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Synthesis, Photophysics, Electrochemistry, and Excited-State Redox Properties of Trinuclear Copper(I) Acetylides with Bis(diphenylphosphino)alkylamines and -arylamines as Bridging Ligands

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A series of soluble trinuclear copper(I) complexes containing bicapped μ_3-η^1 acetylides, $[Cu_3(\mu\text{-PNP})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{CR}')_2]^+$ [PNP = $[(C_6H_5)_2P]_2NR$, R = ^{n}Pr, C_6H_5, C_6H_4-CH_3-*p*, C_6H_4-F-*p*] have been synthesized and shown to exhibit rich photoluminescent behavior at room temperature. The electrochemistry and excited-state redox properties of $[Cu_3(\mu\text{-}^n\text{PrPNP})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{CPh})_2]^+$ have been investigated.

Introduction

There has been a growing interest in the synthesis of alkynyl metal complexes owing to the recent reports on their potential applications as nonlinear optical materials and molecular wire.[1] Moreover, the rich photophysics and photochemical behavior exhibited by a wide variety of polynuclear copper(I) metal complexes[2,3] have attracted our attention. The synthesis and photophysical and photochemical properties of a series of copper(I) acetylides with dppm as bridging ligand have been reported recently.[3a,b,d,f,4] Herein, we report the synthesis and luminescent behavior of a series of trinuclear copper(I) acetylides with PNP [bis(diphenylphosphino)alkyl/-aryl amine] as bridging ligands, $[Cu_3(\mu\text{-PNP})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{CR}')_2]^+$. The Cu_3 framework is stabilized by three bridging PNP ligands which appear to be appropriate supports for the bicapped system. The ease of changing different substituents on the diphenylphosphinoamine allows the design and study of donor−acceptor properties as well as substituent effects on the spectroscopic and electrochemical properties of the complexes, which is advantageous over the use of the dppm ligand.[5]

Experimental Section

Materials and Reagents. Phenylacetylene, 1-octyne, 1-dodecyne, and 3,3-dimethyl-1-butyne were purchased from Aldrich Chemical Co. Ltd. (4-Ethoxyphenyl)acetylene and 4-ethynylbiphenyl were obtained from Maybridge Chemical Co. Ltd. (4-Nitrophenyl)acetylene and 4-ethynylpyridine were prepared by literature procedures.[6] $[Cu(MeCN)_4]X$ (X = BF_4, PF_6) was prepared according to literature procedure.[7] The ligands $[(C_6H_5)_2P]_2N(^n\text{Pr})$,[8] $[(C_6H_5)_2P]_2N(C_6H_5)$,[9] $[(C_6H_5)_2P]_2N(C_6H_4\text{-}CH_3\text{-}p)$,[8] and $[(C_6H_5)_2P]_2N(C_6H_4\text{-F-}p)$[8] were synthesized by literature procedures. The pyridinium acceptors were prepared by refluxing the corresponding substituted pyridine with the appropriate alkylating agent such as methyl iodide in acetone/ethanol (1:1 v/v) for 4 h, followed by metathesis in water using ammonium hexafluorophosphate and recrystallization from acetone/diethyl ether. Tetra-*n*-butylammonium hexafluorophosphate (Aldrich) was recrystallized twice from absolute ethanol before use. All solvents were purified and distilled using standard procedures before use.[10] All other reagents were of analytical grade and were used as received.

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

$[Cu_2(\mu\text{-}^n\text{PrPNP})_2(MeCN)_2](PF_6)_2$ (1), [^{n}PrPNP = $[(C_6H_5)_2P]_2N(^n\text{Pr})$]. A dichloromethane solution (30 mL) of $[Cu(MeCN)_4]PF_6$ (0.59 g, 1.59 mmol) and $[(C_6H_5)_2P]_2N(^n\text{Pr})$ (0.68 g, 1.59 mmol) was stirred at room temperature for 6 h, to give a colorless solution. The product was then filtered and reduced in volume. Subsequent diffusion of diethyl ether into the concentrated solution gave colorless crystals. Yield: 0.75 g (70%). ^{1}H NMR ($CDCl_3$): δ 0.1 (m, 6H, CH_3), 0.5 (m, 4H,

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CH_2), 1.9 (m, 6H, CH_3CN), 2.6 (m, 4H, NCH_2), 7.2−7.7 (m, 40H, PPh_2). Anal. Calcd for $C_{58}H_{60}N_4P_6F_{12}Cu_2\cdot CH_2Cl_2\cdot CH_3CN$: C, 49.50; H, 4.40; N, 4.73. Found: C, 49.85; H, 4.11; N, 4.63.

$[Cu_2(\mu\text{-}ArPNP)_2(MeCN)_2](PF_6)_2$ (2) [ArPNP = $[(C_6H_5)_2P]_2N(C_6H_5)$]. The procedure was similar to that of **1** except ArPNP (0.73 g, 1.59 mmol) was used instead of ^{n}PrPNP. Colorless crystals were obtained. Yield: 0.95 g (84%). ^{1}H NMR ($CDCl_3$): δ 2.1 (m, 6H, CH_3CN), 5.9−7.0 (m, 10H, NPh), 7.2−7.8 (m, 40H, PPh_2). Anal. Calcd for $C_{64}H_{56}N_4P_6F_{12}Cu_2\cdot 2H_2O$: C, 52.71; H, 4.12; N, 3.84. Found: C, 52.42; H, 4.13; N, 3.45.

$[Cu_2(\mu\text{-}MeArPNP)_2(MeCN)_2](PF_6)_2$ (3), [MeArPNP = $[(C_6H_5)_2P]_2N(C_6H_4\text{-}CH_3\text{-}p)$]. The procedure was similar to that of **1** except MeArPNP (0.76 g, 1.59 mmol) was used instead. Colorless crystals were obtained. Yield: 0.86 g (75%). ^{1}H NMR ($CDCl_3$): δ 2.0 (m, 6H, CH_3CN), 2.2 (s, 6H, $NPhCH_3$), 6.5 (dd, 8H, NPh), 7.2−7.6 (m, 40H, PPh_2). Anal. Calcd for $C_{66}H_{60}N_4P_6B_2F_{12}Cu_2\cdot 0.5CH_2Cl_2$: C, 53.50; H, 4.09; N, 3.75. Found: C. 53.75; H, 4.29; N, 3.85.

$[Cu_2(\mu\text{-}FArPNP)_2(MeCN)_2](BF_4)_2$ (4), [FArPNP = $[(C_6H_5)_2P]_2N(C_6H_4\text{-}F\text{-}p)$]. The procedure was similar to that of **1** except $[Cu(MeCN)_4]BF_4$ (0.50 g, 1.59 mmol) and FArPNP (0.76 g, 1.59 mmol) were used instead. Colorless crystals were obtained. Yield: 0.92 g (86%). ^{1}H NMR ($CDCl_3$): δ 2.0 (m, 6H, CH_3CN), 6.4−6.8 (m, 8H, NPh), 7.3−7.7 (m, 40H, PPh_2). Anal. Calcd for $C_{64}H_{54}N_4P_4B_2F_{10}Cu_2\cdot 0.5CH_2Cl_2$: C, 55.96; H, 4.00; N, 4.05. Found: C, 55.74; H, 4.32; N, 3.68.

$[Cu_3(\mu\text{-}^{n}PrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OEt\text{-}p)_2]BF_4$ (5). To a solution of (4-ethoxyphenyl)acetylene (58.0 mg, 0.4 mmol) and $[Cu_2(\mu\text{-}^{n}PrPNP)_2(MeCN)_2](BF_4)_2$ (0.37 mg, 0.3 mmol) in THF was added an excess of KOH to give a yellow turbid solution. The solution was then stirred at room temperature for 24 h. After filtration, the filtrate was evporated to dryness, and the residue was extracted with acetone. Subsequent diffusion of diethyl ether into the concentrated solution gave air stable yellow crystals. Yield: 0.17 g (45%). ^{1}H NMR (acetone-d_6): δ 0.0 (m, 15 H, CH_2CH_3 of ^{n}Pr), 1.6 (t, 6H, CH_3 of OEt), 2.5 (m, 6H, NCH_2), 4.4 (q, 4H, CH_2 of OEt), 7.0−7.8 (m, 68H, Ph). Positive FAB-MS: *m/z* 1762 {M$^+$}. Anal. Calcd for $C_{101}H_{99}N_3O_2P_6BF_4Cu_3\cdot 2H_2O$: C, 64.31; H, 5.47; N, 2.23. Found: C, 64.26; H, 5.29; N, 2.41.

$[Cu_3(\mu\text{-}^{n}PrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4Ph\text{-}p)_2]BF_4$ (6). The procedure was similar to that of **5** except 4-ethynylbiphenyl (71.2 mg, 0.4 mmol) was used instead of (4-ethoxyphenyl)acetylene, to give yellow crystals of **6**. Yield: 0.18 g (47%). ^{1}H NMR (acetone-d_6): δ 0.0 (m, 15 H, CH_2CH_3), 2.5 (m, 6H, NCH_2), 6.9−8.0 (m, 78H, Ph). Positive FAB-MS: *m/z* 1831 {M$^+$}. Anal. Calcd for $C_{109}H_{99}N_3P_6BF_4Cu_3\cdot 2H_2O$: C, 67.13; H, 5.11; N, 2.16. Found: C, 67.08; H, 5.15; N, 2.28.

$[Cu_3(\mu\text{-}^{n}PrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2]BF_4$ (7). The procedure was similar to that of **5** except phenylacetylene (40.8 mg, 0.4 mmol) was used instead to give greenish yellow crystals of **7**. Yield: 0.18 g (50%). ^{1}H NMR (acetone-d_6): δ 0.0 (m, 15 H, CH_2CH_3), 2.5 (m, 6H, NCH_2), 6.8−7.7 (m, 70H, Ph). Positive FAB-MS: *m/z* 1675 {M$^+$}. Anal. Calcd for $C_{97}H_{91}N_3P_6BF_4Cu_3\cdot H_2O$: C, 65.45; H, 5.23; N, 2.36. Found: C, 65.66; H, 5.49; N, 2.35.

$[Cu_3(\mu\text{-}^{n}PrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4\text{-}NO_2\text{-}p)_2]BF_4$ (8). The procedure was similar to that of **5** except (4-nitrophenyl)acetylene (58.8 mg, 0.4 mmol) was used instead to give red crystals of **8**. Yield: 0.13 g (35%). ^{1}H NMR (acetone-d_6): δ 0.0 (m, 15 H, CH_2CH_3), 2.5 (m, 6H, NCH_2), 7.0−8.5 (m, 68H, Ph). Positive FAB-MS: *m/z* 1764 {M$^+$}. Anal. Calcd for $C_{97}H_{89}N_5O_4P_6BF_4Cu_3$: C, 62.91; H, 4.84; N, 3.78. Found: C, 62.74; H, 5.09; N, 3.65.

$[Cu_3(\mu\text{-}^{n}PrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}py\text{-}p)_2]PF_6$ (9). The procedure was similar to that of **5** except $[Cu_2(\mu\text{-}^{n}PrPNP)_2(MeCN)_2](PF_6)_2$ (0.41 g, 0.3 mmol) and 4-ethynylpyridine (41.2 mg, 0.4 mmol) were used instead to give greenish yellow crystals of **9**. Yield: 0.19 g (52%). ^{1}H NMR (acetone-d_6): δ 0.0 (m, 15 H, CH_2CH_3), 2.5 (m, 6H, NCH_2), 6.8−8.9 (m, 68H, Ph). Positive FAB-MS: *m/z* 1677 {M$^+$}. Anal. Calcd for $C_{95}H_{89}N_5P_7F_6Cu_3\cdot H_2O$: C, 62.00; H, 4.98; N, 3.80. Found: C, 61.74; H, 5.08; N, 3.65.

$[Cu_3(\mu\text{-}^{n}PrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C^{t}Bu)_2]PF_6$ (10). The procedure was similar to that of **9** except 3,3-dimethyl-1-butyne (32.8 mg, 0.4 mmol) was used instead to afford pale green crystals of **10**. Yield: 0.11 g (30%). ^{1}H NMR (acetone-d_6): δ 0.0 (m, 15 H, CH_2CH_3), 1.4 (s, 18H, ^{t}Bu), 2.5 (m, 6H, NCH_2), 7.0−7.5 (m, 60H, Ph). Positive FAB-MS: *m/z* 1635 {M$^+$}. Anal. Calcd for $C_{93}H_{99}N_3P_7F_6Cu_3$: C, 62.75; H, 5.57; N, 2.36. Found: C, 62.35; H, 5.46; N, 2.43.

$[Cu_3(\mu\text{-}^{n}PrPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}n\text{-}C_{10}H_{21})_2]PF_6$ (11). The procedure was similar to that of **9** except 1-dodecyne (66.4 mg, 0.4 mmol) was used instead to afford greenish yellow crystals of **11**. Yield: 0.18 g (45%). ^{1}H NMR (acetone-d_6): δ 0.0 (m, 15 H, CH_2CH_3), 0.7−2.9 (m, 48H, $C_{10}H_{21}$, NCH_2), 6.9−7.6 (m, 60H, PPh_2). Positive FAB-MS: *m/z* 1800 {M$^+$}. Anal. Calcd for $C_{105}H_{123}N_3P_7F_6Cu_3\cdot 6H_2O$: C, 61.33; H, 6.57; N, 2.05. Found: C, 61.11; H, 6.05; N, 2.16.

$[Cu_3(\mu\text{-}ArPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OEt\text{-}p)_2]PF_6$ (12). The procedure was similar to **5** except $[Cu_2(ArPNP)_2(MeCN)_2](PF_6)_2$ (0.43 g, 0.3 mmol) was used instead of $[Cu_2(\mu\text{-}^{n}PrPNP)_2(MeCN)_2](PF_6)_2$ to give yellow crystals. Yield: 0.19 g (47%). ^{1}H NMR (acetone-d_6): δ 1.6 (t, 6H, CH_3), 4.4 (q, 4H, CH_2), 5.5−6.8 (m, 15H, NPh), 6.9−7.4 (m, 60H, PPh_2), 7.8 (dd, 8H, Ph). Positive FAB-MS: *m/z* 1868 {M$^+$}. Anal. Calcd for $C_{110}H_{93}N_3O_2P_7F_6Cu_3$: C, 65.72; H, 4.66; N, 2.09. Found: C, 65.69; H, 4.62; N, 2.12.

$[Cu_3(\mu\text{-}ArPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4\text{-}Ph\text{-}p)_2]PF_6$ (13). The procedure was similar to that of **12** except 4-ethynylbiphenyl (71.2 mg, 0.4 mmol) was used instead. Yellow crystals were obtained. Yield: 0.20 g (49%). ^{1}H NMR (acetone-d_6): δ 5.5−6.8 (m, 15H, NPh), 6.9−7.3 (m, 60H, PPh_2), 7.6−8.3 (m, 18H, Bp). Positive FAB-MS: *m/z* 1932 {M$^+$}. Anal. Calcd for $C_{118}H_{93}N_3P_7F_6Cu_3$: C, 68.32; H, 4.52; N, 2.03. Found: C, 68.09; H, 4.43; N, 2.02.

$[Cu_3(\mu\text{-}ArPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2]PF_6$ (14). The procedure was similar to that of **12** except phenylacetylene (40.8 mg, 0.4 mmol) was used instead. Yellow crystals were obtained. Yield: 0.15 g (40%). ^{1}H NMR (acetone-d_6): δ 5.5−6.8 (m, 15H, NPh), 6.9−7.3 (m, 60H, PPh_2), 7.1−8.1 (m, 10H, Ph). Positive FAB-MS: *m/z* 1780 {M$^+$}. Anal. Calcd for $C_{106}H_{85}N_3P_7F_6Cu_3\cdot H_2O$: C, 65.62; H, 4.48; N, 2.17. Found: C, 65.59; H, 4.35; N, 2.20.

$[Cu_3(\mu\text{-}ArPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C\text{-}n\text{-}C_6H_{13})_2]PF_6$ (15). The procedure was similar to that of **12** except 1-octyne (44.0 mg, 0.4 mmol) was used instead. Yellow crystals were obtained. Yield: 0.17 g (45%). ^{1}H NMR (acetone-d_6): δ 1.4−3.2 (m, 26H, C_6H_{13}), 5.5−6.9 (m, 15H, NPh), 7.0−7.6 (m, 60H, PPh_2). Positive FAB-MS: *m/z* 1795 {M$^+$}. Anal. Calcd for $C_{106}H_{101}N_3P_7F_6Cu_3\cdot 4H_2O$: C, 63.33; H, 5.43; N, 2.09. Found: C, 63.36; H, 5.12; N, 2.19.

$[Cu_3(\mu\text{-}MeArPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4OEt\text{-}p)_2]PF_6$ (16). The procedure was similar to that of **5** except $[Cu_2(MeArPNP)_2(MeCN)_2](PF_6)_2$ (0.44 g, 0.3 mmol) was used instead to give yellow crystals of **16**. Yield: 0.18 g (43%). ^{1}H NMR (acetone-d_6): δ 1.6 (t, 6H, CH_3 of OEt), 1.9 (s, 9H, CH_3 of tolyl), 4.4 (q, 4H, OCH_2), 5.8 (dd, 12H, NPh), 6.8−7.3 (m, 60H, PPh_2), 7.7 (dd, 8H, Ph). Positive FAB-MS: *m/z* 1906 {M$^+$}. Anal. Calcd for $C_{113}H_{99}N_3O_2P_7F_6Cu_3\cdot H_2O$: C, 65.55; H, 4.87; N, 2.00. Found: C, 65.37; H, 4.82; N, 2.02.

$[Cu_3(\mu\text{-}MeArPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4\text{-}Ph\text{-}p)_2]PF_6$ (17). The procedure was similar to that of **16** except 4-ethynylbiphenyl (71.2 mg, 0.4 mmol) was used instead to afford yellow crystals of **17**. Yield: 0.17 g (41%). ^{1}H NMR (acetone-d_6): δ 1.9 (s, 9H, CH_3 of tolyl), 5.9 (dd, 12H, NPh), 6.9−7.3 (m, 60H, PPh_2), 7.6−8.3 (m, 18H, Bp). Positive FAB-MS: *m/z* 1973 {M$^+$}. Anal. Calcd for $C_{121}H_{99}N_3P_7F_6Cu_3\cdot 3H_2O$: C, 66.96; H, 4.84; N, 1.94. Found: C, 66.87; H, 4.65; N, 1.97.

$[Cu_3(\mu\text{-}MeArPNP)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_2]PF_6$ (18). The procedure was similar to that of **16** except phenylacetylene (40.8 mg, 0.4 mmol) was used instead to yield yellow crystals of **18**.

Table 1. Photophysical Data for Complexes 1−20

complex	medium (T/K)	absorption λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1})	emission λ_{em}/nm (τ_0/μs)
1	CH_2Cl_2 (298)	262 (20 920)	
		330 (9 180)	
	acetone (298)		425, 515
	solid (298)		449 (0.35)
	solid (77)		451
	MeOH/EtOH (77) (1:4 v/v)		420 sh, 457
2	CH_2Cl_2 (298)	266 (41 390)	
		332 (14 280)	
	acetone (298)		421
	solid (298)		419, 500 sh (0.20)
	solid (77)		463, 530
3	CH_2Cl_2 (298)	268 (55 500)	
		330 (18 240)	
	acetone (298)		416
	solid (298)		396 (<0.1)
	solid (77)		436
4	CH_2Cl_2 (298)	262sh (25 260)	
		340 (9 810)	
	acetone (298)		421
	solid (298)		416 (0.23)
	solid (77)		441, 476
5	CH_2Cl_2 (298)	274 (44 530)	
		310 (32 890)	
		378 (6 760)	
	acetone (298)		467 (4.4)
	solid (298)		459 (3.1)[a]
	solid (77)		453 sh, 482
	MeOH/EtOH (77) (1:4 v/v)		445, 478
6	CH_2Cl_2 (298)	272 (67 770)	
		336 sh (53 220)	
		348 (54 810)	
		388 sh (7 750)	
	acetone (298)		516, 554, 615 sh (26.1)
	solid (298)		521, 558sh, 615 sh (6.6)
	solid (77)		522, 565, 615 sh
	MeOH/EtOH (77) (1:4 v/v)		510, 546, 615 sh
7	CH_2Cl_2 (298)	264 sh (49 740)	
		304 sh (34 470)	
		372 (8 540)	
	acetone (298)		465 (3.4)
	solid (298)		461 (4.0)[a]
	solid (77)		459, 485, 495, 507
	MeOH/EtOH (77) (1:4 v/v)		445, 479
8	CH_2Cl_2 (298)	260 sh (18 380)	
		316 (8 420)	
		378 sh (11 870)	
		402 sh (13 000)	
	acetone (298)		454 (1.6)
	solid (298)		400 (4.0)
	solid (77)		400
	MeOH/EtOH (77) (1:4 v/v)		453, 671
9	CH_2Cl_2 (298)	260 sh (49 310)	
		326 (30 540)	
		390 sh (4 740)	
	acetone (298)		489 (3.2)
	solid (298)		487 (3.9)
	solid (77)		475, 509
	MeOH/EtOH (77) (1:4 v/v)		513
10	CH_2Cl_2 (298)	244 sh (57 650)	
		266 sh (49 160)	
		312 sh (12 280)	
		370 (9 300)	
	acetone (298)		464 (3.2)
	solid (298)		459 (1.0, 5.3)
	solid (77)		485
	MeOH/EtOH (77) (1:4 v/v)		474
11	CH_2Cl_2 (298)	272 (39 160)	
		316 sh (10 700)	
		376 (8 220)	
	acetone (298)		482 (1.0)
	solid (298)		498 (2.7)[a]
	solid (77)		496
	MeOH/EtOH (77) (1:4 v/v)		482, 503 sh
12	CH_2Cl_2 (298)	280 (56 030)	
		306 sh (45 950)	
		378 (11 620)	
	acetone (298)		484, 646 (7.0)
	solid (298)		469 (0.3)
	solid (77)		493

Table 1. (Continued)

complex	medium (*T*/K)	absorption λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1})	emission λ_{em}/nm (τ_0/μs)
13	CH_2Cl_2 (298)	268 sh (45 990) 328 sh (38 590) 346 sh (40 480) 382 sh (9 060)	
	acetone (298)		516, 552, 615 sh (35.0)
	solid (298)		467, 516, 550 sh (5.5)
	solid (77)		515, 560, 615 sh
14	CH_2Cl_2 (298)	280 sh (53 270) 300 sh (42 360) 378 (11 370)	
	acetone (298)		461, 633 (4.8)
	solid (298)		464, 550 sh (5.6)
	solid (77)		462 sh, 487
15	CH_2Cl_2 (298)	268 sh (45 020) 304 sh (17 020) 380 (11 420)	
	acetone (298)		471, 670 (3.4)
	solid (298)		418, 438 sh, 467 (1.2)
	solid (77)		501
16	CH_2Cl_2 (298)	278 (70 850) 304 sh (49 370) 380 (12 290)	
	acetone (298)		464, 632 (2.5)
	solid (298)		466, 550 sh (4.8)
	solid (77)		491
17	CH_2Cl_2 (298)	270 (73 720) 332 sh (57 820) 348 (60 060) 386 sh (11 320)	
	acetone (298)		516, 552, 615 sh (30.0)
	solid (298)		515, 553, 615 sh (10.6)
	solid (77)		517, 557, 615 sh
18	CH_2Cl_2 (298)	270 sh (10 370) 302 sh (38 930) 380 (10 310)	
	acetone (298)		469, 613 (6.4)
	solid (298)		482 (1.4)
	solid (77)		495
19	CH_2Cl_2 (298)	278 (32 010) 306 sh (21 860) 380 (5530)	
	acetone (298)		470 sh, 623 (6.4)
	solid (298)		467, 550 sh (6.6)
	solid (77)		500
20	CH_2Cl_2 (298)	268 sh (57 920) 326 (46 010) 346 (47 890) 382 sh (9 790)	
	acetone		470 sh, 568 (30.0)
	solid (298)		471, 516, 545, 615 sh (6.3)
	solid (77)		516, 556, 615 sh

[a] Slight deviation from mono-exponential character.

Yield: 0.18 g (45%). ^{1}H NMR (acetone-d_6): δ 1.9 (s, 9H, CH_3 of tolyl), 5.9 (dd, 12H, NPh), 6.9−7.3 (m, 60H, PPh_2), 7.7−8.1 (m, 10H, Ph). Positive FAB-MS: *m*/*z* 1818 {M$^+$}. Anal. Calcd for $C_{109}H_{91}N_3P_7F_6Cu_3{\cdot}H_2O$: C, 66.04; H, 4.70; N, 2.12. Found: C, 65.86; H, 4.76; N, 2.15.

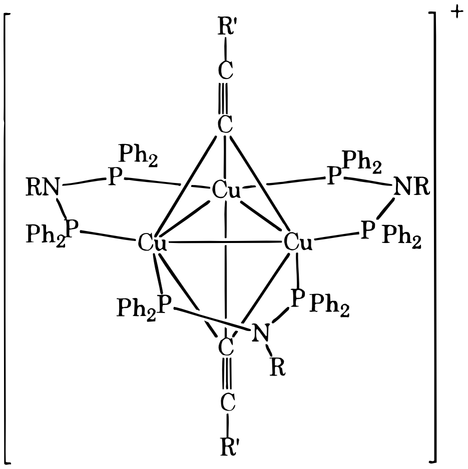
$[Cu_3(\mu\text{-FArPNP})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CC_6H_4OEt\text{-}p)_2]PF_6$ (19). The procedure was similar to that of **5** except $[Cu_2(FArPNP)_2(MeCN)_2](PF_6)_2$ (0.44 g, 0.3 mmol) was used instead to give yellow crytals of **19**. Yield: 0.18 g (44%). ^{1}H NMR (acetone-d_6): δ 1.6 (t, 6H, CH_3), 4.4 (q, 4H, OCH_2), 5.5−6.3 (m, 12H, NPh), 6.9−7.3 (m, 60H, PPh_2), 7.8 (dd, 8H, Ph). Positive FAB-MS: *m*/*z* 1918 {M$^+$}. Anal. Calcd for $C_{110}H_{90}N_3O_2P_7F_9Cu_3$: C, 64.00; H, 4.36; N, 2.04. Found: C, 63.67; H, 4.23; N, 2.01.

$[Cu_3(\mu\text{-FArPNP})_3(\mu_3\text{-}\eta^1\text{-C}{\equiv}CC_6H_4\text{-Ph-}p)_2]PF_6$ (20). The procedure was similar to that of **19** except 4-ethynylbiphenyl (71.2 mg, 0.4 mmol) was used instead to give yellow crystals of **20**. Yield: 0.20 g (48%). ^{1}H NMR (acetone-d_6): δ 5.5−6.3 (m, 12H, NPh), 6.9−7.4 (m, 60H, PPh_2), 7.5−8.4 (m, 18H, Bp). Positive FAB-MS: *m*/*z* 1983 {M$^+$}. Anal. Calcd for $C_{118}H_{90}N_3P_7F_9Cu_3$: C, 66.59; H, 4.23; N, 1.98. Found: C, 66.74; H, 4.30; N, 1.96.

Physical Measurements and Instrumentation. UV−visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra 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 either a JEOL JNM-GSX270 or a Bruker DPX300 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 Butterworth Laboratories Ltd.

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, 2 Gs/s) digital oscilloscope and analyzed using a program for exponential fits. Time-resolved transient absorption spectroscopy was performed using the 355 nm output (third harmonic) of the Quanta-Ray Q-switched GCR-150 pulsed Nd−YAG laser as the excitation source, with the monitoring light beam generated from a 250 W quartz−tungsten−halogen lamp placed perpendicular to the excitation beam. The output of the quartz−tungsten−halogen lamp with wavelength selected

Chart 1



5: R = $CH_2CH_2CH_3$, R' = C_6H_4OEt-*p*
6: R = $CH_2CH_2CH_3$, R' = C_6H_4Ph-*p*
7: R = $CH_2CH_2CH_3$, R' = Ph
8: R = $CH_2CH_2CH_3$, R' = C_6H_4-NO_2-*p*
9: R = $CH_2CH_2CH_3$, R' = py-*p*
10: R = $CH_2CH_2CH_3$, R' = ^{t}Bu
11: R = $CH_2CH_2CH_3$, R' = *n*-$C_{10}H_{21}$
12: R = Ph, R' = C_6H_4OEt-*p*
13: R = Ph, R' = C_6H_4Ph-*p*
14: R = Ph, R' = Ph
15: R = Ph, R' = *n*-C_6H_{13}
16: R = C_6H_4-CH_3-*p*, R' = C_6H_4OEt-*p*
17: R = C_6H_4-CH_3-*p*, R' = C_6H_4-Ph-*p*
18: R = C_6H_4-CH_3-*p*, R' = Ph
19: R = C_6H_4-F-*p*, R' = C_6H_4OEt-*p*
20: R = C_6H_4-F-*p*, R' = C_6H_4Ph-*p*

by passing through two monochromators (Oriel 77250, $^1/_8$ m, and 77200, $^1/_4$ m). The transient absorption signals were detected by a Hamamatsu R928 photomultiplier tube and the signal amplified using a Tektronix AM 502 differential amplifier and digitized on a Tektronix Model TDS-620A (500 MHz, 2GS/s) digital oscilloscope interfaced to an IBM personal computer for data acquisition and analysis. The transient absorption difference spectra were generated using the point-to-point method.

All solutions for photophysical studies were prepared under vacuum in a 10 cm^3 round-bottom flask equipped with a side arm 1 cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four 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 486 DX2 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. Ag/$AgNO_3$ (0.1 mol dm^{-3} in 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 $^nBu_4NPF_6$). 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.[11]

Results and Discussion

Analogous to the preparation of the dppm analogues,[3a,d,4b,c] the *triangulo*-Cu_3 complexes **5**−**20** $[Cu_3(\mu\text{-PNP})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_2]^+$ (Chart 1) were prepared by the reaction of the respective binuclear copper(I) complexes **1**−**4**, $[Cu_2(\mu\text{-PNP})_2(MeCN)_2]^{2+}$ with alkynes in the presence of an excess of KOH in THF under anaerobic and anhydrous conditions. All the newly synthesized complexes gave satisfactory elemental analyses and were characterized by positive FAB-MS and ^{1}H NMR spectroscopy.

The electronic absorption and photophysical data for the newly synthesized copper(I) complexes are summarized in Table 1. Several characteristic peaks can be observed in the series of trinuclear copper(I) acetylide complexes with ^{n}PrPNP as bridging ligand. For the precursor dinuclear complex **1**, the dominant band at 262 nm is likely to arise from an intraligand $\pi \rightarrow \pi^*$ transition which has been red-shifted from 253 nm in the free ligand to 262 nm in complex **1**. The lower energy band at 330 nm is possibly assigned as a metal-perturbed intraligand ($\sigma \rightarrow a_\pi$) transition.[12] Similar assignments have been made for a related $[Cu_2(dppm)_2(MeCN)_4]^{2+}$ complex.[13] The absorption spectra for the trinuclear acetylide complexes show, in addition to the absorption bands at *ca.* 260−274 and 304−336 nm, low-energy bands at *ca.* 370−402 nm. Such bands, which are absent in the precursor complexes, are likely to involve the trinuclear acetylide unit. The energies of this band do not differ much upon changing the acetylide unit, though a close scrutiny suggests a very subtle trend. Complexes with more electron deficient acetylides such as (4-nitrophenyl)acetylide in **8** have the lowest absorption energy, while those of the relatively more electron-rich acetylide such as *tert*-butylacetylide in **10** are highest in energy. Such trends are in line with the π^* energy levels of the acetylide ligands. It is likely that the absorption band at 370−402 nm involves a metal-perturbed $\pi \rightarrow \pi^*$ ($RC\equiv C^-$) or MLCT [$d\sigma^*$(Cu) $\rightarrow \pi^*(RC\equiv C^-)$] transition.

Similarly, complexes **2**−**4** all show absorption bands at *ca.* 260 and 330 nm, which have been assigned accordingly to a $\pi \rightarrow \pi^*$ and $\sigma \rightarrow a_\pi$ transition, respectively. The low-energy bands at *ca.* 380 nm in the acetylide complexes of bridging ArPNP, MeArPNP, and FArPNP ligands are assigned similarly to that for complexes **5**−**11**. An alternative assignment of the low-energy absorption band as a metal cluster centered d−s transition is also likely in view of the relative insensitivity of the transition energy to the nature of the acetylide.

Excitation of the trinuclear copper(I) acetylide complexes at $\lambda > 350$ nm results in long-lived dual luminescence, typical of this class of compounds.[3a,b,d,14] The long-lived excited states in the microsecond range are suggestive of a triplet parentage.

A representative emission spectrum of complex **19**

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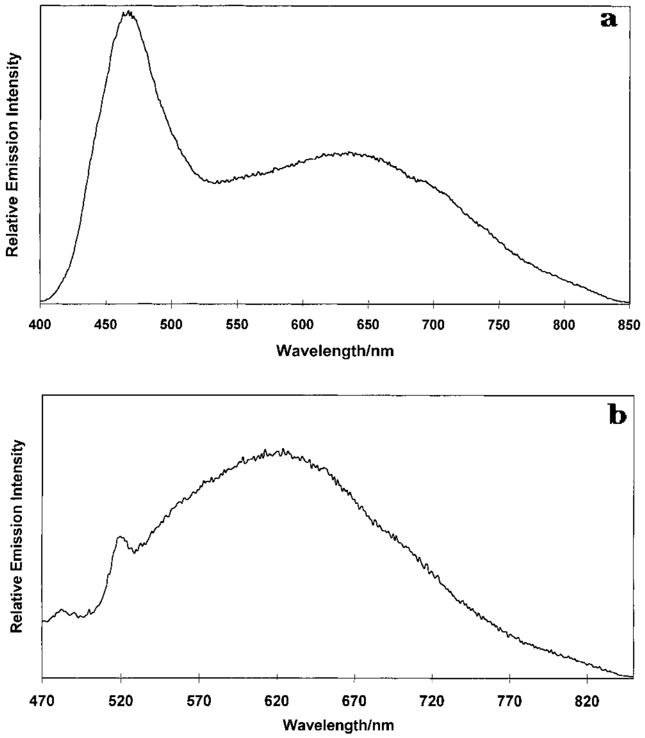

Figure 1. Emission spectrum of **19** in degassed acetone at 298 K with excitation wavelength at (a) 370 and (b) 450 nm.

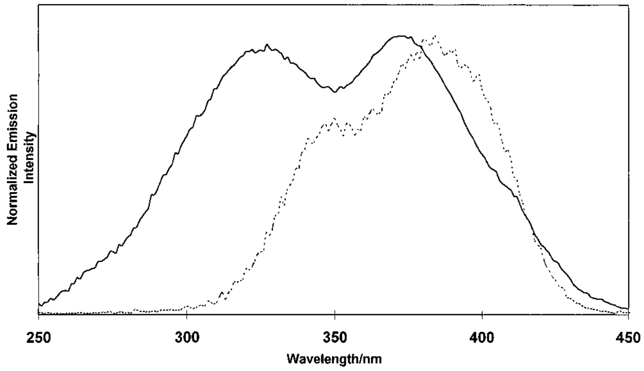

Figure 2. Excitation spectra of **16** in degassed acetonitrile at 298 K with emission wavelengths monitored at 470 (—) and 660 nm (- - -).

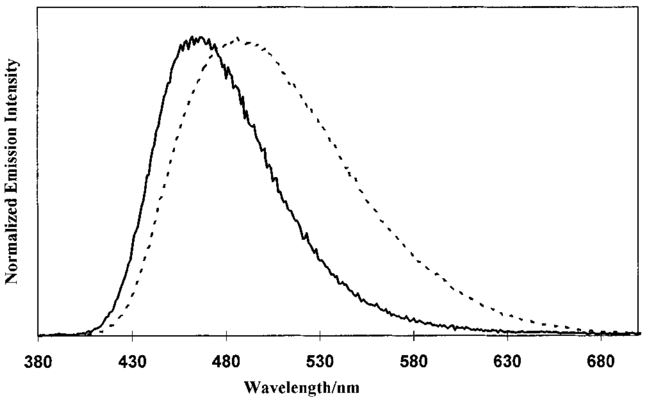

Figure 3. Emission spectra of **7** (—) and **11** (- - -) in degassed acetone at 298 K.

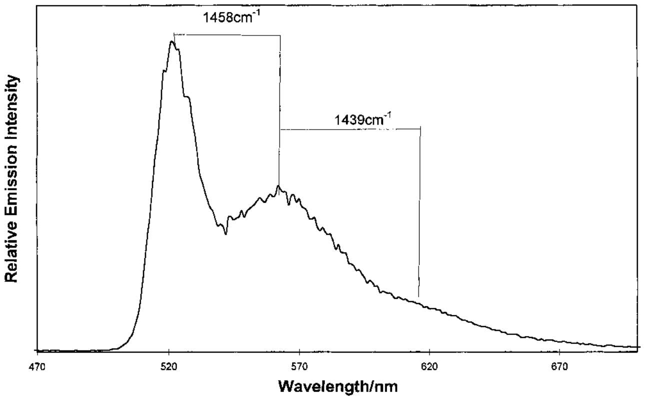

Figure 4. Emission spectrum of **6** in the solid state at 77 K.

excited at 370 nm is shown in Figure 1a. Figure 1b shows the emission spectrum with excitation wavelength at 450 nm. The low-energy emission band at *ca.* 613−670 nm is probably derived from a ligand-to-metal charge transfer LMCT [$\mathrm{RC{\equiv}C^-} \rightarrow \mathrm{Cu_3}$] state mixed with a metal cluster centered d−s state. Similar assignments have been suggested in other related systems.[3a,c−g] Figure 2 shows the typical excitation spectra of complex **16** monitored at the respective high-energy and low-energy emission bands. An excited state of large LMCT parentage is substantiated on the following grounds. Complexes with electron-rich acetylides are found to emit at lower energies. For example, the emission energies for the series of complexes with ArPNP and MeArPNP as bridging ligands follow the order **14** > **12** > **15** and **18** > **16**. This is consistent with the donating ability of the acetylide ($\mathrm{RC{\equiv}C^-}$) ligand which decreases in the order R = $\mathrm{C_6H_{13}}$ > $\mathrm{C_6H_4}$-OEt-*p* > $\mathrm{C_6H_5}$. On the other hand, the trend in the ^{n}PrPNP series is less obvious and less well defined. The emission spectra of complexes **7** and **11** are shown in Figure 3. The emission bands are highly unsymmetrical with the low-energy emission only appearing as a shoulder at *ca.* 500−550 nm to the red of the high-energy emission band. It is likely that the intense high-energy band at *ca.* 460−465 nm, which is derived from the ligand-centered ^{n}PrPNP ligand, has obscured the low-energy emission of large LMCT [$\mathrm{RC{\equiv}C^-} \rightarrow \mathrm{Cu_3}$] parentage. However, there are certain exceptions to the assignments. For complexes **6**, **13**, **17**, and **20**, which contain the biphenylacetylide unit, the emission spectra are very similar with vibronically structured bands. Figure 4 shows the emission spectrum of complex **6**. The vibrational progressional spacings of *ca.* 1400−1500 cm^{-1} are typical of the $\nu(\mathrm{C}{\cdots}\mathrm{C})$ stretching frequency of the biphenyl ring. It is likely that such emission originates from the ligand-centered biphenylacetylide unit. Similarly, for complex **8** which contains the (*p*-nitrophenyl)acetylide ligand, a low-energy emission band appears at *ca.* 671 nm upon cooling at 77 K in MeOH−EtOH glass, which is typical of the (*p*-nitrophenyl)acetylide unit and is indicative of its ligand-centered origin. Thus, it is likely that for the very electron deficient acetylides, such as biphenylacetylide and (*p*-nitrophenyl)acetylide, the lowest lying excited states are no longer LMCT in nature, instead they are dominated by an intraligand $\pi \rightarrow \pi^*$ ($\mathrm{RC{\equiv}C^-}$) character.

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(14) Comparison of the emissive lifetimes of the high-energy emission band with those of the free ligands and the binuclear copper(I) precursors, as well as their emission and excitation spectra, did not favor the presence of contamination by impurities such as free ligands and precursor complexes.

Table 2. Electrochemical Data for Complexes 5−20

complex	$E_{1/2}$(V vs Fc$^+$/Fc)[a]	complex	$E_{1/2}$(V vs Fc$^+$/Fc)[a]
5	+0.30	**13**	+0.37
6	+0.34	**14**	+0.41
7	+0.32	**15**	+0.31
8	+0.45	**16**	+0.35
9	+0.44	**17**	+0.37
10	+0.29	**18**	+0.38
11	+0.23	**19**	+0.40
12	+0.38	**20**	+0.44

[a] In MeCN (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$), glassy-carbon electrode, scan rate 100 mV s^{-1}, 298 K. For these quasi-reversible couples, $E_{1/2}$ is the average of E_{pa} and E_{pc}.

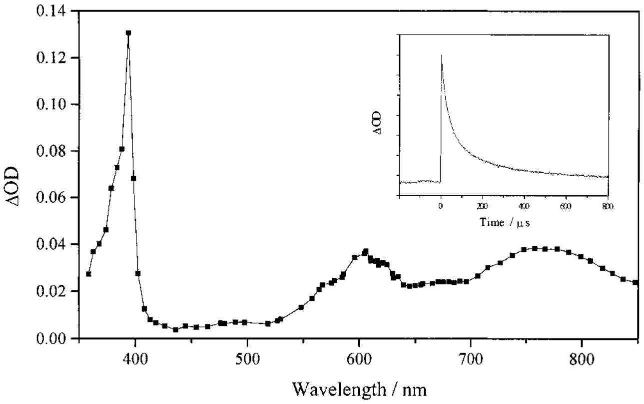

Figure 5. Transient absorption difference spectrum recorded 20 μs after laser flash for a degassed acetonitrile of **7** (1 × 10^{-4} M) and MV^{2+} (0.0033 M) at 298 K. The inset shows the decay trace of MV$^{•+}$ at 394 nm.

A comparison of the emission energies for the complexes with the same acetylide but different PNP bridging ligands, such as **5**, **12**, and **16**, shows that the emission energies follow the order **5** > **16** > **12**, which is in line with the electron richness of the ligand: ^{n}PrPNP > MeArPNP > ArPNP. It is likely that the presence of an electron-rich substituent on the PNP ligand would destabilize the metal-centered LUMO, leading to a higher energy LMCT transition, and hence a higher lying LMCT emissive state. Although an alternative assignment of the emissive state as derived from an acetylide-to-phosphine ligand-to-ligand charge transfer (LLCT) transition could also account for the observed trend, we favor the LMCT assignment in view of the small change in emission energies observed along the series, suggesting that the PNP ligands are only indirectly involved in the transition. However, one should be aware that the assignments of electronic transitions between metal and/or ligand localized orbitals are only rough approximations because of the possible extensive orbital mixing in these complexes.

Cyclic voltammetric studies of complexes **5**−**20** in MeCN (0.1 M ^{n}Bu$_4$NPF$_6$) show the presence of a quasi-reversible oxidation couple, assignable to a one-electron oxidation at the copper(I) center. The electrochemical data for complexes **5**−**20** are shown in Table 2. Further oxidation of the cluster probably resulted in decomposition, as suggested by the irreversibility of the couples at more anodic potentials. Similar assignments have also been suggested for the trinuclear copper(I) acetylide complexes with dppm as bridging ligand.[3a,d] In general, complexes with electron-rich acetylides are found to be more easily oxidized, with the potential values decreasing for the series **8** ≥ **9** > **6** > **7** > **5** ≥ **10** > **11**; **14** > **12** > 15; **18** ≥ **17** > **16**, and **20** > **19**. The observed increased ease of oxidation is in line with the increasing electron-donating ability of the acetylide ligands, which would preferentially stabilize the higher oxidation state of copper(II). Moreover, for the same acetylide but with different PNP ligands, it is found that the ease of oxidation is in the order **7** > **18** > **14**; **5** > **16** > **12** > **19** and **6** > 17 ≈ **13** > **20**, which is in line with the electron richness of the PNP ligand with ^{n}PrPNP > MeArPNP > ArPNP > FArPNP; the more electron rich of which would preferentially stabilize the copper(II) center to a larger extent.

The trinuclear copper(I) acetylide complexes have also been found to be strong reducing agents in the excited state. Laser flash photolysis of a degassed acetone solution (0.1 M ^{n}Bu$_4$NPF$_6$) of complex 7 with 4-(methoxycarbonyl)-*N*-methylpyridinium salt generated a transient absorption difference spectrum with bands at *ca.* 400 and 770 nm. The 400 nm band is characteristic of the pyridinyl radical.[15] Similarly, the transient absorption difference spectrum of complex **7** with methyl viologen in degassed acetone (0.1 M ^{n}Bu$_4$NPF$_6$) shown in Figure 5 shows intense absorption bands at *ca.* 395 and 605 nm which are typical of MV$^{•+}$ radical,[16] and a band at *ca.* 770 nm

$$[\mathrm{Cu_3(^nPrPNP)_3(PhC{\equiv}C)_2}]^{+*} + \mathrm{MV^{2+}} \rightarrow [\mathrm{Cu_3(^nPrPNP)_3(PhC{\equiv}C)_2}]^{2+} + \mathrm{MV^{\bullet+}}$$

It is likely that the presence of the 770 nm band in both spectra, which is not characteristic of the pyridinyl radicals, is derived from the intervalence charge transfer transition of the mixed valence Cu^{I}Cu^{I}Cu^{II} species[3b,d,17]

$$\mathrm{Cu^ICu^ICu^{II}} + h\nu \rightarrow \mathrm{Cu^ICu^{II}Cu^I}*$$

The transient signal decays via second-order kinetics, in line with the back electron transfer reaction. The decay trace of MV$^{•+}$ radical at 394 nm is shown in the inset diagram of Figure 5

$$[\mathrm{Cu_3(PNP)_3(PhC{\equiv}C)_2}]^{2+} + \mathrm{MV^{\bullet+}} \rightarrow [\mathrm{Cu_3(PNP)_3(PhC{\equiv}C)_2}]^{+} + \mathrm{MV^{2+}}$$

This provides spectroscopic evidence for the electron transfer quenching mechanism for the bimolecular quenching reactions of the phosphorescent state with pyridinium acceptors.

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