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Synthesis and luminescence behaviour of mixed-metal rhenium(I)–copper(I) and –silver(I) alkynyl complexes

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Contents

Abstract

A series of luminescent mixed-metal acetylide complexes, $[\mathrm{Cu_3}(\mu\text{-LL})_3\{\mu_3\text{–}\eta^1\text{-C}{\equiv}\mathrm{CC_6H_2R_2C}{\equiv}\text{C–}p\text{-Re(NN)(CO)}_3\}_2]^+$ (LL = dppm, ^{n}PrPNP; NN = bpy, $^t\mathrm{Bu_2bpy}$; R = H, Me) and $[\mathrm{M_3}(\mu\text{-LL})_3\{\mu_3\text{–}\eta^1\text{-C}{\equiv}\text{CC}{\equiv}\text{C–Re(NN)(CO)}_3\}_2]^+$ (M = Cu, Ag; LL = dppm, dppa; NN = bpy, $\mathrm{Me_2bpy}$, $^t\mathrm{Bu_2bpy}$) have been synthesized and characterized. All of them display rich photoluminescence and their low-energy emission are assigned as derived from states of ^{3}MLCT [$d\pi(\mathrm{Re})\rightarrow\pi^*(\mathrm{NN})$] character. The X-ray crystal structures of $[\mathrm{Cu_3}(\mu\text{-dppm})_3\{\mu_3\text{–}\eta^1\text{-C}{\equiv}\text{CC}{\equiv}\text{C–Re}(\mathrm{Me_2bpy})\text{(CO)}_3\}_2]\mathrm{PF_6}$ and $[\mathrm{Ag_3}(\mu\text{-dppm})_3\{\mu_3\text{–}\eta^1\text{-C}{\equiv}\text{CC}{\equiv}\text{C–Re(bpy)(CO)}_3\}_2]\mathrm{PF_6}$ have been determined.

Keywords: Mixed-metal; Metal alkynyl; Building block; MLCT and luminescence behaviour

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1. Introduction

Carbon-rich polymers containing extended π-systems and their transition metal complexes have attracted considerable attention due to their potential technological applications as precursors for non-linear optical materials and rigid-rod molecular wires [1,2]. Recent work by a number of groups have shown that extended conjugated alkynyls, such as 1,4-diethynylbenzene and butadiyne, could serve as ideal building blocks for the synthesis of homometallic and mixed-metal complexes [3]. With our recent interest in both polynuclear Cu(I) and Ag(I) alkynyl and rhenium(I) alkynyl complexes [1b,4], we believe that with appropriate design and the judicious choice of ligands, the design and synthesis of interesting luminescent mixed-metal molecular rods of rhenium–copper and –silver could be achieved. Although examples of mixed-metal rhenium(I)–copper(I) alkynyl complexes are known [5,6], most of them involve the use of the alkynyl ligand as an η^2-ligand to π-bond to the Cu^I centre such as in $[ReCu(C\equiv CC_6F_5)_2(CO)_3(PPh_3)_2]$ [5a] and $[\{\eta^2\text{-}Re(CO)_3(bpy)(C\equiv CPh)\}_2Cu]PF_6$ [6]. Herein, we report the synthesis of a series of mixed-metal Re(I)–Cu(I) and –Ag(I) alkynyl complexes, $[M_3(\mu\text{-}LL)_3\{\mu_3\text{–}\eta^1\text{-}C\equiv C\text{–}C_6H_2R_2\text{–}C\equiv C\text{–}p\text{-}Re(NN)(CO)_3\}_2]^+$ and $[M_3(\mu\text{-}LL)_3\{\mu_3\text{–}\eta^1\text{-}C\equiv CC\equiv C\text{–}Re(NN)(CO)_3\}_2]^+$, by employing the ‘metal complex as ligand’ or the so-called metalloligand approach. Through a systematic variation of the nature of the trinuclear metal core and the diimine ligands on the Re^I centre, the emission properties of this class of compounds could be readily tuned.

2. Experimental

2.1. Materials and reagents

The ligands bis(diphenylphosphino)methane (dppm) and *N*,*N*-bis(diphenylphosphino)amine (dppa) were purchased from Lancaster Synthesis Ltd. 1,4-Bis(trimethylsilyl)-1,3-butadiyne was purchased from GFS Chemicals. $Re(CO)_5Cl$, 4,4′-dimethyl-2,2′-bipyridine and 2,2′-bipyridine were obtained from Aldrich Chemical Co. Bis(diphenylphosphino)-*n*-propylamine (^{n}PrPNP) [7], 1,4-diethynylbenzene [8], 1,4-diethynyl-2,5-dimethylbenzene [9], $[Re(^tBu_2bpy)(CO)_3\text{–}(C\equiv CC_6H_4C\equiv CH\text{-}p)]$ ($^tBu_2bpy$=4,4′-di-*tert*-butyl-2,2′-bipyridine) [10], $[Re(bpy)(CO)_3(C\equiv CC_6H_4C\equiv CH\text{-}p)]$ (bpy=2,2′-bipyridine) [10], $[Re(bpy)(CO)_3(C\equiv CC_6H_2\text{-}2,5\text{-}C\equiv CH\text{-}p)]$ [10], $[Re(^tBu_2bpy)(CO)_3(C\equiv CC\equiv CH)]$ [11], $[Re(Me_2bpy)(CO)_3(C\equiv CC\equiv CH)]$ (Me_2bpy = 4,4′-2,2′-bipyridine) [11,12], $[Re(bpy)(CO)_3(C\equiv CC\equiv CH)]$ [11,12], $[Cu_2(\mu\text{-}LL)_2(MeCN)_2](X)_2$ [13] (LL = dppm, dppa, ^{n}PrPNP; X = BF_4^-, PF_6^-) and $[Ag_2(\mu\text{-}dppm)_2(MeCN)_2](PF_6)_2$ [14] were prepared according to literature procedures. All solvents were purified and distilled using standard procedures before use [15]. All other reagents were of analytical grade and were used as received.

2.2. Syntheses of Re(I)–Cu(I)/Ag(I) complexes

All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.

2.2.1. $[Cu_3(\mu\text{-}dppm)_3\{\mu_3\text{–}\eta^1\text{-}C\equiv CC_6H_4C\equiv C\text{–}p\text{-}Re(bpy)(CO)_3\}_2]PF_6$ (**1**)

Complex **1** was prepared by the reaction of $[Cu_2(\mu\text{-}dppm)_2(MeCN)_2](PF_6)_2$ (0.11g, 0.09 mmol) with $[Re(bpy)(CO)_3(C\equiv CC_6H_4C\equiv CH\text{-}p)]$ (0.066 g, 0.12 mmol) in the presence of excess KOH in CH_2Cl_2/MeOH (15 ml/5 ml). The mixture was stirred at room temperature for 24 h. After evaporation to dryness, the resulting solid residue was extracted with CH_2Cl_2 (20 ml) and the solution was filtered and concentrated. Diffusion of diethyl ether vapour into a concentrated solution of the complex gave **1** as orange crystals. Yield: 0.06 g (38%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 262sh (102 640), 300sh (78 350), 354sh (69 340), 372 (77 380), 428sh (5110). IR (Nujol mull, KBr), ν/cm^{-1}: 2089w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 3.2 (m, 6H, –CH_2–), 6.7–7.3 (m, 68H, –Ph), 7.9 (t, 4H, bipyridyl H’s, $J_{H–H}$, 6.6 Hz), 8.4 (t, 4H, bipyridyl H’s, $J_{H–H}$, 7.8 Hz), 8.8 (d, 4H, bipyridyl H’s, $J_{H–H}$, 8.2 Hz), 9.3 (d, 4H, bipyridyl H’s, $J_{H–H}$, 5.0 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ −4.8 (s). Positive FAB-MS: *m/z* 2443 $[M-PF_6]^+$. Anal. Calc. for $C_{121}H_{92}Cu_3F_6N_4P_7O_6Re_2$: C, 56.12; H, 3.48; N, 2.16. Found: C, 56.14; H, 3.34; N, 2.02%.

2.2.2. $[Cu_3(\mu\text{-}dppm)_3\{\mu_3\text{–}\eta^1\text{-}C\equiv CC_6H_2\text{-}2,5\text{-}Me_2\text{-}C\equiv C\text{-}p\text{-}Re(bpy)(CO)_3\}_2]PF_6$ (**2**)

Complex **2** was prepared by a method similar to that of **1** except $[Re(bpy)(CO)_3(C\equiv C\text{–}C_6H_2\text{–}Me_2\text{–}2,5\text{-}C\equiv CH\text{-}p)]$ (0.069 g, 0.12 mmol) was used in place of $[Re(bpy)(CO)_3\text{-}(\mu_3\text{–}\eta^1\text{-}C\equiv CC_6H_4C\equiv CH\text{-}p)]$. Orange crystals of **2** were obtained. Yield: 0.057 g (35%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 298 (51 820), 364sh (50 720), 378 (53 020), 424sh (4920). IR (Nujol mull, KBr), ν/cm^{-1}: 2084w [ν(C≡C)]. ^{1}H-NMR (300 MHz, $CDCl_3$)/ppm: δ 1.9 (s, 6H, –CH_3), 2.3 (s, 6H, –CH_3), 2.9 (m, 6H, –CH_2–), 6.5–7.3 (m, 64H, –Ph), 7.6 (t, 4H, bipyridyl H’s, $J_{H–H}$, 5.9 Hz), 8.2 (t, 4H, bipyridyl H’s, $J_{H–H}$, 7.9 Hz), 8.6 (d, 4H, bipyridyl H’s, $J_{H–H}$, 8.2 Hz), 9.2 (d, 4H, bipyridyl H’s, $J_{H–H}$, 4.6 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ −5.9 (s). Positive FAB-MS: *m/z* 2500 $[M-PF_6]^+$. Anal. Calc. for $C_{125}H_{98}Cu_3F_6N_4O_6P_7Re_2\cdot 0.5CH_2Cl_2$: C, 56.07; H, 3.69; N, 2.08. Found: C, 56.06; H, 3.63; N, 1.78%.

2.2.3. $[Cu_3(\mu\text{-}dppm)_3\{\mu_3\text{–}\eta^1\text{-}C\equiv CC_6H_4C\equiv C\text{-}p\text{-}Re(^tBu_2bpy)(CO)_3\}_2]BF_4$ (**3**)

Complex **3** was prepared by a method similar to that of **1** except $[Cu_2(\mu\text{-}dppm)_2(MeCN)_2](BF_4)_2$ (0.10 g, 0.09 mmol) and $[Re(^tBu_2bpy)(CO)_3(C\equiv CC_6H_4C\equiv CH\text{-}p)]$ (0.078 g, 0.12 mmol) were used in place of $[Re(bpy)(CO)_3(C\equiv CC_6H_4C\equiv CH\text{-}p)]$ and $[Cu_2(\mu\text{-}dppm)_2(MeCN)_2](PF_6)_2$. Orange crystals of **3** were obtained. Yield: 0.048 g (30%).

UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 296 (103 100), 356sh (101 210), 374 (117 100), 424sh (9230). IR (Nujol mull, KBr), ν/cm^{-1}: 2096w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 1.6 (s, 36H, butyl H's), 6.7–7.3 (m, 68H, –Ph), 7.9 (dd, 4H, bipyridyl H's), 8.8 (s, 4H, bipyridyl H's, $J_{H–H}$, 2.0 Hz), 9.2 (d, 4H, bipyridyl H's, $J_{H–H}$, 6.1 Hz). Positive FAB-MS: *m/z* 2669 [M−BF$_4$]$^+$. Anal. Calc. for $C_{137}H_{122}Cu_3BF_4N_4O_6P_6Re_2\cdot1.5CH_2Cl_2$: C, 57.69; H, 4.34; N, 1.94. Found: C, 57.65; H, 4.45; N, 1.92%.

2.2.4. [$Cu_3(\mu$-^{n}PrPNP$)_3\{\mu_3$–η^1-C≡CC_6H_4C≡C-*p*-Re(bpy)$(CO)_3\}_2$]PF_6 (**4**)

Complex **4** was prepared by a method similar to that of **1** except [$Cu_2(\mu$-^{n}PrPNP$)_2(MeCN)_2$]$(PF_6)_2$ (0.12 g, 0.09 mmol) was used in place of [$Cu_2(\mu$-dppm$)_2(MeCN)_2$]$(PF_6)_2$. Orange crystals of **4** were obtained. Yield: 0.045 g (28%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 276sh (91 810), 292 (94 310), 348sh (95 440), 370 (145 080), 434sh (5310). IR (Nujol mull, KBr), ν/cm^{-1}: 2088w [ν(C≡C)]. ^{1}H-NMR (300 MHz, CD_2Cl_2, 298 K)/ppm: δ 0.0 (m, 15H, –N–CH_2–C*H*$_2$–C*H*$_3$), 2.4 (m, 6H, –N–C*H*$_2$–CH_2–CH_3), 6.7–7.4 (m, 68H, –Ph), 7.7 (t, 4H, bipyridyl H's, $J_{H–H}$, 6.4 Hz), 8.3 (t, 4H, bipyridyl H's, $J_{H–H}$, 7.8 Hz), 8.5 (d, 4H, bipyridyl H's, $J_{H–H}$, 8.2 Hz), 9.3 (d, 4H, bipyridyl H's, $J_{H–H}$, 5.5 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ 68.9 (s). Positive FAB-MS: *m/z* 2573 [M−PF$_6$]$^+$. Anal. Calc. for $C_{127}H_{105}Cu_3F_6N_7O_6P_7Re_2\cdot0.5CH_2Cl_2$: C, 55.45; H, 3.84; N, 3.55. Found: C, 55.06; H, 3.88; N, 3.25%.

2.2.5. [$Cu_3(\mu$-^{n}PrPNP$)_3\{\mu_3$–η^1-C≡CC_6H_2-2,5-Me_2-C≡C-Re(bpy)$(CO)_3\}_2$]PF_6 (**5**)

Complex **5** was prepared by a method similar to that of **2** except [$Cu_2(\mu$-^{n}PrPNP$)_2\{MeCN\}_2$]$(PF_6)_2$ (0.12 g, 0.09 mmol) was used in place of [$Cu_2(\mu$-dppm$)_2(MeCN)_2$]$(PF_6)_2$. Orange crystals of **5** were obtained. Yield: 0.051 g (30%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 244sh (23 380), 278sh (41 640), 294 (16 100), 350sh (15 527), 372 (22 060), 428sh (950). IR (Nujol mull, KBr), ν/cm^{-1}: 2086w [ν(C≡C)]. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K)/ppm: δ 0.0 (m, 15H, –N–CH_2–C*H*$_2$-C*H*$_3$), 1.8 (s, 6H, –CH_3), 1.9 (s, 6H, –CH_3), 2.4 (m, 6H, –N–C*H*$_2$–CH_2-CH_3), 6.7–7.2 (m, 64H, –Ph), 7.5 (t, 4H, bipyridyl H's, $J_{H–H}$, 6.4 Hz), 8.2 (t, 4H, bipyridyl H's, $J_{H–H}$, 8.0 Hz), 8.6 (d, 4H, bipyridyl H's, $J_{H–H}$, 8.3 Hz), 9.2 (d, 4H, bipyridyl H's, $J_{H–H}$, 4.2 Hz). Positive FAB-MS: *m/z* 2630 [M−PF$_6$]$^+$. Anal. Calc. for $C_{131}H_{113}Cu_3F_6N_7O_6P_7Re_2\cdot0.5CH_2Cl_2$: C, 56.04; H, 4.08; N, 3.48. Found: C, 55.95; H, 4.08; N, 3.31%.

2.2.6. [$Cu_3(\mu$-dppm$)_3\{\mu_3$–η^1-C≡CC≡C-Re(bpy)$(CO)_3\}_2$]PF_6 (**6**)

Complex **6** was prepared by a method similar to that of **1** except [Re(bpy)$(CO)_3$(C≡CC≡CH)] (0.055 g, 0.12 mmol) was used in place of [Re(bpy)$(CO)_3$(C≡CC_6H_4C≡CH-*p*)] and acetone was used as the solvent. Red crystals of **6** were obtained by layering *n*-hexane onto a acetone solution of the complex. Yield: 0.046 g (31%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 292 (92 510), 326sh (60 470), 368sh (19 820), 482 (2570). IR (Nujol mull, KBr), ν/cm^{-1}: 2076w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 3.0 (m, 6H, –CH_2–), 6.7–7.1 (m, 60H, –Ph), 7.9 (t, 4H, bipyridyl H's, $J_{H–H}$, 6.4 Hz), 8.5 (t, 4H, bipyridyl H's, $J_{H–H}$, 7.3 Hz), 8.9 (d, 4H, bipyridyl H's, $J_{H–H}$, 9.1 Hz), 9.4 (d, 4H, bipyridyl H's, $J_{H–H}$, 5.3 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ −4.7. Positive FAB-MS: *m/z* 2293 [M−PF$_6$]$^+$. Anal. Calc. for $C_{109}H_{82}Cu_3F_6Re_2N_4O_6P_7$: C, 53.71; H, 3.40; N, 2.30. Found: C, 53.71; H, 3.35; N, 2.00%.

2.2.7. [$Cu_3(\mu$-dppm$)_3\{\mu_3$–η^1-C≡CC≡C-Re(Me_2bpy)$(CO)_3\}_2$]PF_6 (**7**)

This was prepared by a method similar to that of **6** except [Re(Me_2bpy)$(CO)_3$(C≡CC≡CH)] (0.058 g, 0.12 mmol) was used in place of [Re(bpy)$(CO)_3$(C≡CC≡CH)]. Orange crystals of **7** were obtained. Yield: 0.11 g (76%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 294 (88 730), 324sh (61 150), 366sh (23 000), 470 (2770). IR (Nujol mull, KBr), ν/cm^{-1}: 2086w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 2.7 (s, 12H, –Me) 3.1 (m, 6H, –CH_2–), 6.7–7.1 (m, 60H, –Ph), 7.8 (d, 4H, bipyridyl H's, $J_{H–H}$, 5.4 Hz), 8.8 (s, 4H, bipyridyl H's), 9.2 (d, 4H, bipyridyl H's, $J_{H–H}$, 5.4 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ −4.8. Positive FAB-MS: *m/z* 2350 [M−PF$_6$]$^+$. Anal. Calc. for $C_{113}H_{90}Cu_3F_6Re_2N_4O_6P_7$: C, 54.47; H, 3.64; N, 2.23. Found: C, 54.71; H, 3.63; N, 2.09%.

2.2.8. [$Cu_3(\mu$-dppm$)_3\{\mu_3$–η^1-C≡CC≡C-Re(^{t}Bu$_2$bpy)$(CO)_3\}_2$]PF_6 (**8**)

This was prepared by a method similar to that of **6** except [Re(^{t}Bu$_2$bpy)$(CO)_3$(C≡CC≡CH)] (0.071 g, 0.12 mmol) was used in place of [Re(bpy)$(CO)_3$(C≡CC≡CH)]. Orange crystals of **8** were obtained. Yield: 0.13 g (84%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 292 (89 880), 322sh (59 460), 368sh (21 590), 470 (2790). IR (Nujol mull, KBr), ν/cm^{-1}: 2074w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 1.4 (s, 36H, butyl H's), 2.9 (m, 6H, –CH_2–), 6.6–7.0 (m, 60H, –Ph), 7.8 (d, 4H, bipyridyl H's, $J_{H–H}$, 5.9 Hz), 8.9 (s, 4H, bipyridyl H's), 9.1 (d, 4H, bipyridyl H's, $J_{H–H}$, 5.9 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ −4.8. Positive FAB-MS: *m/z* 2518 [M−PF$_6$]$^+$. Anal. Calc. for $C_{125}H_{114}Cu_3F_6Re_2N_4O_6P_7$: C, 56.40; H, 4.32; N, 2.10. Found: C, 56.42; H, 4.37; N, 2.02%.

2.2.9. [$Cu_3(\mu$-dppa$)_3\{\mu_3$–η^1-C≡CC≡C-Re(bpy)$(CO)_3\}_2$]PF_6 (**9**)

This was prepared by a method similar to that of **6** except [$Cu_2(\mu$-dppa$)_2(MeCN)_2$]$(PF_6)_2$ (0.11 g, 0.09 mmol) was used in place of [$Cu_2(\mu$-dppm$)_2(MeCN)_2$]$(PF_6)_2$. Orange crystals of **9** were obtained. Yield: 0.059 g (43%). UV–vis (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 262sh (106 900), 296 (99 110), 324sh (64 475), 370sh (22 970), 486 (2865). IR (Nujol mull, KBr), ν/cm^{-1}: 2070w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 289 K)/ppm: δ 5.0 (s, 3H, –NH), 6.8–7.2 (m, 60H, –Ph), 8.0 (t, 4H, bipyridyl H's, $J_{\text{H–H}}$, 7.7 Hz), 8.5 (t, 4H, bipyridyl H's, $J_{\text{H–H}}$, 6.6 Hz), 8.9 (d, 4H, bipyridyl H's, $J_{\text{H–H}}$, 8.0 Hz), 9.4 (d, 4H, bipyridyl H's, $J_{\text{H–H}}$, 5.5 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ 46.8 (s). Positive FAB-MS: m/z 2297 [M−PF$_6$]$^+$. Anal. Calc. for $C_{106}H_{79}Cu_3F_6Re_2N_7O_6P_7$: C, 52.17; H, 3.26; N, 4.02. Found: C, 52.31; H, 3.31; N, 3.98%.

*2.2.10. [Cu$_3$(μ-dppa)$_3${μ$_3$–η^1-C≡CC≡C-Re(Me$_2$bpy)(CO)$_3$}$_2$]PF$_6$ (**10**)*

This was prepared by a method similar to that of **7** except [Cu$_2$(μ-dppa)$_2$(MeCN)$_2$](PF$_6$)$_2$ (0.11 g, 0.09 mmol) was used in place of [Cu$_2$(μ-dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$. Orange crystals of **10** were obtained. Yield: 0.071 g (50%). UV–vis (CH$_2$Cl$_2$), λ/nm ($\varepsilon_{\max}$/dm^3 mol^{-1} cm^{-1}): 268 (135 310), 298 (119 520), 324sh (76 505), 368sh (20 275), 482 (2740). IR (Nujol mull, KBr), ν/cm^{-1}: 2077w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 2.7 (s, 12H, –Me), 5.0 (s, 3H, –NH), 6.8–7.2 (m, 60H, –Ph), 7.8 (d, 4H, bipyridyl H's, $J_{\text{H–H}}$, 5.6 Hz), 8.7 (s, 4H, bipyridyl H's), 9.2 (d, 4H, bipyridyl H's, $J_{\text{H–H}}$, 5.6 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ 46.6 (s). Positive FAB-MS: m/z 2353 [M−PF$_6$]$^+$. Anal. Calc. for $C_{110}H_{87}Cu_3F_6Re_2N_7O_6P_7\cdot CH_2Cl_2$: C, 51.64; H, 3.47; N, 3.8. Found: C, 51.78; H, 3.40; N, 3.76%.

*2.2.11. [Ag$_3$(μ-dppm)$_3${μ$_3$–η^1-C≡CC≡C-Re(bpy)(CO)$_3$}$_2$]PF$_6$ (**11**)*

This was prepared by a method similar to that of **6** except [Ag$_2$(μ-dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$ (0.12 g, 0.09 mmol) was used in place of [Cu$_2$(μ-dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$. Orange crystals of **11** were obtained. Yield: 0.041 g (28%). UV–vis (CH$_2$Cl$_2$), λ/nm ($\varepsilon_{\max}$/dm^3 mol^{-1} cm^{-1}): 256 (98 725), 301sh (64 050), 359sh (8045), 473 (3450). IR (Nujol mull, KBr), ν/cm^{-1}: 2088w [ν(C≡C)]. ^{1}H-NMR (300 MHz, acetone-d_6, 298 K)/ppm: δ 3.2 (s, 6H, –CH$_2$), 6.6–7.4 (m, 60H, –Ph), 7.8 (t, 4H, bipyridyl H's, $J_{\text{H–H}}$, 6.4 Hz), 8.4 (t, 4H, bipyridyl H's, $J_{\text{H–H}}$, 6.1 Hz), 8.7 (d, 4H, bipyridyl H's, $J_{\text{H–H}}$, 8.1 Hz), 9.2 (d, 4H, bipyridyl H's, $J_{\text{H–H}}$, 5.0 Hz). ^{31}P{^{1}H}-NMR (202 MHz, acetone-d_6, 298 K)/ppm: δ 1.4 (d, $J_{\text{Ag–P}}$, 31.1 Hz). Positive FAB-MS: m/z 2423 [M−PF$_6$]$^+$. Anal. Calc. for $C_{109}H_{82}Ag_3F_6Re_2N_4O_6P_7\cdot 1.5C_3H_6O$: C, 51.29; H, 3.45; N, 2.11. Found: C, 51.56; H, 3.18; N, 2.11%.

2.3. Physical measurements and instrumentation

All infrared spectra were obtained as Nujol mull on KBr disk on a Bio-Rad FTS-7 spectrophotometer. The electronic absorption spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Steady state emission spectra recorded at room temperature and at 77 K were obtained on a Spex Fluorolog-2 Model 111 fluorescence spectrophotometer with or without corning filters. All solutions for photophysical studies were prepared under 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. Solid-state photophysical measurements were carried out with the solid sample loaded in a quartz tube inside a quartz-walled Dewar flask. Liquid nitrogen was placed into the Dewar flask for low temperature (77 K) solid-state photophysical measure-

Table 1
Crystal and structure determination of **7** and **11**

Complex	**7**	**11**
Empirical formula	$C_{125}H_{108}Cu_3F_6N_4O_{10}P_7Re_2$	$C_{109}H_{82}Ag_3F_6N_4O_6P_7Re_2$
Formula weight	2719.96	2570.59
Temperature (K)	253(2)	301(2)
Wavelength (Å)	0.71069	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pna2_1$
Unit cell dimensions		
a (Å)	14.589(3)	28.739(6)
b (Å)	18.979(4)	29.990(6)
c (Å)	23.688(5)	30.199(6)
α (°)	89.27(3)	90
β (°)	81.74(3)	90
γ (°)	83.26(3)	90
Volume (Å^3)	6446(2)	26028(9)
Z	2	8
D_{calc} (Mg m^{-3})	1.401	1.312
Absorption coefficient (mm^{-1})	2.508	2.435
F(000)	2724	10 096
Crystal size (mm^3)	0.4×0.2×0.1	0.2×0.2×0.1
θ Range for data collection (°)	0.87–25.34	0.96–23.66
Index ranges	$16 \leq h \leq 17$, $-22 \leq k \leq 22$, $-28 \leq l \leq 27$	$-31 \leq h \leq 31$, $-31 \leq k \leq 32$, $-31 \leq l \leq 31$
Reflections collected	31 604	73 605
Independent reflections	17 334 ($R_{\text{int}} = 0.0407$)	23 271 ($R_{\text{int}} = 0.0630$)
Completeness to $\theta = 25.34°$ (%)	73.4	64.6
$(\Delta/\sigma)_{\max}$	−0.002 (av. 0.001)	−0.017 (av. 0.002)
Parameters	1293	780
Goodness-of-fit on F^2	0.943	1.034
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0586$, $wR_2 = 0.1705$	$R_1 = 0.0798$, $wR_2 = 0.2245$
R indices (all data)	$R_1 = 0.1008$, $wR_2 = 0.1913$	$R_1 = 0.1236$, $wR_2 = 0.2489$
Largest difference peak and hole (e Å^{-3})	1.398 and −1.452	1.961 and −0.914

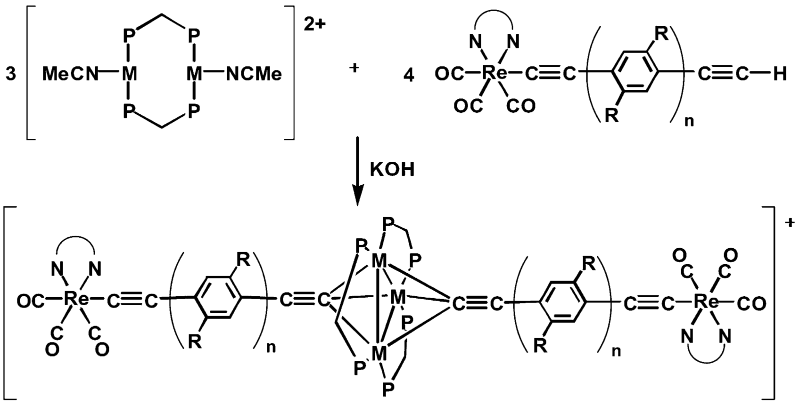
$R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$. Goodness-of-fit $= S = \{\sum [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

ments. ^{1}H- and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker DPX-300 and Bruker AM-500 NMR spectrometer. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the newly synthesized complexes were performed either by Butterworth Labratories Ltd. or on a Carlo Erba 1106 elemental analyzer at 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 Spectra-Physics 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, 2GS/s) digital oscilloscope, and analyzed using a program for exponential fits.

2.4. *Crystal structure determination*

The crystal data for **1** have been communicated previous by literature [16]. Single crystals of **7** and **11** suitable for X-ray crystallography were obtained by *n*-hexane onto a concentrated solution of **7** and **11** in acetone, respectively. The crystallographic data and experimental details for complexes **7** and **11** are summarized in Table 1. The X-ray diffraction data were collected at 253 and 301 K for **7** and **11**, respectively on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The images were interpreted and intensities integrated using program DENZO [17]. The structure was solved by direct methods employing SIR-97 program [18]. Full-matrix least-squares refinement on F^2 was used in the structure refinement. All non-hydrogen atoms were refined anisotropically except for the non-hydrogen atoms of solvent molecules and disordered atoms were refined isotropically for **7**. Only Ag, Re and P atoms of the molecule cations were refined anisotropically, other non-hydrogen atoms were refined isotropically for **11**. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final *R*-indices. One crystallographic asymmetric unit consists of one formula unit, including four acetone solvent molecules [19] and one PF$_6^-$ anion [20] for **7**. One crystallographic asymmetric unit consists of two formula units for **11**; restraints had to be applied for phenyl rings, bpy and PF$_6^-$ anions [21] due to incompleteness and poor quality of data set.



1: M = Cu, P∧P = dppm, N∩N = bpy, R = H, n = 1

2: M = Cu, P∧P = dppm, N∩N = bpy, R = Me, n = 1

3: M = Cu, P∧P = dppm, N∩N = ^{t}Bu$_2$bpy, R = H, n = 1

4: M = Cu, P∧P = ^{n}PrPNP, N∩N = bpy, R = H, n = 1

5: M = Cu, P∧P = ^{n}PrPNP, N∩N = bpy, R = Me, n = 1

6: M = Cu, P∧P = dppm, N∩N = bpy, n = 0

7: M = Cu, P∧P = dppm, N∩N = Me$_2$bpy, n = 0

8: M = Cu, P∧P = dppm, N∩N = ^{t}Bu$_2$bpy, n = 0

9: M = Cu, P∧P = dppa, N∩N = bpy, n = 0

10: M = Cu, P∧P = dppa, N∩N = Me$_2$bpy, n = 0

11: M = Ag, P∧P = dppm, N∩N = bpy, n = 0

Scheme 1. The synthetic route of mixed-metal rhenium(I)–copper(I) and –silver(I) complexes.

3. Results and discussion

3.1. Syntheses and X-ray crystallography

Complexes **1**–**5** were prepared by the reaction of the corresponding $[M_2(\mu\text{-LL})_2(MeCN)_2]X_2$ (M = Cu, Ag; X = BF_4^-, PF_6^-) with $[Re(NN)(CO)_3(C{\equiv}CC_6H_2R_2{-}C{\equiv}CH\text{-}p)]$ in a 3:4 molar ratio in the presence of an excess of KOH in CH_2Cl_2/acetone–MeOH at room temperature under anaerobic and anhydrous conditions. Complexes **6**–**11** were similarly prepared except $[Re(NN)(CO)_3(C{\equiv}CC{\equiv}CH)]$ was used in place of $[Re(NN)(CO)_3(C{\equiv}CC_6H_2R_2{-}C{\equiv}CH\text{-}p)]$. The synthetic routes of the complexes are shown in Scheme 1. All complexes gave satisfactory elemental analyses and have been characterized by ^{1}H-, ^{31}P{^{1}H}-NMR, IR spectroscopy and positive FAB-mass spectrometry. The X-ray crystal structures for complexes **1**, **7** and **11** have also been determined.

The perspective drawings of the complex cations of **7** and **11** with atomic numbering are depicted in Fig. 1. Both complex cations are isostructural and consist of an isosceles triangle of copper or silver atoms with a dppm ligand bridging each edge to form a roughly planar $[M_3P_6]$ core, with two Re butadiynyl metalloligands capping the triangular M^I in a μ_3–η^1 fashion. The bridging mode of the alkynyl group is asymmetric, with Cu–C bond distances in **7** and Ag–C bond distances in **11** in the range of 2.063(11)–2.290(9) and 2.11(3)–2.50(3) Å, respectively. Similar structures have been observed in complex **1** [4b,4d] and in the related bicapped trinuclear metal alkynyl systems [22]. The C≡C bond lengths in both complexes are typical of a metal–alkynyl σ bond [23]. The Cu···Cu (2.552(7)–2.659(3) Å) and Ag···Ag (2.869(3)–3.071(3) Å) separations are smaller than the sum of van der Waals radii for copper (2.8 Å) and for silver (3.4 Å), respectively [24], and may suggest the presence of weak Cu···Cu and Ag···Ag interactions. The Re–C≡CC≡C units are essentially linear with bond angles of 177.7(11)–178.7(11) and 172(3)–178(3)° for **7** and **11**, respectively [11,25].

3.2. Electronic absorption and emission spectroscopy

The electronic absorption spectra of all complexes in CH_2Cl_2 solution exhibit absorption bands at ca. 244–378 nm and a low-energy band at ca. 440–482 nm. The electronic absorption and photophysical data for the newly synthesized

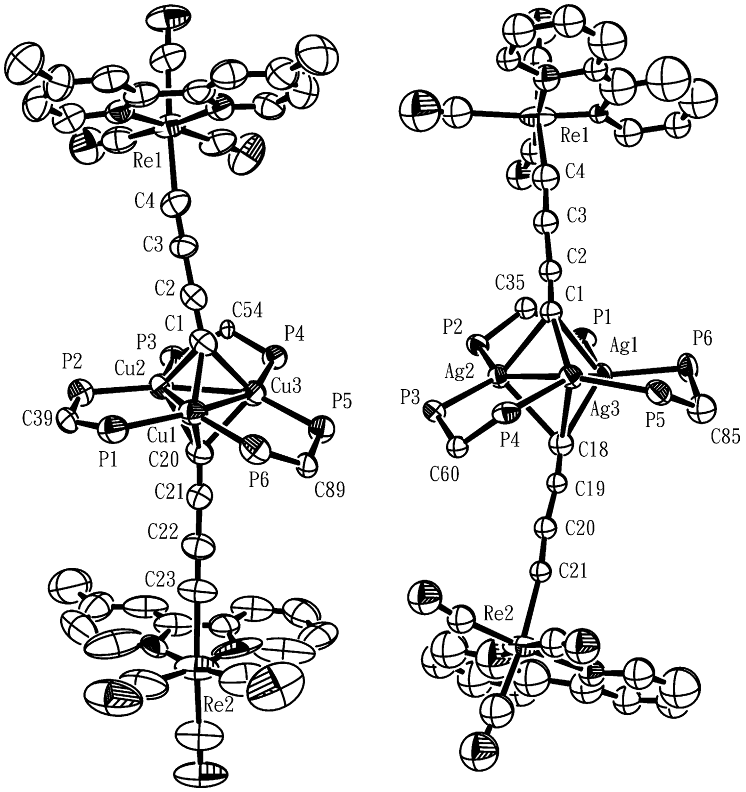


Fig. 1. Perspective drawings of the complex cations of **7** (left) and **11** (right) with atomic numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and bond angles (°) for **7**: C(1)–C(2) 1.244(13), C(3)–C(4) 1.180(13), C(20)–C(21) 1.226(13), C(22)–C(23) 1.223(14), Re(1)–C(4) 2.148(11), Re(2)–C(23) 2.137(11), Cu(1)···Cu(2) 2.6593(17), Cu(2)···Cu(3) 2.5527(18), Cu(3)···Cu(1) 2.5737(18); Cu(1)–Cu(2)–Cu(3) 59.14(5), Cu(2)–Cu(3)–Cu(1) 62.50(5), Cu(3)–Cu(1)–Cu(2) 58.37(5), C(4)–Re(1)–C(5) 175.4(4), C(23)–Re(2)–C(24) 173.6(5). Selected bond distances (Å) and bond angles (°) for **11**: C(1)–C(2) 1.18(3), C(3)–C(4) 1.32(3), C(18)–C(19) 1.14(3), C(20)–C(21) 1.25(3), Re(1)–C(4) 2.02(3), Re(2)–C(21) 2.14(2), Ag(1)···Ag(2)2.898(3), Ag(2)···Ag(3) 2.914(3), Ag(3)···Ag(1) 3.020(3); Ag(1)–Ag(2)–Ag(3) 62.60(8), Ag(2)–Ag(3)–Ag(1) 58.43(7), Ag(3)–Ag(1)–Ag(2) 58.97(7), C(4)–Re(1)–C(5) 173.8(13), C(21)–Re(2)–C(22) 173.2(13).

Table 2
Photophysical data for complexers **1–11**

Complex	Medium (T/K)	λ_{abs}/nm (dm^{-3} mol^{-1} cm^{-1})	λ_{em}/nm (τ_o/µs)
1	CH_2Cl_2 (298)	262sh (102 600), 300sh (78 400), 354sh (69 300), 372 (77 400), 428sh (5110)	642 (<0.1)
	Solid (298)		616 (<0.1)
	Solid (77)		605
2	CH_2Cl_2 (298)	298 (51 800), 360sh (50 700), 378 (53 000), 424sh (4920)	650 (<0.1)
	Solid (298)		615 (0.14)
	Solid (77)		608
3	CH_2Cl_2 (298)	296 (103 100), 356sh (101 200), 374 (117 000), 424sh (9230)	615 (<0.1)
	Solid (298)		613 (0.1)
	Solid (77)		605
4	CH_2Cl_2 (298)	276sh (91 800), 292 (94 300), 348sh (95 400), 370 (145 100), 434sh (5310)	660 (<0.1)
	Solid (298)		616 (0.12)
	Solid (77)		623
5	CH_2Cl_2 (298)	244sh (23 400), 278sh (41 600), 294 (16 100), 350sh (15 500), 372 (22 100), 428sh (950)	650 (<0.1)
	Solid (298)		618 (0.13)
	Solid (77)		615
6	CH_2Cl_2 (298)	264sh (102 700), 292 (92 510), 326sh (60 470), 368sh (19 820), 482 (2570)	706 (<0.1)
	Solid (298)		641 (<0.1)
	Solid (77)		655
7	CH_2Cl_2 (298)	260 (106 500), 294 (88 730), 324sh (61 150), 366sh (23 000), 470 (2770)	688 (<0.1)
	Solid (298)		605 (<0.1)
	Solid (77)		607
8	CH_2Cl_2 (298)	258sh (102 500), 292 (89 880), 322sh (59 460), 368sh (21 590), 470 (2790)	678 (<0.1)
	Solid (298)		634 (<0.1)
	Solid (77)		630
9	CH_2Cl_2 (298)	262sh (106 900), 296 (99 110), 324sh (64 475), 370sh (22 970), 486 (2865)	701 (<0.1)
	Solid (298)		647 (<0.1)
	Solid (77)		645
10	CH_2Cl_2 (298)	268 (135 310), 298 (119 520), 324sh (76 505), 368sh (20 275), 482 (2740)	677 (<0.1)
	Solid (298)		642 (<0.1)
	Solid (77)		635
11	CH_2Cl_2 (298)	256 (98 725), 301sh (64 050), 359sh (8045), 473 (3450)	656 (<0.1)
	Solid (298)		625 (<0.1)
	Solid (77)		629

Re(I)–Cu(I)/Ag(I) mixed-metal complexes are summarized in Table 2. The high-energy absorptions are assigned as intraligand π→π* transitions of the diphosphines, alkynyl and the bipyridines, since the free ligands also absorb strongly in this region [4d,4e,26]. The low-energy absorptions at ca. 440–482 nm are assigned as [dπ(Re)→π*(NN)] MLCT transition. The absorption energies for the low-energy absorption bands follow the trend: **3** (424 nm)>**1** (428 nm); **8** (470 nm)≈**7** (470 nm)>**6** (482 nm); and **10** (482 nm)>**9** (486 nm), consistent with the higher π* orbital energy of $^tBu_2$bpy and Me_2bpy than bpy as a result of its poorer π-accepting ability derived from the presence of the more electron-rich *tert*-butyl substituents on the bipyridine ligand. A blue shift in the low-energy absorption band is observed in the 1,4-diethynylbenzene-bridged complexes, **1** and **3**, with the respect to the butadiynyl analogues **6** and **8**. A higher MLCT absorption energy for silver(I) complex **11** (473 nm) than the related copper(I) analogue **6** (482 nm) is consistent with the poorer electron donating ability of the Ag_3^I core than the Cu_3^I counterpart, which would render the

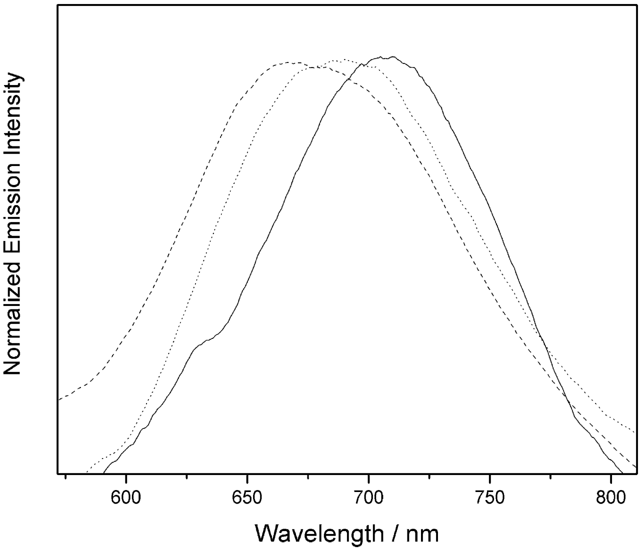


Fig. 2. Normalised emission spectra of [Cu_3(μ-dppm)$_3${$μ_3$–$η^1$-C≡CC≡C–Re(bpy)(CO)$_3$}$_2$]PF_6 (**6**) (—), [Cu_3(μ-dppm)$_3${$μ_3$–$η^1$-C≡CC≡C–Re(Me_2bpy)(CO)$_3$}$_2$]PF_6 (**7**) (···) and [Cu_3(μ-dppm)$_3${$μ_3$–$η^1$-C≡CC≡C–Re(^{t}Bu_2bpy)(CO)$_3$}$_2$]PF_6 (**8**) (---) in degassed CH_2Cl_2 at 298 K.

Re(I) centre less electron rich, leading to a larger MLCT energy gap.

Excitation of complexes **1**–**11** in the solid state and in CH_2Cl_2 solution at $\lambda>400$ nm resulted in strong orange luminescence at ca. 628–706 nm. The emission energies were found to be sensitive to the nature of the diimine and phosphine ligands and the nature of the trinuclear metal core. The emission energies of the complexes with the same bidentate phosphine ligands but different bipyridine ligands in CH_2Cl_2 follow the order: **3** (615 nm)>**1** (642 nm); **8** (678 nm)≈**7** (688 nm)>**6** (706 nm); and **10** (677 nm)>**9** (701 nm), consistent with the higher π* orbital energies of ^{t}Bu_2bpy and Me_2bpy than bpy as a result of the electron-donating effect of the *tert*-butyl and methyl groups on the bipyridine ligand, which would raise the π* orbital energy of ^{t}Bu_2bpy and Me_2bpy over that of bpy. With reference to previous spectroscopic work on rhenium(I) diimine systems, the intense low-energy emission is assigned as derived from states of ^{3}MLCT [dπ(Re)→π*(NN)] origin. A similar red shift in emission energy has also been observed on going from [Re(^{t}Bu_2bpy)(CO)$_3$Cl] [27] and [Re(Me_2bpy)(CO)$_3$Cl] [25] to [Re(bpy)(CO)$_3$Cl] [28]. Similar energy trends have also been observed in the electronic absorption spectra. Fig. 2 shows the emission spectral trend of the complexes with different bipyridine ligands. With the same bipyridine ligand, a slight blue shift in emission energy is observed on going from **6** (706 nm) to **9** (701 nm) and from **7** (688 nm) to **10** (677 nm). This can be rationalized by the fact that the stronger electron-donating ability of dppm than dppa would render the Cu^I-coordinated alkynyl more electron rich, which in turn would render the Re^I centre more electon rich, raising the energy of the dπ(Re) orbitals, causing a lower energy ^{3}MLCT emission. The corresponding 1,4-diethynylbenzene-bridged complexes, **1** and **3**, are blue shifted with the respect to the butadiynyl analogues **6** and **8**. In addition, a red shift in emission energy of the lowest-lying emission band from **11** to **6** in CH_2Cl_2 has been observed. The fact that Cu^I is much more easily oxidized, given the higher energy of the Cu^I 3d orbitals relative to those of the Ag^I 4d orbitals [29], would imply that the trinuclear Cu^I_3 core is more electron rich, leading to a stronger π-donor ability of the alkynyl unit which raises the dπ(Re) orbital energy to give a lower energy ^{3}MLCT emission. Similar to the corresponding rhenium(I) alkynyl system [1b,25], which exhibits short luminescence lifetimes, the relatively short lifetimes in the submicrosecond range in Re(I)–Cu(I)/Ag(I) complexes are further supportive of an emissive state of predominantly ^{3}MLCT [dπ(Re)→π*(NN)] character, possibly with some mixing of a π(C≡C)→π*(NN) ligand-to-ligand charge transfer (^{3}LLCT) character.

4. Conclusion

By employing ‘metal complex as ligand’ or so-called metalloligand approach, a series of Re(I)–Cu(I)/Ag(I) were successfully synthesized and characterized. The origin of the emission was assigned as dervied from states of a ^{3}MLCT [dπ(Re)→π*(NN)] character. The spectroscopic and emission properties of these complexes can be readily tuned by a systematic variation of the diimine ligands, the alkynyl ligands, and the trinuclear metal core. Moreover, rhenium(I) alkynyl systems have been shown to serve as versatile and powerful building blocks for the synthesis of various luminescent mixed-metal carbon-rich molecular rods.

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[19] One of the acetone molecules was treated with disorder. Due to high thermal parameters, the acetones were restrained to be flat, with similar C–C and C=O distances.

[20] The PF_6^- anion was also located with high disorder of the F atoms and only four F atoms were located.

[21] Restraints were applied: (i) PF_6^- anions were restrained to be in octahedral geometry with F atoms around the P atom and similar P–F bond lengths and thermal parameters; (ii) phenyl rings were restrained to be normal hexagonal rings with bond lengths of 1.39 Å; (iii) some C atoms have unexpectedly high thermal parameters, atoms in the phenyl rings concerned were restrained to have the same thermal parameters; (iv) some extra individual restraints had to be applied to prevent unusual structure.

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