hz), and −9.6 (s) for **2**, **3**, and **4**, respectively, indicating the equivalence of the P atoms in these compounds. In the ^{31}P NMR spectrum of **5** (Figure S2, Supporting Information), however, two singlets occur at −8.4 and −14.9 ppm, respectively, coinciding well with the presence of two sets of inequivalent P atoms in the $\mathrm{Cu_{14}}$ complex cation.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**

Ag1−Ag2	3.038(5)	Ag1−Ag3	3.053(4)
Ag2−Ag3	3.115(5)	Ag1−C11	2.277(7)
Ag1−P1	2.469(4)	Ag1−P5	2.425(4)
Ag2−C11	2.277(7)	Ag2−P2	2.476(4)
Ag2−P3	2.432(4)	Ag3−C11	2.279(6)
Ag3−P4	2.442(4)	Ag3−P6	2.444(4)
Re−N1A	2.050(8)	Re−N2	2.078(8)
Re−C1	1.954(14)	Re−C2	1.909(18)
Re−C3	1.926(9)	Re−Cl	2.462(9)
C11−C12	1.215(7)	C12−C13	1.423(7)
Ag2−Ag1−Ag3	61.52(10)	Ag1−Ag2−Ag3	59.48(9)
Ag1−Ag3−Ag2	59.01(10)	C11−Ag1−P5	128.62(16)
C11−Ag1−P1	102.74(14)	P5−Ag1−P1	120.40(10)
C11−Ag2−P3	126.79(16)	C11−Ag2−P2	102.81(16)
P3−Ag2−P2	123.08(11)	C11−Ag3−P4	113.77(17)
C11−Ag3−P6	116.12(17)	P4−Ag3−P6	126.02(11)
C2−Re−C3	88(2)	C2−Re−C1	86.0(6)
C3−Re−C1	84.9(19)	C2−Re−N1A	95.2(6)
C3−Re−N1A	95.1(19)	C1−Re−N1A	178.8(5)
C2−Re−N2	178.6(5)	C3−Re−N2	90.5(19)
C1−Re−N2	94.3(5)	N1A−Re−N2	84.5(4)
C2−Re−Cl	93.3(6)	C3−Re−Cl	178.7(19)
C1−Re−Cl	95.3(5)	N1A−Re−Cl	84.7(3)
N2−Re−Cl	88.1(3)	Ag1−C11−Ag2	83.61(19)
Ag1−C11−Ag3	84.05(18)	Ag2−C11−Ag3	86.3(2)

ORTEP drawings of **1** and the complex cations of **3** and **4** with atom-labeling schemes are depicted in Figures 1, 2, and 3, respectively. For **1**, the $\mathrm{Re^I}$ center is six-coordinated with $\mathrm{C_3ClN_2}$ donors to afford a distorted octahedral geometry with three CO groups being *fac*-oriented. The relevant

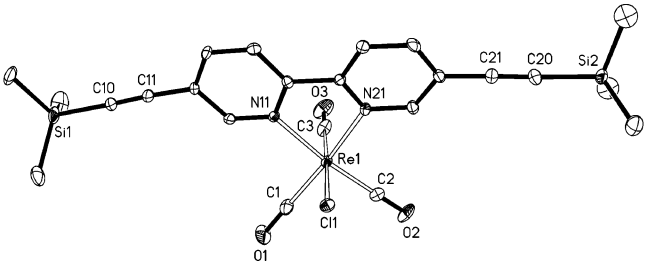


Figure 1. ORTEP drawing of of **1** with atom labeling scheme showing 30% thermal ellipsoids.

bonding lengths and angles around the Re^I center are in the normal ranges as observed in similar Re(N−N)$(CO)_3$Cl (N−N = diimine) complexes.[14b,39] The C(10)−C(11) [1.197(8) Å] and C(20)−C(21) [1.198(8) Å] bonds are typical of C≡C triple bonding.

The heteroheptanuclear $ReAg_6$ assembly of **3** consists of two triangular trinuclear Ag_3 cluster units and one $Re(CO)_3Cl$ fragment bound to the diacetylides and 2,2′-bipyridyl in the bridging ligand, respectively. The Ag_3 cluster is symmetrically capped by an acetylide in a μ_3-η^1-bonding mode, contrasting to the asymmetric μ_3-bridging fashion found in most of the alkynyl complexes with triangular trinuclear $M^I{}_3$ (M = Cu, Ag) cluster units.[26−32] The intracluster Ag−Ag distances [3.038(5)−3.115(5) Å] are shorter than the sum of the van der Waals radii (3.4 Å) and lie within the ranges found in other complexes with trinuclear $Ag^I{}_3$ cluster units.[4] The Ag−C and Ag−P distances are comparable to those found in other tri- and hexanuclear alkynyl complexes with triangular trinuclear $Ag^I{}_3$ cluster units described by Gimeno and Yam et al.[27,28,32] The bonding parameters in the fragment *fac*-Re(bpy)$(CO)_3$Cl are similar to those observed in the precursor complex **1**. The Re^I center is located in a distorted octahedral environment with C_3ClN_2 donors, and the Ag^I center exhibits an approximately trigonal-planar geometry composed of CP_2 donors. The C≡C length (1.217(7) Å) is slightly elongated as compared with that in the parent complex **1** (1.197 (8) Å) due to formation of the Ag−C bonds that weaken the C≡C bonding to some extent. The intramolecular Re−Ag separations are ca. 7.7−8.7 Å. The intercluster Ag···Ag separations across the bridging 2,2′-bipyridyl-diacetylide are ca. 15.0−15.5 Å.

Compound **4** exhibits a binuclear structure with each Cu^I center chelated by 2,2′-bipyridyl and bridged doubly by dppm to form an eight-membered ring composed of two Cu^I and two dppm. The Cu^I center is located in a distorted tetrahedral geometry built by N_2P_2 donors. The Cu···Cu separation through doubly bridging dppm is 4.75 Å, which is much longer than that (3.76 Å) found in the precursor complex $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$[36] but close to those in the similar complexes $[Cu_2(\mu\text{-dppm})_2(N-N)_2]^{2+}$ (N−N = diimine).[40,41]

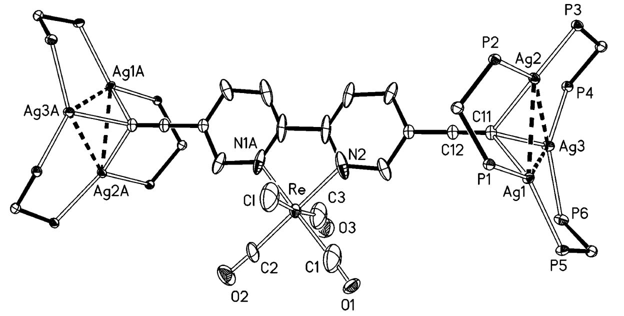


Figure 2. ORTEP drawing of the complex cation of **3** with atom labeling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms are omitted for clarity.

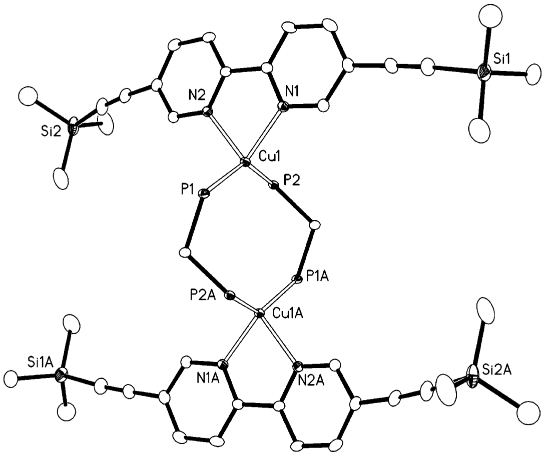


Figure 3. ORTEP drawing of the complex cation of **4** with atom labeling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms are omitted for clarity.

The photophysical data of **1**−**5** are presented in Table 3. The UV−vis absorption spectra of **1**−**3** in dichloromethane are characterized by intense high-energy absorption bands at 220−300 nm, medium energy bands at ca. 350−400 nm, and broad low-energy bands at 410−550 nm, which are typical of ligand-centered π−π* (diphosphine), metal-perturbed π−π* (C≡C), and [d(Re) → π*(bpy)] MLCT transitions,[14b] respectively. It is noteworthy that the absorption bands due to metal-perturbed $\pi \rightarrow \pi^*$ (C≡C) and [d(Re) → π*(bpy)] MLCT transitions in **2** and **3** are distinctly red-shifted to a lower energy as compared with those in the precursor complex **1** (Figure 4). This phenomenon arises probably from the more extended π-conjugation induced by μ_3-η^1-acetylide coordination upon the formation of the ReM_6 heteroheptanuclear cluster assembly, which would lower the π* orbital (LUMO) energy of 2,2′-bipyridyl-5,5′-diacetylides and thus reduce the energy gap between HOMO and LUMO.

The electronic absorption spectrum of **4** is dominated by high-energy bands below 280 nm and broad absorption bands in the vicinity of 350−400 nm. The former is due to dppm-centered transitions, whereas the latter originates probably from $\pi \rightarrow \pi^*$ (C≡C) and [d(Cu) → π*(bpy)] MLCT transitions.[42] Upon formation of the Cu_{14} complex **5**, the broad absorption bands due to $\pi \rightarrow \pi^*$ (C≡C) and [d(Cu) → π*(bpy)] MLCT transitions shift significantly to 450 nm

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[39] (a) Polo, A. S.; Itokazu, M. K.; Frin, K, M.; Patrocinio, A. O. D.; Iha, N. Y. M. *Coord. Chem. Rev.* **2006**, *250*, 1669. (b) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (c) Fredericks, S. M.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415. (d) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888. (e) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104.

[40] Kitagawa, S.; Maruyama, H.; Wada, S.; Munakata, M.; Nakamura, M.; Masuda, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2809.

[41] Jin, D.-M.; Yang, R.-N.; Wang, D.-M.; Hu, X.-Y. *Chin. J. Inorg. Chem.* **2000**, *16*, 335.

Table 3. Photophysical Data for Compounds **1**−**5**

compound	medium	λ_{abs} (nm) (ϵ/dm^3 mol^{-}1 cm^{-}1)	λ_{em} (nm) (τ_{em}/μs)^a (298 K)	λ_{em} (nm) (77 K)
1	Solid		598 (0.10)	598
	CH_2Cl_2	295 (30650), 343 (45680), 363 (56310), 410 (4090)	387, 659 (<0.1)	575
2	Solid		716 (0.60)	695, 605
	CH_2Cl_2	260 (49270), 350 (16960), 460 (11650)	710 (0.45, 38.7)	709
3	Solid		620 (0.6, 5.8), 635	590, 636
	CH_2Cl_2	260 (112160), 350 (24550), 396 (25650), 424 (20970)	570 (0.7, 2.6) 609 (0.7, 2.6)	590, 639
4	Solid		570 (4.0)	530, 572
	CH_2Cl_2	274 (44320), 339 (43360), 354 (35140)	386, 640 (0.1)	535, 633
5	Solid		624 (0.9, 35.6)	606, 656
	CH_2Cl_2	266 (182020), 349 (26980) 449 (16160)	616 (8.0)	591, 550sh, 634sh

[a] The excitation wavelength in the lifetime measurement is 397 nm. The lifetimes were measured in solid states or degassed fluid solutions.

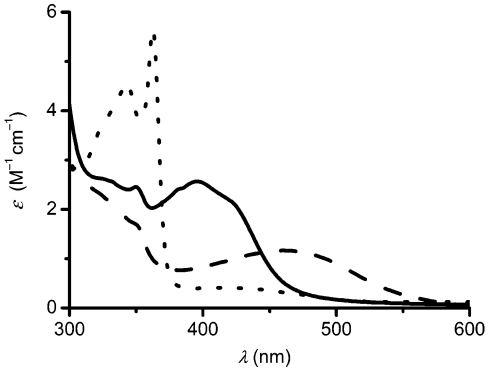

Figure 4. UV−vis absorption spectra of **1** (dot), **2** (dash), and **3** (solid) in dichloromethane at room temperature.

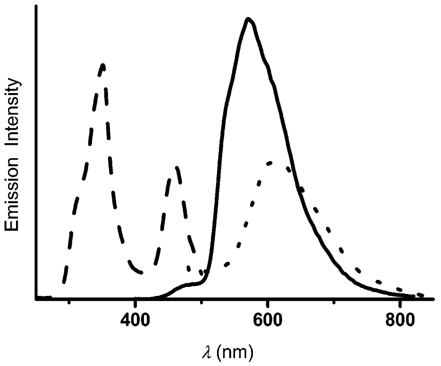

Figure 5. Excitation (dash) and emission (solid: 300 ≤ λ_{ex} ≤ 400 nm and dot: λ_{ex} > 410 nm) spectra of **3** in fluid dichloromethane solution.

because of the more extended π-conjugation induced by μ_3-η^1-acetylide coordination.

With excitations at λ_{ex} ≥ 350 nm, compounds **1**−**5** luminesce in both solid states and degassed chloromethane at both 298 and 77 K. The lifetimes in solid states and in degassed dichloromethane at room temperature are in the microsecond ranges (Table 3), revealing that the emission is most likely associated with a spin-forbidden triplet parentage. Vibronic-structured emission bands with vibrational progressional spacings of ca. 1200−1600 and 1900−2150 cm^{-1} are observed at 77 K in some cases, which are typical of aromatic ν(CH=CH) and ν(C≡C) stretching modes of 5,5′-diethynyl-2,2′-bipyridine in the ground states. The appearance of vibronic progressions suggests the involvement of the transitions from 5,5′-diethynyl-2,2′-bipyridine in the excited states.

The mononuclear Re^I complex **1** displays emission at ca. 598 nm in solid states at both 298 and 77 K. The emission in dichloromethane at room temperature, however, is red-shifted 2217 cm^{-1} as compared to that at 77 K (Table 3). This phenomenon is typical for the phosphorescence from the [d(Re) → π*(bpy)] ^{3}MLCT excited state, which has been reported in many rhenium(I) diimine tricarbonyl complexes in the literature.[39] In fluid dichloromethane solution, intense 5,5′-diethynyl-2,2′-bipyridine ligand-centered luminescence is also observed at 387 nm besides the emission at 659 nm from MLCT transition. Upon formation of the M_6Re complexes, ligand-centered emission with high energy is completely quenched probably due to an efficient energy transfer occurring from the ligand to the triangular trinuclear M_3 cluster centers.

In excitation of the Cu_6Re complex **2** with λ_{ex} ≥ 350 nm, a broad emission band occurs with the maximum at ca. 716 nm in the solid state and ca. 710 nm (Figure S6) in dichloromethane at 298 K. The decay curves measured in dichloromethane, however, are best fitted by biexponential functions with shorter (0.45 μs) and a longer lifetime (38.7 μs) components, suggesting that two different lowest excited states are likely operative and that their energy is likely very close. Alternately, the Ag_6Re complex **3** distinctly shows a dual emission. As depicted in Figure 5, the excitation spectrum of **3** in the fluid chloromethane solution exhibits two maximum bands at 351 and 458 nm, respectively. Although an emissive maximum occurs at 570 nm with excitation at 300 ≤ λ_{ex} ≤ 400 nm, irradiation of the solution of **3** with λ_{ex} > 410 nm affords a lower energy emission with the maximum at 609 nm. As the excitation spectrum is close to the low-energy absorption features, the bands at 351 and 458 nm probably arise from metal-perturbed $\pi \rightarrow \pi^*$ (C≡C) and [d(Re) → π*(bpy)] MLCT transitions, respectively. Therefore, the emissive origin at 570 nm induced by excitation with 300 ≤ λ_{ex} ≤ 400 nm is likely involved in the acetylides, whereas the emission at 609 nm (with λ_{ex} > 410 nm) is probably induced by the [d(Re) → π*(bpy)] MLCT transition.[14b,39] It is noteworthy that both the absorption and the emission bands of **2** occur at a lower energy than those of **3**. A red-shift for the emission of **2**

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(42) (a) Cuttell, D. G.; Kuang, S.-M.; Fanwick, P. E.; McMillin, D. R.; Walton, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 6. (b) Kuag, S.-M.; Cuttell, D. G.; McMillin, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **2002**, *41*, 3313.

(λ_{em} = 710 nm) relative to that of **3** (λ_{em} = 570 nm) is 0.43 eV in the fluid dichloromethane solution, comparable to the values in emission energy differences on going from Ag^I to Cu^I acetylide or chalcogenido cluster complexes, in which an admixture of d → s and LMCT emissive origin has been suggested by Yam et al.[14,27,32] Another possible assignment involving the excited state derived from the MLCT [d(M) → π* (acetylide)] transition should induce a red-shift in energy with ΔE > 1.0 eV from Ag^I to Cu^I counterparts because the ionization energy for Ag^+(g) is 10^4 cm^{-1} larger than that for Cu^+(g).[27] Consequently, with reference to previous spectroscopic and photophyical studies on the mononuclear rhenium tricarbonyl complexes[39] and trinuclear coinage metal alkynyl complexes,[14,27,32] the dual emission of **2** or **3** is tentatively assigned to originate from both [d(Re) → π*(bpy)] MLCT transition and LMCT (acetylide → M_3) excited states modified by metal−metal interactions in view of the short metal−metal contacts in the triangular trinuclear M_3 clusters.

Compound **4** shows photoluminescence in both solid states and dichloromethane at 298 and 77 K. With reference to the literature work on related complexes,[42] its emissive state is ascribed tentatively to the MLCT [d(Cu) → π*(bpy)] transition. As found in mononuclear Re^I complex **1**, intense ligand-centered luminescence is also observed at 386 nm in a fluid dichloromethane solution besides the emission at 640 nm induced by MLCT transition. Upon formation of Cu^I_{14} complex **5**, ligand-centered emission is completely quenched, whereas the emission originating from the MLCT transition is broadened and enhanced significantly in intensity (ca. four times in dichloromethane) relative to the precursor compound **4** at 298 K. A biexponential fitting in the calculation of lifetime implies (Table 3) that the emissive state is probably derived from the admixture of the MLCT [d(Cu) → π*(bpy)] and LMCT (acetylide → Cu_3) transitions.

Summary

Designed syntheses of heteroheptanuclear $Re^IM^I_6$ (M = Cu, Ag) and tetradecanuclear Cu^I_{14} complexes of 5,5′-diethynyl-2,2′-bipyridine capped with triangular trinuclear M_3 cluster units were achieved by reaction of $[M_2(dppm)_2(MeCN)_2]^{2+}$ with diacetylides in the bridging ligand. These heteronuclear or multicomponent complexes exhibit photoluminescence with the emissive lifetimes in the microsecond time scale in both solid states and dichloromethane at room temperature. They exhibit dual emission ascribed to two different excited states originating from two types of organometallic chromophores. This synthetic route opens a feasible approach for the design of heteronuclear and/or multicomponent materials with long-lived luminescence by introducing different types of emissive organometallic chromophores using bipyridyl- or terpyridyl-functionalized alkynyl ligands. Further studies are underway in this laboratory.

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Supporting Information Available: ESI-MS (Figure S1) and ^{31}P NMR spectrum (Figure S2) of **5**, ORTEP drawing (Figure S3) of the complex cation of **3** showing the statistical distribution, UV−vis absorption spectra (Figure S4) of **4** and **5** in dichloromethane, emission spectra (Figure S5) of **2** and **3** in solid states at 298 K, excitation and emission spectra of **2** (Figure S6) in fluid dichloromethane solutions, and X-ray crystallographic files in CIF format for the structure determination of compounds **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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