Can 2-pyridyl-1,2,3-triazole “click” ligands be used to develop Cu(I)/Cu(II) molecular switches?

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1 Experimental

1.1 General

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. 2,6-bis((trimethylsilyl)ethynyl)pyridin-4-yl-methanol (1), 5-ethynyl-2,2′-bipyridine, 6,6′-dimesityl-2,2′-bipyridine (diMesbpy), 2-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (pytri), 5-(1-benzyl-1H-1,2,3-triazol-4-yl)-2,2′-bipyridine (bpytri), 2,6-bis(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (tripy), [Cu(diMesbpy)(MeCN)2](PF6), [Cu(bpy)(diMesbpy)](PF6) and [Cu(pytri)(diMesbpy)](PF6) were synthesised according to literature methods. Solvents were laboratory reagent grade, with the exception of dry toluene which was obtained by passing the solvent through an activated alumina column on a PureSolv solvent purification system (Innovative Technologies, Inc., Amesbury, MA). Pet. Ether refers to the fraction of petroleum ether boiling in the range 40-60 °C. 1H and 13C NMR spectra were recorded on either a 400 MHz Varian 400 MR or Varian 500 MHz VNMRS spectrometer. Chemical shifts are reported in parts per million and referenced to residual solvent peaks (CDCl3: 1H δ 7.26 ppm, 13C δ 77.16 ppm; d6-acetone: 1H δ 2.05 ppm, 13C δ 29.84, 206.26 ppm; d6-DMSO: 1H δ 2.50 ppm, 13C δ 39.52). Coupling constants (J) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, q = quartet, t = triplet, dt = double triplet, d = doublet, dd = double doublet, s = singlet. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. High resolution electrospray ionisation mass spectra (HRESI-MS) were collected on either a Bruker microTOF-Q spectrometer or a Shimadzu LCMS-9030 spectrometer.

Safety Note: Whilst no problems were encountered during the course of this work, azide compounds are potentially explosive and appropriate precautions should be taken when working with them.
1.2 (2,6-diethynyl)pyridin-4-yl)methanol (2)

1 (531 mg, 1.76 mmol) and Na$_2$CO$_3$ (417 mg, 3.88 mmol) were stirred in MeOH (20 mL) at room temperature for 30 minutes. After filtering through celite and removal of the solvent in vacuo, the light brown residue was dissolved in CHCl$_3$ (50 mL) and washed with water (50 mL) and brine (50 mL). The pale-yellow solution was dried over sodium sulfate and the solvent removed in vacuo to provide the product as a light brown solid. Yield: 246 mg, 89%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ 7.47 (s, 2H, H$_b$), 4.74 (s, 2H, H$_a$), 3.14 (s, 2H, H$_c$). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ 151.3, 142.8, 124.6, 82.2, 62.8, 29.5. HRESI-MS: $m/z$ = 156.0432 [2 - H] (calc. C$_{10}$H$_6$NO, 156.0454).

Figure S1 - $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of 2.

Figure S2 - $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of 2.
Figure S3 – HRESI-MS (DCM/MeOH) of 2.
1.3  (2,6-bis-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridin-4-yl)methanol (3)

Sodium azide (122 mg, 1.87 mmol), sodium L-ascorbate (176 mg, 0.891 mmol), CuSO₄•5H₂O (111 mg, 0.445 mmol) and benzyl bromide (305 mg, 1.78 mmol) were added to a DMF/water (4:1, 60 mL) solution of 2 (140 mg, 0.891 mmol). The resulting solution was stirred at room temperature for 20 hours, DCM (100 mL) and 0.1 M EDTA/NH₄OH (aq) (75 mL) were then added and the biphasic mixture stirred for a further 2 hours. The organic phase was extracted and washed with washed with 0.1 M EDTA/NH₄OH (aq) (50 mL), water (2 x 75 mL) and brine (2 x 100 mL), dried over sodium sulfate and the solvent removed under reduced pressure. Column chromatography (silica, gradient: 10% acetone/90% DCM to 100% acetone) provided the product as a white solid. Yield: 320 mg, 84%. ¹H NMR (400 MHz, d₆-DMSO, 298 K) δ 8.66 (s, 2H, Hᵥ), 7.94 (s, 2H, Hᵥ), 7.44 – 7.30 (m, 10H, Hₑ-g), 5.69 (s, 4H, Hᵤ), 5.57 (t, J = 5.8 Hz, 1H, HᵥHᵤ), 4.67 (d, J = 5.8 Hz, 2H, HᵥHᵤ). ¹³C (¹H) NMR (100 MHz, d₆-DMSO, 298 K) δ 154.0, 149.6, 147.5, 136.0, 128.8, 128.2, 127.9, 123.6, 115.7, 61.6, 53.1. HRESI-MS: m/z = 424.1854 [3 + H]⁺ (calc. C₂₄H₂₂N₇O₂, 424.1880), 446.1677 [3 + Na]⁺ (calc. C₂₄H₂₁N₇ONa, 446.1700). Anal. calc. for C₂₄H₂₁N₇O·0.5H₂O: C, 66.65; H, 5.13; N, 22.67%. Found: C, 66.93; H, 5.29; N, 22.28%.

Figure S4 - ¹H NMR (400 MHz, d₆-DMSO, 298 K) of 3.
Figure S5 - $^{13}$C ($^1$H) NMR (100 MHz, $d_6$-DMSO, 298 K) of 3.

Figure S6 – HRESI-MS (DCM/MeOH) of 3.
1.4 2,6-bis(1-benzyl-1H-1,2,3-triazol-4-yl)-4-(bromomethyl)pyridine (4a)

Dry DCM (150 mL) was added to 3 (802 mg, 1.89 mmol), triphenylphosphine (596 mg, 2.27 mmol) and carbon tetrabromide (942 mg, 2.84 mmol) under an N₂ atmosphere. The resulting solution was stirred at room temperature under N₂ for 19 hours, at which point the solvent was removed under reduced pressure. Column chromatography (silica, 15% acetone/85% DCM) provided the product as a white powder. Yield: 644 mg, 70%. ¹H NMR (400 MHz, d₆-DMSO, 298 K) δ 8.70 (s, 2H, H₉), 8.04 (s, 2H, H₆), 7.42 – 7.33 (m, 10H, Hₑ⁻ᵍ), 5.71 (s, 4H, H₄), 4.84 (s, 2H, H₃). ¹³C {¹H} NMR (100 MHz, d₆-DMSO, 298 K) δ 150.3, 148.9, 147.0, 135.9, 128.8, 128.2, 127.9, 123.8, 118.4, 53.1, 31.6. HRESI-MS: m/z = 486.1052 [4a + H]⁺ (calc. C₂₄H₂₂N₇Br, 486.1036), 508.0868 [4a + Na]⁺ (calc. C₂₄H₂₀N₇BrNa, 508.0856). Anal. calc. for C₂₄H₂₀N₇Br·1acetone: C, 59.56; H, 4.81; N, 18.01%. Found: C, 59.54; H, 5.04; N, 18.05%.

![Figure S7](image1)

Figure S7 - ¹H NMR (400 MHz, d₆-DMSO, 298 K) of 4a.

![Figure S8](image2)

Figure S8 - ¹³C{¹H} NMR (100 MHz, d₆-DMSO, 298 K) of 4a.
Figure S9 – HREESI-MS (DCM/MeOH) of 4a.
1.5 (2,6-bis(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine-4-yl)methyl 4-methylbenzenesulphonate (4b)

Sodium hydroxide (94 mg, 2.36 mmol) was added to an Ar degassed THF (30 mL) solution of 3 (500 mg, 1.18 mL) and cooled to 0°C. An Ar degassed THF (30 mL) solution of p-toluenesulphonyl chloride (225 mg, 1.18 mmol) was added dropwise and the resulting solution allowed to warm to room temperature. After stirring for 2 hours, diethyl ether (50 mL) and 3M NaOH (aq) (20 mL) were added, and the organic phase extracted. The organic layer was washed with water (50 mL) and brine (50 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure to provide the product as a white solid. Yield: 594 mg, 87%. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ 8.03 (s, 2H, H$_c$), 7.93 (s, 2H, H$_b$), 7.84 (d, $J = 8.3$ Hz, 2H, H$_h$), 7.40-7.27 (m, 12H, H$_{e-g,i}$), 5.56 (s, 4H, H$_d$), 5.12 (s, 2H, H$_a$), 2.38 (s, 3H, H$_j$). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ 150.5, 148.2, 145.4, 144.5, 134.6, 132.7, 130.2, 129.9, 129.0, 128.3, 128.2, 122.4, 117.7, 69.4, 54.5, 21.7. HRESI-MS: $m/z$ = 578.1947 [4b + H]$^+$ (calc. C$_{31}$H$_{28}$N$_7$O$_3$S, 578.1969), 600.1766 [4b + Na]$^+$ (calc. C$_{31}$H$_{27}$N$_7$O$_3$SNa, 600.1788). Anal. calc. for C$_{31}$H$_{27}$N$_7$O$_3$S: C, 64.46; H, 4.71; N, 16.97%. Found: C, 64.29; H, 4.67; N, 17.36%.

Figure S10 - $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of 4b.
Figure S11 - $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of 4b.

Figure S12 – HRESI-MS (CHCl$_3$/MeOH) of 4b.
1.6 4-(azidomethyl)-2,6-bis(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (5)

A) Synthesised from 4a:
A DMF (5 mL) solution of 4a (155 mg, 0.319 mmol) and sodium azide (31 mg, 0.477 mmol) were stirred at room temperature for 18 hours. Water (80 mL) was added, and the solution stirred for a further 1 hour. The white precipitate was collected by vacuum filtration and washed with water (2 x 10 mL). The solid was dissolved in DCM/isopropanol (3:1, 120 mL) then dried over sodium sulfate. The solvent was removed under reduced pressure providing the product as an off white solid. Yield: 117 mg, 82%.

B) Synthesised from 4b:
A DMF (5 mL) solution of 4b (50 mg, 0.087 mmol) and sodium azide (6.20 mg, 0.095 mmol) were stirred at room temperature for 21 hours. DCM/isopropanol (3:1, 100 mL) and water (80 mL) was added, and the organic phase extracted. The organic layer was washed with brine (2 x 50 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure to provide the product as an off white solid. Yield: 39 mg, 97%.

1H NMR (400 MHz, CDCl3, 298 K) δ 8.09 (s, 2H, Hc), 8.06 (s, 2H, Hb), 7.39 – 7.35 (m, 6H, Hf,g), 7.31 – 7.27 (m, 4H, He), 5.57 (s, 4H, Hd), 4.51 (s, 2H, Ha).

13C {1H} NMR (100 MHz, CDCl3, 298 K) δ 150.6, 148.2, 146.8, 134.6, 129.3, 129.0, 128.2, 122.6, 118.2, 54.5, 53.6. HRESI-MS: m/z = 449.1938 [5 + H]+ (calc. C24H21N10, 449.1945), 471.1758 [5 + Na]+ (calc. C24H20N10Na, 471.1765). Anal. calc. for C24H20N10·2H2O: C, 59.49; H, 4.99; N, 28.91%. Found: C, 59.12; H, 5.28; N, 29.02%.

Figure S13 - 1H NMR (400 MHz, CDCl3, 298 K) of 5.
Figure S14 - $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$, 298 K) of 5.

Figure S15 – HRESI-MS (DCM/MeOH) of 5.
1.7 2,6-bis(1-benzyl-1H-1,2,3-triazol-4-yl)-4-((4-(pyridine-2-yl)-1H-1,2,3-triazol-1-yl)methyl)pyridine (L1)

A DMF/water (4:1, 25 mL) suspension of 5 (480 mg, 1.07 mmol), sodium L-ascorbate (212 mg, 1.07 mmol), CuSO₄•5H₂O (134 mg, 0.535 mmol) and 2-ethynylpyridine (132 mg, 1.28 mmol) was stirred at room temperature for 24 hours. Additional sodium L-ascorbate (120 mg) and CuSO₄•5H₂O (70 mg) were added and the suspension stirred for a further 14 hours. 0.1 M EDTA/NH₄OH (aq) (40 mL) and DCM (40 mL) were added and the biphasic solution stirred for 1.5 hours. The organic phase was extracted and washed with 0.1 M EDTA/NH₄OH (aq) (3 x 50 mL), water (100 mL) and brine (2 x 100 mL). The organic layer was then dried over sodium sulfate and the solvent removed under reduced pressure. Column chromatography (silica, 5% MeOH/95% DCM) provided the product as a light brown powder. Yield: 563 mg, 95%. ¹H NMR (400 MHz, d₆-DMSO, 298 K) δ 8.85 (s, 1H, Hₙ), 8.69 (s, 2H, Hₐ), 8.60 (d, J = 4.6 Hz, 1H, Hₗ), 8.06 (d, J = 7.9 Hz, 1H, Hₗ), 7.96 – 7.85 (m, 3H, Hₖj), 7.43 – 7.29 (m, 11H, Hₖf,g,k), 5.91 (s, 2H, Hₐ), 5.69 (s, 4H, Hₗ). ¹³C (¹H) NMR (100 MHz, d₆-DMSO, 298 K) δ 150.4, 149.7, 149.7, 147.7, 147.1, 147.0, 137.3, 135.9, 128.8, 128.2, 127.9, 124.1, 123.9, 123.1, 119.5, 116.9, 53.1, 51.8. HRESI-MS: m/z = 574.2191 [L1 + Na]⁺ (calc. C₃₁H₂₅N₁₁Na, 574.2187). Anal. calc. for C₃₁H₂₅N₁₁·0.5H₂O: C, 66.42; H, 4.67; N, 27.48%. Found: C, 66.52; H, 4.59; N, 27.65%.

![Figure S16 - ¹H NMR (400 MHz, d₆-DMSO, 298 K) of L1.](image-url)
Figure S17 - $^{13}$C ($^1$H) NMR (100 MHz, $d_6$-DMSO, 298 K) of L1.

Figure S18 – HRESI-MS (DMSO/MeOH) of L1.
A DMF/water (4:1, 25 mL) suspension of 5 (195 mg, 0.435 mmol), sodium L-ascorbate (129 mg, 0.652 mmol), CuSO₄·5H₂O (109 mg, 0.435 mmol), 5-ethynyl-2,2'-bipyridine (78 mg, 0.435 mmol) was stirred at room temperature for 24 hours. Additional sodium L-ascorbate (60 mg) and CuSO₄·5H₂O (50 mg) were added and the suspension stirred for a further 4 hours. 0.1 M EDTA/NH₄OH (aq) (50 mL) and DCM (50 mL) were added and the biphasic solution stirred for 1.5 hours. The organic phase was extracted and washed with 0.1 M EDTA/NH₄OH (aq) (3 x 80 mL), water (80 mL) and brine (2 x 100 mL). The organic layer was then dried over sodium sulfate and the solvent removed under reduced pressure.

Column chromatography (silica, 3% MeOH/97% CHCl₃, then 10% MeOH/90% CHCl₃) provided the product as a pale-yellow powder. Yield: 188 mg, 69%. ¹H NMR (500 MHz, d₆-DMSO, 298 K) δ 9.17 (d, J = 2.2 Hz, 1H, Hᵢ), 8.94 (s, 1H, Hₖ), 8.68 (s, 3H, H_c,o), 8.46 (d, J = 8.3 Hz, 1H, Hₗ), 8.44 – 8.38 (m, 2H, H_j,l), 7.94 (td, J = 7.7, 1.8 Hz, 1H, H_m), 7.88 (s, 2H, Hₘ), 7.45 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H, Hₙ), 7.39 – 7.30 (m, 10H, H_e,f,g), 5.93 (s, 2H, H_a), 5.68 (s, 4H, H_d). ¹³C [¹H] NMR (125 MHz, d₆-DMSO, 298 K) δ 154.8, 154.6, 150.4, 149.3, 149.3, 147.0, 146.9, 146.1, 143.8, 137.3, 135.9, 133.6, 128.8, 128.2, 127.9, 126.6, 124.2, 123.9, 123.1, 120.6, 120.5, 117.0, 53.1, 52.0. HRESI-MS: m/z = 651.2401 [L₂ + Na⁺] (calc. C₃₆H₂₈N₁₂ 1acetone-1MeOH: C, 66.84; H, 5.33; N, 23.38%. Found: C, 67.14; H, 5.32; N, 23.40%.

Figure S19 - ¹H NMR (500 MHz, d₆-DMSO, 298 K) of L₂.
Figure S20 - $^{13}$C ($^1$H) NMR (125 MHz, $d_6$-DMSO, 298 K) of L2.

Figure S21 – HRESI-MS (DMSO/MeOH) of L2.
1.9 [Cu($\kappa^2$-terpy)(diMesbpy)](PF$_6$)

A $d_6$-acetone (0.75 mL) solution of terpy (1.65 mg, 0.007 mmol) was added to [Cu(diMesbpy)(MeCN)$_2$](PF$_6$) (5 mg, 0.007 mmol). The mixture was sonicated for 10 minutes, and the resulting deep red solution subjected to $^1$H and $^{13}$C NMR spectroscopy and HRESI-MS. $^1$H NMR (500 MHz, $d_6$-acetone, 298 K) $\delta$ 8.72 (d, $J = 8.1$ Hz, 2H, $H_a$), 8.31 (t, $J = 7.8$ Hz, 2H, $H_j$), 8.25 (d, $J = 6.9$ Hz, 2H, $H_b$), 8.20 (d, $J = 6.8$ Hz, 1H, $H_d$), 8.14 (m, 2H, $H_i$), 8.06 (d, $J = 7.6$ Hz, 2H, $H_c$), 7.84 (t, $J = 7.0$ Hz, 2H, $H_a$), 7.59 (d, $J = 7.4$ Hz, 2H, $H_i$), 7.38 (m, 2H, $H_m$), 6.17 (s, 4H, $H_b$), 1.87 (s, 6H, $H_g$), 1.55 (s, 12H, $H_i$). $^{13}$C ($^1$H) NMR (125 MHz, $d_6$-acetone, 298 K) $\delta$ 159.5, 153.8, 153.6, 149.2, 139.4, 139.3, 138.2, 138.1, 136.4, 135.7, 128.3, 128.1, 127.9, 122.7, 121.4, 121.2, 20.3, 20.1. HRESI-MS: $m/z$ = 688.2502 [M – PF$_6$]$^+$ (calc. C$_{43}$H$_{39}$N$_5$Cu 688.2496), $m/z$ = 344.1254 [M – PF$_6$]$^{2+}$ (calc. C$_{23}$H$_{19}$N$_3$Cu 344.1245).

Figure S22 - $^1$H NMR (500 MHz, $d_6$-acetone, 298 K) of [Cu($\kappa^2$-terpy)(diMesbpy)](PF$_6$).
Figure S23 – $^{13}$C ($^1$H) NMR (125 MHz, $d_6$-acetone, 298 K) of [Cu(κ²-terpy)(diMesbpy)]($\text{PF}_6$).

Figure S24 – HRESI-MS (acetone/MeOH) of [Cu(κ²-terpy)(diMesbpy)]($\text{PF}_6$).
1.10 General procedure for preparation of \([\text{Cu}_n(\text{L})(\text{diMesbpy})_n](\text{PF}_6)_n\) complexes

A DCM (typically 5-8 mL) solution of diMesbpy was added to a solution of \([\text{Cu}(\text{MeCN})_4](\text{PF}_6)\) (1 equiv. of each per binding pocket) in acetone (5-10 mL) and the resulting yellow solution stirred for 30 minutes. This was then filtered through celite into an acetone (5-10 mL) solution/suspension of \(\text{L}\) (1 equiv.) and stirred at room temp for 1 hour. The solution was filtered through celite and the product obtained by precipitation from solution using a petroleum ether/diethyl ether (3:1) solution, and isolated by vacuum filtration.

1.10.1 \([\text{Cu(bpytri)(diMesbpy)}]_2(\text{PF}_6)_2\)

Prepared according to the general procedure. DiMesbpy (45 mg, 0.115 mmol), \([\text{Cu}(\text{MeCN})_4](\text{PF}_6)\) (43 mg, 0.115 mmol) and bpytri (34 mg, 0.109 mmol). Yield: 90 mg, 90%. \(^1\text{H}\) NMR (400 MHz, \(d_6\)-acetone, 298 K) \(\delta\) 8.83 (d, \(J = 1.3\) Hz, 1H, \(H_g\)), 8.72 (d, \(J = 8.2\) Hz, 2H, \(H_r\)), 8.61 (s, 1H, \(H_h\)), 8.46 (dd, \(J = 8.4, 2.1\) Hz, 1H, \(H_f\)), 8.40 – 8.34 (m, 3H, \(H_a,q\)), 8.22 (d, \(J = 8.3\) Hz, 1H, \(H_l\)), 8.16 (d, \(J = 8.2\) Hz, 1H, \(H_e\)), 8.06 (td, \(J = 7.8, 1.6\) Hz, 1H, \(H_b\)), 7.69 (d, \(J = 7.6\) Hz, 2H, \(H_p\)), 7.55 (ddd, \(J = 7.4, 5.1, 1.1\) Hz, 1H, \(H_d\)), 7.44 – 7.36 (m, 5H, \(H_i,j,k,l\)), 6.11 (s, 2H, \(H_n\)), 6.06 (s, 2H, \(H_{n'}\)), 5.73 (s, 2H, \(H_i\)), 1.80 (s, 6H, \(H_m\)), 1.77 (s, 6H, \(H_{m'}\)), 1.72 (s, 6H, \(H_{m''}\)). \(^{13}\text{C}\) \(^{1}\text{H}\) NMR (100 MHz, \(d_6\)-acetone, 298 K) \(\delta\) 159.3, 153.2, 151.7, 150.9, 149.4, 146.0, 139.6, 138.5, 138.1, 138.1, 136.6, 135.5, 133.9, 129.8, 129.7, 129.4, 129.1, 128.1, 128.0, 127.9, 126.3, 123.0, 121.8, 121.6, 121.0, 54.7, 20.7, 20.4, 20.3. HRESI-MS: \(m/z = 768.2861\) [M – \(\text{PF}_6\)]\(^+\) (calc. \(\text{C}_{47}\text{H}_{53}\text{CuN}_{7}\text{PF}_{6}\cdot\text{H}_{2}\text{O}\)). Anal. calc. for \(\text{C}_{47}\text{H}_{53}\text{CuN}_{7}\text{PF}_{6}\cdot\text{H}_{2}\text{O}\): C, 60.54; H, 4.86; N, 10.52%. Found: C, 60.91; H, 4.69; N, 10.19%.
Figure S25 - $^1$H NMR (400 MHz, $d_6$-acetone, 298 K) of [Cu(bpy)tri(diMesbpy)](PF$_6$).

Figure S26 - $^{13}$C ($^1$H) NMR (100 MHz, $d_6$-acetone, 298 K) of [Cu(bpy)tri(diMesbpy)](PF$_6$).
Figure S27 – HRESI-MS (acetone) of \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6)\).
1.10.2 [Cu(κ²-tripy)(diMesbpy)][PF₆]

Prepared according to the general procedure but under inert conditions. DiMesbpy (29 mg, 0.076 mmol), [Cu(MeCN)₄][PF₆] (30 mg, 0.076 mmol) and tripy (29 mg, 0.073 mmol). Yield: 64 mg, 88%. ¹H NMR (400 MHz, d₆-acetone, 298 K) δ 8.71 (dd, J = 8.1, 0.9 Hz, 2H, Hₘ), 8.36-8.30 (m, 4H, Hₗ), 7.99 (dd, J = 8.3, 7.4 Hz, 1H, Hₙ), 7.83 (d, J = 7.8 Hz, 2H, Hₖ), 7.57 (d, J = 7.6 Hz, 2H, Hₛ), 7.48 – 7.39 (m, 6H, Hₑₑ), 7.32 (dd, J = 7.7, 1.8 Hz, 4H, Hₗ), 6.05 (s, 4H, Hᵢ), 5.58 (s, 4H, Hᵣ), 1.83 (s, 6H, Hₗ), 1.47 (s, 12H, Hⱼ); ¹³C {¹H}NMR (100 MHz, d₆-acetone, 298 K) δ 159.7, 152.8, 148.6, 146.5, 139.9, 138.9, 138.0, 136.1, 135.8, 129.9, 129.6, 129.2, 127.9, 127.8, 123.0, 121.7, 121.5, 54.9, 20.8, 20.0; HRESI-MS: m/z = 848.3265 [M – PF₆]⁺ (calc. for C₅₁H₄₇CuN₉F₆P·0.8MeCN C, 61.50; H, 4.85; N, 13.36%. Found C, 61.20; H, 4.62; N, 13.71%.

Figure S28 - ¹H NMR (400 MHz, d₆-acetone, 298 K) of [Cu(κ²-tripy)(diMesbpy)][PF₆].
Figure S29 – $^{13}$C ($^1$H) NMR (100 MHz, $d_6$-acetone, 298 K) of [Cu($\kappa^2$-tripy)(diMesbpy)](PF$_6$).

Figure S30 – HRESI-MS (acetone/MeOH) of [Cu($\kappa^2$-tripy)(diMesbpy)](PF$_6$).
Prepared according to the general procedure. DiMesbpy (28 mg, 0.073 mmol), [Cu(MeCN)]$_4$(PF$_6$) (27 mg, 0.073 mmol) and L$_1$ (20 mg, 0.036 mmol). Yield: 60 mg, 94%. $^1$H NMR (500 MHz, $d_6$-acetone, 298 K) $\delta$ 8.81 (s, 1H, H$_h$), 8.71 (d, $J$ = 4.2 Hz, 2H, H$_s$), 8.69 (d, $J$ = 4.3 Hz, 2H, H$_n$), 8.38 (t, $J$ = 7.9 Hz, 2H, H$_m$), 8.35 – 8.32 (m, 4H, H$_{e,g,k}$), 8.23 (d, $J$ = 5.0 Hz, 1H, H$_l$), 8.08 (s, 2H, H$_b$), 7.97 (td, $J$ = 8.0, 1.5 Hz, 1H, H$_j$), 7.69 (d, $J$ = 7.7 Hz, 2H, H$_o$), 7.62 (d, $J$ = 8.2 Hz, 1H, H$_i$), 7.54 (d, $J$ = 7.6 Hz, 2H, H$_u$), 7.44 – 7.39 (m, 7H, H$_{e,g,k}$), 7.29 – 7.27 (m, 4H, H$_i$), 6.11 (s, 2H, H$_q$), 6.01 (s, 4H, H$_w$), 5.94 (s, 2H, H$_a$), 5.78 (s, 2H, H$_e$), 5.57 (s, 4H, H$_d$), 1.78 – 1.77 (m, 12H, H$_{p,x}$), 1.72 (s, 6H, H$_r$), 1.58 (s, 6H, H$_{p'}$), 1.48 (s, 12H, H$_v$). $^{13}$C ($^1$H) NMR (125 MHz, $d_6$-acetone, 298 K) $\delta$ 159.9, 159.6, 153.0, 152.8, 149.5, 149.3, 147.0, 146.5, 146.2, 146.0, 140.2, 139.9, 138.5, 138.3, 138.2, 137.7, 136.0, 135.7, 135.5, 130.0, 129.6, 129.1, 128.0, 127.9, 127.8, 125.3, 123.3, 123.3, 122.9, 121.8, 121.7, 121.0, 55.0, 53.8, 20.8, 20.3, 20.3, 20.2, 20.2, 20.1, 20.1. HRESI-MS: $m/z$ = 731.7696 [M – (PF$_6$)$_2$]$^{2+}$ (calc. for C$_{87}$H$_{81}$Cu$_2$N$_{15}$P$_2$F$_{12}$·1H$_2$O: C, 58.98; H, 4.72; N, 11.86%). Found: C, 58.80; H, 4.87; N, 12.21%.

Figure S31 - $^1$H NMR (500 MHz, $d_6$-acetone, 298 K) of [Cu$_2$(L1)(diMesbpy)$_2$](PF$_6$)$_2$. 

S26
Figure S32 – $^{13}$C {$^1$H} NMR (125 MHz, $d_6$-acetone, 298 K) of $[\text{Cu}_2(\text{L}1)(\text{diMesbpy})_2](\text{PF}_6)_2$.

Figure S33 – HRESI-MS (acetone/MeOH) of $[\text{Cu}_2(\text{L}1)(\text{diMesbpy})_2](\text{PF}_6)_2$. 

S27
1.10.4 \([\text{Cu}_2(L2)(\text{diMesbpy})_2](\text{PF}_6)_2\)

Prepared according to the general procedure. DiMesbpy (25 mg, 0.064 mmol), \([\text{Cu}(\text{MeCN})_4](\text{PF}_6)\) (23 mg, 0.062 mmol) and \(L_2\) (19 mg, 0.030 mmol). Yield: 47 mg, 85%. \(^{1}H\) NMR (500 MHz, \(d_6\)-acetone, 298 K) \(\delta\) 8.90 (s, 1H, H_h), 8.86 (s, 1H, H_i), 8.73 – 8.68 (m, 4H, H_p,v), 8.48 (d, \(J = 8.4\) Hz, 1H, H_j), 8.39 – 8.35 (m, 5H, H_o,w), 8.29 (s, 2H, H_e), 8.23 (d, \(J = 8.5\) Hz, 1H, H_d), 8.17 (d, \(J = 7.9\) Hz, 1H, H_h), 8.07 (m, 1H, H_i), 7.90 (s, 2H, H_b), 7.69 (d, \(J = 7.6\) Hz, 2H, H_h), 7.59 – 7.53 (m, 3H, H_m,\_l), 7.43 – 7.39 (m, 6H, H_a,\_g), 7.32 – 7.29 (m, 4H, H_i), 6.12 (s, 2H, H_t'), 6.04 (s, 2H, H_t'), 5.96 (s, 4H, H_d), 5.89 (s, 2H, H_a), 5.55 (s, 4H, H_b), 1.83 – 1.72 (m, 24H, H_s,\_u,\_A), 1.45 (s, 12H, H_y). \(^{13}C\) \(^{1}H\) NMR (125 MHz, \(d_6\)-acetone, 298 K) \(\delta\) 159.7, 159.3, 153.3, 153.2, 152.7, 151.6, 151.3, 151.1, 149.4, 149.2, 147.4, 146.2, 145.9, 144.5, 140.0, 139.7, 138.6, 138.5, 138.2, 138.1, 138.0, 136.0, 135.8, 135.6, 135.5, 135.4, 130.0, 129.6, 129.2, 128.2, 127.9, 127.7, 123.7, 123.2, 123.1, 121.7, 121.6, 121.1, 121.0, 55.0, 53.2, 20.8, 20.8, 20.5, 20.4, 20.1, 20.1. HRESI-MS: \(m/z = 770.2816 \ [M - (\text{PF}_6)_2]^{2+}\) (calc. for \(\text{C}_{92}\text{H}_{84}\text{N}_{16}\text{Cu}_2\text{P}_2\text{F}_{12}\cdot 2.5\text{DCM} \cdot 2\text{MeCN}\): C, 55.67; H, 4.51; N, 11.86%). Found: C, 55.81; H, 4.49; N, 12.10%.

Figure S34 - \(^{1}H\) NMR (500 MHz, \(d_6\)-acetone, 298 K) of \([\text{Cu}_2(L2)(\text{diMesbpy})_2](\text{PF}_6)_2\).
**Figure S35** - $^{13}$C ($^1$H) NMR (125 MHz, $d_6$-acetone, 298 K) of [Cu$_2$(L2)(diMesbpy)$_2$](PF$_6$)$_2$.

**Figure S36** – HRESI-MS (acetone/MeOH) of [Cu$_2$(L2)(diMesbpy)$_2$](PF$_6$)$_2$.

Where $C_{12}H_9N_5$ may be:

[Chemical structure image]
1.11 [Cu(tripy)(diMesbpy)](PF₆)$_2$

CuCl$_2$ (14.0 mg, 0.104 mmol) was combined with AgPF$_6$ (54.1 mg, 0.214 mmol) in acetone (5 mL) and the mixture was stirred in the dark at room temperature for 2 hours. The resulting suspension was filtered through celite and added to a suspension of diMesbpy (40.0 mg, 0.102 mmol) in acetone (5 mL) and the resulting mixture was stirred at room temperature for 1 hour. The solution was then filtered through Celite and added to an acetone (5 mL) solution of L3 (40.1 mg, 0.102 mmol) and the mixture was stirred at room temperature for 1 hour. The resulting green solution was again filtered through celite and the product was recrystallised via slow diffusion of diisopropyl ether into the acetone solution. The crystals were filtered, rinsed with diethyl ether (2 x 5 mL) and redissolved in acetonitrile. The product was again recrystallised via slow diffusion of diisopropyl ether into acetonitrile solution giving blue X-ray quality crystals. Yield: 71.0 mg, 61%. IR (ATR): ν (cm$^{-1}$) 3160, 2962, 1591, 1468, 875, 555. HRESI-MS: m/z = 993.2888 [M – PF$_6$]$^+$ (calc. for C$_{51}$H$_{47}$N$_9$CuPF$_{12}$ 993.2887), 848.3239 [M – (PF$_6$)$_2$]$^{2+}$ (calc. for C$_{51}$H$_{47}$N$_9$Cu 848.3245). UV-Vis (MeCN) $\lambda_{\text{max}}$ (ε/L mol$^{-1}$ cm$^{-1}$) 670 (97).

Anal. calc. for C$_{51}$H$_{47}$N$_9$CuP$_2$F$_{12}$·0.1MeCN C, 53.78; H, 4.17; N, 11.15%. Found C, 54.17; H, 4.25; N, 11.21%.
Figure S37 – HRESI-MS (acetone/MeOH) of \([\text{Cu(tripy)(diMesbpy)}]\)(PF_6)_2
1.12 [Cu(L1)(diMesbpy)][PF₆]₂

DiMesbpy (10.0 mg, 0.025 mmol) was added to an acetone (3 mL) solution of Cu(NO₃)₂·3H₂O (61.0 mg, 0.025 mmol) and the resulting solution stirred for 30 minutes. L1 (14.0 mg, 0.025 mmol) was added followed by MeOH (3 mL) and MeCN (3 mL) and the resulting blue solution stirred for 1 hour. After passing through a 0.45 μm PTFE syringe filter, the solution was heated to 85 °C and treated with saturated NH₄PF₆(aq) (15 mL) dropwise. The resulting suspension was stirred at 85 °C for 1 hour before the precipitate was isolated by vacuum filtration. The pale blue solid was dissolved in MeCN (5 mL), water (100 mL) was added and the suspension stirred for a further 1 hour at room temperature. The precipitate was collected by vacuum filtration, dissolved in MeCN (5 mL) and diethyl ether (60 mL) was added resulting in a pale blue precipitate. After vacuum filtration, washing with diethyl ether (3 x 10 mL) and drying under the vacuum the product was isolated as a pale blue powder. Yield: 24.4 mg, 76%.

IR (ATR): ν (cm⁻¹) 3158, 2980, 1593, 1458, 838, 556. HRESI-MS: m/z = 503.1884 [M – (PF₆)₂]²⁺ (calc. for C₅₉H₅₃N₁₃Cu 503.1916), 1006.3784 [M – (PF₆)₂]⁺ (calc. for C₅₉H₅₃N₁₃CuPF₆ 1006.3837). UV-Vis (MeCN) λₘₐₓ (ε/L mol⁻¹ cm⁻¹) 670 (93) Anal. calc. for C₅₉H₅₃N₁₃CuPF₆·0.5NH₄PF₆ C, 51.38; H, 4.02; N, 13.71%. Found C, 51.35; H, 3.88; N, 13.97%.
Figure S38 – HRESI-MS (acetone/MeOH) of \([\text{Cu(L1)(diMesbpy)}](\text{PF}_6)_2\)
DiMesbpy (10.0 mg, 0.025 mmol) was added to an acetone (5 mL) solution of Cu(NO$_3$)$_2$·3H$_2$O (62.0 mg, 0.025 mmol) and the resulting solution stirred for 30 minutes. L2 (16.0 mg, 0.025 mmol) was added followed by MeOH (5 mL) and MeCN (5 mL) and the resulting blue solution stirred for 1 hour. After passing through a 0.45 μm PTFE syringe filter, the solution was heated to 85 °C and treated with saturated NH$_4$PF$_6$(aq) (15 mL) dropwise. The resulting suspension was stirred at 85 °C for 1 hour before the precipitate was isolated by vacuum filtration. The pale blue solid was dissolved in MeCN (8 mL), water (100 mL) was added and the suspension stirred for a further 1 hour at room temperature. The precipitate was collected by vacuum filtration, dissolved in MeCN (8 mL) and diethyl ether (80 mL) added resulting in a pale blue precipitate. After vacuum filtration, washing with diethyl ether (3 x 10 mL) and drying under vacuum the product was isolated as a pale blue powder. Yield: 27 mg, 78%. IR (ATR): ν (cm$^{-1}$) 3144, 2987, 1595, 1459, 832, 556. HRESI-MS: $m/z$ = 541.7039 [M – (PF$_6$)$_2$]$^{2+}$ (calc. for C$_{64}$H$_{56}$N$_{14}$CuPF$_6$ 541.7049). UV-Vis (MeCN) $\lambda_{max}$ (ε/L mol$^{-1}$ cm$^{-1}$) 670 (95) Anal. calc. for C$_{64}$H$_{56}$N$_{14}$CuP$_2$F$_{12}$·1NH$_4$PF$_6$·2H$_2$O C, 48.85; H, 4.10; N, 13.35%. Found C, 48.76; H, 3.65; N, 12.98%.
2 Cu(II) complexes of L1 & L2 using AgPF$_6$

Initially the Cu(II) complexes of L1 and L2 were attempted to be synthesised using AgPF$_6$ and CuCl$_2$, the general procedure is outlined below.

AgPF$_6$ (2 equiv.) was added to an MeCN (10 mL) solution of CuCl$_2$ (1 equiv.) and the resulting mixture stirred in the dark for 30 minutes. After filtering through celite to remove AgCl, the filtrate was added to diMesbpy (1 equiv.). The pale green/blue solution was stirred for 30 minutes, then filtered through celite. The filtrate was added to L1 or L2 (1 equiv.) and stirred for 2 hours. Addition of diethyl ether gave a pale blue/green precipitates that were isolated by vacuum filtration.

Despite mass spec evidence of the desired [Cu(L1/L2)(diMesbpy)]$^{2+}$ molecular ions (Figure S40 for L1 complex & Figure 5 in main manuscript for L2), suitable fits for the elemental analysis of the products could only be achieved when AgPF$_6$ was included, e.g. for Cu(II) complex of L2: [Cu(L2)(diMesbpy)](PF$_6$)$_2$·0.5AgPF$_6$·1H$_2$O C 50.60%, H 3.85%, N 12.91%, found C 50.20%, H 3.80%, N 13.32%.
The presence of a species containing a Ag ion and PF$_6$ species was confirmed by X-ray crystallography. X-ray quality crystals were obtained from the vapour diffusion of diisopropyl ether into a MeCN solution of the suspected [Cu(L1)(diMesbpy)](PF$_6$)$_2$ complex obtained from the reaction using CuCl$_2$ and AgPF$_6$, the structure is shown in Figure S41. Based on the structure a suitable fit for the elemental analysis of the complex could be found, i.e. anal. calc. for C$_{120}$H$_{114}$N$_{26}$AgCu$_2$P$_5$F$_{30}$·5MeCN C, 50.61; H, 4.21; N, 14.07%. Found C, 50.35; H, 3.84; N, 14.23%, suggesting a complex such as that shown in Figure S42.

Figure S40 - HRESI-MS (Acetone/MeOH) of the product from the attempted synthesis of [Cu(L1)(diMesbpy)](PF$_6$)$_2$ using CuCl$_2$ and AgPF$_6$. 
Figure S41 - Crystal structure of [(Cu(L1)(diMesbpy))₂Ag(PF₆)₂][PF₆]₃. Ellipsoids shown at the 50% probability level. Non-bonding counter-anions, hydrogen atoms and solvent molecules omitted for clarity. Colour scheme: carbon grey/dark grey, nitrogen blue, copper(II) turquoise, silver silver, phosphorous yellow, fluorine green.

Figure S42 – Chemdraw of [(Cu(L1)(diMesbpy))₂Ag(PF₆)₂][PF₆]₃.
3 Additional NMR data

3.1 Cu(II) complexes $^1$H NMR

$[\text{Cu(L1)(diMesbpy)}](\text{PF}_6)_2$

$[\text{Cu(L2)(diMesbpy)}](\text{PF}_6)_2$

Figure S43 – Stacked $^1$H NMR spectra (400 MHz, $d_6$-acetone, 298 K) of Cu(II) complexes of L1 (top) and L2 (bottom).

3.2 Cu(I) complexes $^1$H NMR

L1 + 1 eq. $[\text{Cu(diMesbpy)}](\text{PF}_6)_2$

L2 + 1 eq. $[\text{Cu(diMesbpy)}](\text{PF}_6)_2$

Figure S44 – Partial $^1$H NMR (400 MHz, CDCl$_3$, 298 K) stacked spectra of the products from the attempted synthesis of the monometallic Cu(I) complexes of L1 (top) and L2 (bottom).
Figure S45 - Partial $^1$H NMR (400 MHz, CDCl$_3$, 298 K) stacked spectra of a) the 1:1 mixture of L1:[Cu(diMesbpy)](PF$_6$)$_2$ without sodium ascorbate (top) and with sodium ascorbate (bottom), and b) the 1:1 mixture of L2:[Cu(diMesbpy)](PF$_6$)$_2$ without sodium ascorbate (top) and with sodium ascorbate (bottom).
Figure S46 — Partial $^1$H NMR (400 MHz, CDCl$_3$, 298 K) stacked spectra of a) L1 with 1 equiv. of [Cu(diMesbpy)](PF$_6$) (top) and 2 equiv. of [Cu(diMesbpy)](PF$_6$) (bottom) and b) L2 with 1 equiv. of [Cu(diMesbpy)](PF$_6$) (top) and 2 equiv. of [Cu(diMesbpy)](PF$_6$) (bottom).
3.3 Representative 2D NMR data

Figure S47 – 2D $^1$H NMR (500 MHz, $d_6$-acetone, 298 K) spectra of [Cu$_2$(L1)(diMesbpy)](PF$_6$)$_2$, a) partial 2D COSY, b) partial 2D NOESY and c) partial 2D COSY of the aromatic region.
3.4 NMR titration data

400 μL of a CDCl$_3$ stock solution of the relevant ligand (1.1 mM for L1 and 0.5 mM for L2) were added to a clean dry NMR tube. To this was added a $d_6$-acetone solution of [Cu(diMesbpy)(MeCN)$_2$](PF$_6$) in equivalents ranging from 0-3 with respect to the ligand (18 different points). The volume of solvent in each NMR tube was then made up to 600 μL via addition of neat $d_6$-acetone. The mixed solvent solutions were sonicated for 30 seconds to ensure thorough mixing before a $^1$H NMR spectrum was collected at room temperature.

Figure S48 shows the results of the titration of [Cu(diMesbpy)(MeCN)$_2$](PF$_6$) into L2. The resonances labelled i and c represent the alpha pyridyl proton H$_i$ and the triazole proton of the tripy pocket H$_c$, as labelled above in section 1.10.4.

3.5 VT NMR data

Variable temperature $^1$H NMR studies were carried out on [Cu(κ$_2$-tripy)(diMesbpy)](PF$_6$) and the products of the 1:1 reactions of L1 or L2 and [Cu(diMesbpy)](PF$_6$). Due to spectrometer limitations temperatures below -40 °C could not be achieved.
Figure S49 – Partial VT $^1$H NMR (500 MHz, $d_6$-acetone) stack plot of the [Cu(κ$^2$-tripy)(diMesbpy)](PF$_6$).
Figure S50 – Partial VT $^1$H NMR (500 MHz, $d_6$-acetone) stack plot of the reaction product from 1:1 mixture of L1:[Cu(diMesbpy)][PF$_6$]
Figure S51 – Partial VT $^1$H NMR (500 MHz, $d_6$-acetone) stack plot of the reaction product from 1:1 mixture of L2:[Cu(diMesbpy)]PF$_6$
4 X-ray Data

X-ray data were collected at 100 K on an Agilent Technologies Supernova system using Cu Kα or Mo Kα radiation with exposures over 1.0°, and data were treated using CrysAlisPro software. The structures were solved using SHELXT and weighted full-matrix refinement on $F^2$ was carried out using SHELXL-97, both running within the OLEX2-v1.2.9 package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbons were placed in calculated positions and refined using a riding model.

4.1 [Cu(bpytri)(diMesbpy)](PF₆)

CCDC #: 2065123. X-ray quality crystals of [Cu(bpytri)(diMesbpy)](PF₆) were obtained by the vapour diffusion of diethyl ether into a MeCN solution of [Cu(bpytri)(diMesbpy)](PF₆). The structure was solved in the triclinic space group $P\overline{1}$ and refined to an R1 value of 6.34%. The asymmetric unit (Figure S52) consists of one [Cu(bpytri)(diMesbpy)] molecule and one PF₆ counterion.

![Figure S52 - Mercury ellipsoid plot of the asymmetric unit of [Cu(bpytri)(diMesbpy)](PF₆). Ellipsoids shown at the 50% probability level. Colour scheme: carbon grey, nitrogen blue, hydrogen white, copper(I) orange, phosphorous yellow, fluorine green.](image)

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4.2 \([\text{Cu(tripy)(diMesbpy)}(\text{PF}_6)_2]\)

**CCDC #: 2094328.** X-ray quality crystals of \([\text{Cu(tripy)(diMesbpy)}(\text{PF}_6)_2]\) were obtained by the vapour diffusion of diisopropyl ether into a MeCN solution of \([\text{Cu(tripy)(diMesbpy)}(\text{PF}_6)_2]\). The structure was solved in the monoclinic space group \(C2/c\) and refined to an R1 value of 8.30%. The asymmetric unit (Figure S53) consists of one \([\text{Cu(tripy)(diMesbpy)}]\) molecule and two \(\text{PF}_6\) counterions.

![Mercury ellipsoid plot of the asymmetric unit of \([\text{Cu(tripy)(diMesbpy)}(\text{PF}_6)_2]\); a) a side view, b) a top view. Ellipsoids shown at the 50% probability level. Colour scheme: carbon grey, nitrogen blue, hydrogen white, copper(II) turquoise, phosphorous yellow, fluorine green.](image_url)
4.3 [[Cu(L1)(diMesbpy)]$_2$Ag(PF$_6$)$_2$](PF$_6$)$_3$

CCDC #: 2065120. X-ray quality crystals of [[Cu(L1)(diMesbpy)]$_2$Ag(PF$_6$)$_2$](PF$_6$)$_3$ were obtained by the vapour diffusion of diisopropyl ether into a MeCN solution of the product from the attempted synthesis of [Cu(L1)(diMesbpy)](PF$_6$)$_2$ using AgPF$_6$ and CuCl$_2$. The structure was solved in the triclinic space group $Par{1}$ and refined to an $R1$ value of 20.55%. The asymmetric unit (Figure S54) consists of one [Cu(L1)(diMesbpy)AgPF$_6$] molecule, two non-coordinating PF$_6$ counterions and four MeCN solvent molecules.

![Figure S54 - Mercury ellipsoid plot of the asymmetric unit of [[Cu(L1)(diMesbpy)]$_2$Ag(PF$_6$)$_2$](PF$_6$)$_3$; a) a top view, b) a side view. Ellipsoids shown at the 50% probability level. Colour scheme: carbon grey, nitrogen blue, hydrogen white, copper(II) turquoise, silver silver, phosphorous yellow, fluorine green.](image-url)
4.4 \([\text{Cu}_2(\text{L1})(\text{diMesbpy})_2]\)(\text{PF}_6)_2

CCDC #: 2065122. X-ray quality crystals of \([\text{Cu}_2(\text{L1})(\text{diMesbpy})_2]\)(\text{PF}_6)_2\) were obtained by the vapour diffusion of diethyl ether into a MeCN solution of \([\text{Cu}_2(\text{L1})(\text{diMesbpy})_2]\)(\text{PF}_6)_2\). The structure was solved in the triclinic space group \(P\overline{1}\) and refined to an R1 value of 5.80%. The asymmetric unit (Figure S55) consists of two \([\text{Cu}_2(\text{L1})(\text{diMesbpy})_2]\) molecules (P and M helices), four PF\(_6\) counterions and one MeCN solvent molecule. One of the \([\text{Cu}_2(\text{L1})(\text{diMesbpy})_2]\) molecules is flipped 180° relative to the other.

Figure S55 - Mercury ellipsoid plot of the asymmetric unit of \([\text{Cu}_2(\text{L1})(\text{diMesbpy})_2]\)(\text{PF}_6)_2\). Ellipsoids shown at the 50% probability level. Colour scheme: carbon grey, nitrogen blue, hydrogen white, copper(I) orange, phosphorous yellow, fluorine green.
4.5  [Cu₂(L2)(diMesbpy)₂](PF₆)₂
CCDC #: 2065119. X-ray quality crystals of [Cu₂(L2)(diMesbpy)₂](PF₆)₂ were obtained by the vapour diffusion of diethyl ether into a MeCN solution of a 1:1 mixture of L2:[Cu(MeCN)₂(diMesbpy)](PF₆). The structure was solved in the triclinic space group Pī and refined to an R1 value of 5.51%. The asymmetric unit (Figure S56) consists of one [Cu₂(L2)(diMesbpy)₂] molecule, two PF₆ counterions and one MeCN solvent molecule.

Figure S56 - Mercury ellipsoid plot of the asymmetric unit of [Cu₂(L2)(diMesbpy)₂](PF₆)₂. Ellipsoids shown at the 50% probability level. Colour scheme: carbon grey, nitrogen blue, hydrogen white, copper(I) orange, phosphorous yellow, fluorine green.
4.6  [Cu(κ²-tripy)(diMesbpy)](PF₆)

CCDC #: 2094327. X-ray quality crystals of [Cu(κ²-tripy)(diMesbpy)](PF₆) were obtained by the vapour diffusion of diisopropyl ether into an acetone solution of [Cu(κ²-tripy)(diMesbpy)](PF₆). The structure was solved in the monoclinic space group P2₁/n and refined to an R1 value of 3.75%. The asymmetric unit (Figure S57) consists of one [Cu(κ²-tripy)(diMesbpy)] molecule and one PF₆ counterion.

Figure S57 - Mercury ellipsoid plot of the asymmetric unit of [Cu(κ²-tripy)(diMesbpy)](PF₆). Ellipsoids shown at the 50% probability level. Colour scheme: carbon grey, nitrogen blue, hydrogen white, copper(I) orange, phosphorous yellow, fluorine green.
4.7 κ²-tripy comparison

Figure S58 below shows ellipsoid plots of the three crystal structures featuring κ²-tripy type coordination presented in this paper, and the crystal structure obtained by Goldup and co-workers\textsuperscript{11} of their [2]rotaxane system that also displays κ²-Rtripy coordination to a Cu(I) metal ion.

Figure S58 – Mercury ellipsoid plots of a) [Cu₂(L1)(diMesbpy)]₂[(PF₆)₆], b) [Cu₂(L2)(diMesbpy)]₂[(PF₆)₆], c) [Cu(κ²-tripy)(diMesbpy)](PF₆) and d) Goldup and co-workers Cu(I) [2]rotaxane that also displays κ²-Rtripy coordination. Ellipsoids shown at the 50% probability level. Hydrogen atoms, counter-anions and solvent molecules omitted for clarity. Colour scheme: carbon grey/dark grey, nitrogen blue, oxygen red, copper (I) orange.
### 4.8 Crystallographic Data

| Identification code | [Cu(bpytri)(diMesbpy)](PF$_6$) | [Cu(tripy)(diMesbpy)](PF$_6$)$_2$ |
|---------------------|-------------------------------|----------------------------------|
| CCDC #              | 2065123                       | 2094328                         |
| Empirical formula   | C$_{47}$H$_{43}$CuF$_6$N$_7$P  | C$_{51}$H$_{47}$CuF$_{12}$N$_9$P$_2$ |
| Formula weight      | 914.39                        | 1139.45                         |
| Temperature/K       | 99.97(10)                     | 100.01(10)                      |
| Crystal system      | triclinic                     | monoclinic                      |
| Space group         | P-1                           | C2/c                            |
| a/Å                 | 12.2365(4)                    | 21.0885(2)                      |
| b/Å                 | 13.7855(4)                    | 20.0942(2)                      |
| c/Å                 | 14.7658(4)                    | 25.9382(3)                      |
| α/°                 | 91.427(2)                     | 90                              |
| β/°                 | 113.765(3)                    | 99.5050(10)                     |
| γ/°                 | 107.915(3)                    | 90                              |
| Volume/Å$^3$        | 2137.13(12)                   | 10840.6(2)                      |
| Z                   | 2                             | 8                               |
| ρcalc/g/cm$^3$      | 1.421                         | 1.396                           |
| μ/mm$^{-1}$         | 1.666                         | 1.873                           |
| F(000)              | 944.0                         | 4664.0                          |
| Crystal size/mm$^3$ | 0.652 × 0.390 × 0.268         | 0.41 × 0.267 × 0.227            |
| 2Θ range for data collection/° | 6.84 to 149.932 | 7.362 to 148.528 |
| Index ranges        | -15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18 | -25 ≤ h ≤ 26, -21 ≤ k ≤ 24, -32 ≤ l ≤ 31 |
| Reflections collected | 38758                      | 50953                           |
| Independent reflections | 8664  [R$_{int}$ = 0.0392, R$_{sigma}$ = 0.0236] | 10821  [R$_{int}$ = 0.0203, R$_{sigma}$ = 0.0109] |
| Data/restraints/parameters | 8664/36/610                 | 10821/113/718                   |
| Goodness-of-fit on F$^2$ | 1.046                      | 1.036                           |
| Final R indexes [I>2σ (I)] | R$_1$ = 0.0634, wR$_2$ = 0.1654 | R$_1$ = 0.0830, wR$_2$ = 0.2301 |
| Final R indexes [all data] | R$_1$ = 0.0661, wR$_2$ = 0.1675 | R$_1$ = 0.0840, wR$_2$ = 0.2309 |
| Largest diff. peak/hole / e Å$^3$ | 1.82/-1.31 | 1.48/-1.48 |
| Identification code | [Cu(L1)(diMesbpy)$_2$Ag(PF$_6$)$_3$](PF$_6$)$_3$ | [Cu$_2$(L1)(diMesbpy)$_3$](PF$_6$)$_2$ |
|---------------------|-----------------------------------------------|-----------------------------------------------|
| CCDC #              | 2065120                                       | 2065122                                       |
| Empirical formula   | C$_{67}$H$_{65}$Ag$_{0.5}$CuF$_{18}$N$_{17}$P$_3$ | C$_{68}$H$_{82}$Cu$_{2}$F$_{12}$N$_{15.5}$P$_2$ |
| Formula weight      | 1660.74                                        | 1774.21                                       |
| Temperature/K       | 100.02(13)                                     | 100.02(16)                                    |
| Crystal system      | triclinic                                      | triclinic                                    |
| Space group         | P-1                                            | P-1                                          |
| a/Å                 | 10.2735(4)                                     | 18.0237(4)                                    |
| b/Å                 | 17.6829(13)                                    | 20.4237(4)                                    |
| c/Å                 | 21.5578(15)                                    | 27.0667(5)                                    |
| α/°                 | 73.521(6)                                      | 68.756(2)                                     |
| β/°                 | 84.071(4)                                      | 76.003(2)                                     |
| γ/°                 | 81.219(4)                                      | 70.192(2)                                     |
| Volume/Å$^3$        | 3704.0(4)                                      | 8656.1(3)                                     |
| Z                   | 2                                              | 4                                            |
| ρ$_{calc}$/g/cm$^3$  | 1.489                                          | 1.361                                         |
| μ/mm$^{-1}$         | 0.586                                          | 0.608                                         |
| F(000)              | 1691.0                                         | 3660.0                                        |
| Crystal size/mm$^3$ | 0.398 × 0.17 × 0.043                           | 0.78979 × 0.514 × 0.259                      |
| Radiation           | MoKα ($λ$ = 0.71073)                           | MoKα ($λ$ = 0.71073)                          |
| 2θ range for data collection/° | 6.586 to 59.248 | 6.52 to 59.24 |
| Index ranges        | -13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -27 ≤ l ≤ 29     | -24 ≤ h ≤ 23, -27 ≤ k ≤ 26, -37 ≤ l ≤ 37    |
| Reflections collected | 48741                                         | 193734                                        |
| Independent reflections | 17954 [R$_{int}$ = 0.0906, R$_{sigma}$ = 0.1288] | 44204 [R$_{int}$ = 0.0512, R$_{sigma}$ = 0.0545] |
| Data/restraints/parameters | 17954/0/971                                   | 44204/198/2177                                |
| Goodness-of-fit on F$^2$ | 1.852                                         | 1.019                                         |
| Final R indexes [I>2σ (I)] | R$_1$ = 0.2055, wR$_2$ = 0.5085 | R$_1$ = 0.0580, wR$_2$ = 0.1438 |
| Final R indexes [all data] | R$_1$ = 0.2507, wR$_2$ = 0.5313 | R$_1$ = 0.0946, wR$_2$ = 0.1644 |
| Largest diff. peak/hole / e Å$^3$ | 4.39/-3.91 | 0.93/-0.74 |
Table S3 - Crystallographic data for [Cu₂(L₂)(diMesbpy)₂]([PF₆]₂) and [Cu(κ²-tripy)(diMesbpy)][PF₆].

|                          | [Cu₂(L₂)(diMesbpy)₂]([PF₆]₂) | [Cu(κ²-tripy)(diMesbpy)][PF₆]   |
|--------------------------|-----------------------------|---------------------------------|
| Identification code      | DR050                       | JAF477                          |
| CCDC #                   | 2065119                     | 2094327                         |
| Empirical formula        | C₉₄H₈₇Cu₂F₁₂N₁₇P₂            | C₅₁H₇₂CuF₆N₉P                  |
| Formula weight           | 1871.82                     | 994.48                          |
| Temperature/K            | 99.99(10)                   | 99.97(10)                       |
| Crystal system           | triclinic                   | monoclinic                      |
| Space group              | P-1                         | P2₁/n                           |
| a/Å                      | 11.2007(2)                  | 11.82100(10)                    |
| b/Å                      | 18.6987(3)                  | 25.7863(2)                      |
| c/Å                      | 24.2051(4)                  | 15.5079(2)                      |
| α/°                      | 103.2070(10)                | 90                              |
| β/°                      | 103.189(2)                  | 104.1770(10)                    |
| γ/°                      | 101.657(2)                  | 90                              |
| Volume/Å³                | 4629.22(14)                 | 4583.15(8)                      |
| Z                        | 2                           | 4                               |
| ρcalc g/cm³              | 1.343                       | 1.441                           |
| μ/mm⁻¹                   | 1.561                       | 1.616                           |
| F(000)                   | 1932.0                      | 2056.0                          |
| Crystal size/mm³         | 0.208 x 0.141 x 0.075       | 0.755 x 0.221 x 0.096           |
| Radiation                | CuKα (λ = 1.54184)          | CuKα (λ = 1.54184)              |
| 2Θ range for data collection/° | 7.22 to 150.16             | 8.442 to 148.568               |
| Index ranges             | -13 ≤ h ≤ 14, -23 ≤ k ≤ 22, -30 ≤ l ≤ 30 | -14 ≤ h ≤ 14, -31 ≤ k ≤ 31, -19 ≤ l ≤ 19 |
| Reflections collected    | 88785                       | 49944                           |
| Independent reflections  | 18749 [Rint = 0.0663, Rsigma = 0.0429] | 9252 [Rint = 0.0324, Rsigma = 0.0179] |
| Data/restraints/parameters | 18749/74/1256             | 9252/75/833                     |
| Goodness-of-fit on F²    | 1.051                       | 1.023                           |
| Final R indexes [I>2σ (I)] | R₁ = 0.0551, wR₂ = 0.1452 | R₁ = 0.0375, wR₂ = 0.0964       |
| Final R indexes [all data]| R₁ = 0.0689, wR₂ = 0.1578 | R₁ = 0.0387, wR₂ = 0.0974       |
| Largest diff. peak/hole / e Å⁻³ | 0.86/-0.79               | 0.69/-0.50                     |
5 Competition Experiments

NMR samples were made up using stock solutions of the reactants such that: the volume of the sample was always 0.75 ml, the concentration with respect to the initial complex was 2 mM, the equivalents of initial complex to competing ligand was always 1:1 and that there was 5% of an internal standard (tetrakis(trimethylsilyl)silane). The integrations for the methyl peaks of the mesyl moieties or the methylene of the tripy coordination site, for the complexes, gave the ratio of the initial complex:exchange complex. All NMR spectra were collected at 298 K on a 400 MHz spectrometer and samples were also analysed using HRESI-MS under pseudo cryospray conditions (-10 °C).

5.1 \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})]([\text{PF}_6]) + \text{pytri}\)

![Scheme for the competition study carried out using \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})]([\text{PF}_6])\) and \(\text{pytri}\), products shown are those observed in the \(^1H\) NMR spectrum of the exchange mixture. Also shown is the partial \(^1H\) NMR (400 MHz, \(d_6\)-acetone, 298 K) stacked spectra a) \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})]([\text{PF}_6])\), b) the mixture of \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})][\text{PF}_6]\) and \(\text{pytri}\) ligand and c) \([\text{Cu}(\text{pytri})(\text{diMesbpy})][\text{PF}_6]\). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed tripy marked with *.

Figure S59 - Scheme for the competition study carried out using \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})]([\text{PF}_6])\) and \(\text{pytri}\), products shown are those observed in the \(^1H\) NMR spectrum of the exchange mixture. Also shown is the partial \(^1H\) NMR (400 MHz, \(d_6\)-acetone, 298 K) stacked spectra a) \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})]([\text{PF}_6])\), b) the mixture of \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})][\text{PF}_6]\) and \(\text{pytri}\) ligand and c) \([\text{Cu}(\text{pytri})(\text{diMesbpy})][\text{PF}_6]\). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed tripy marked with *.
Figure S60 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of [Cu(κ²-tripy)(diMesbpy)](PF₆) and terpy.
5.2 \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6) + \text{tripy}\)

Figure S61 - Scheme for the competition study carried out using \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6)\) and tripy, products shown are those observed in the \(^1\text{H} \text{NMR} \) spectrum of the exchange mixture. Also shown is the partial \(^1\text{H} \text{NMR} \) (400 MHz, \(d_6\)-acetone, 298 K) stacked spectra a) \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6)\), b) the mixture of \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6)\) and tripy ligand and c) \([\text{Cu(κ2-tripy)(diMesbpy)}](\text{PF}_6)\). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed tripy marked with *.

\[\text{S}58\]
Figure S62 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of [Cu(bpytri)(diMesbpy)](PF$_6$) and tripy.
Figure S63 - Scheme for the competition study carried out using [Cu(κ²-tripy)(diMesbpy)](PF₆) and bpytri, products shown are those observed in the ¹H NMR spectrum of the exchange mixture. Also shown is the partial ¹H NMR (400 MHz, d₆-acetone, 298 K) stacked spectra a) [Cu(bpytri)(diMesbpy)](PF₆), b) the mixture of [Cu(κ²-tripy)(diMesbpy)](PF₆) and bpytri ligand and c) [Cu(κ²-tripy)(diMesbpy)](PF₆). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed tripy marked with *.
Figure S64 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of [Cu(κ²-tripy)(diMesbpy)](PF₆) and bpytri.
5.4  [Cu(bpy)(diMesbpy)](PF₆) + tripy

Figure S65 - Scheme for the competition study carried out using [Cu(bpy)(diMesbpy)](PF₆) and tripy, products shown are those observed in the ¹H NMR spectrum of the exchange mixture. Also shown is the partial ¹H NMR (400 MHz, d₆-acetone, 298 K) stacked spectra a) [Cu(bpy)(diMesbpy)](PF₆), b) the mixture of [Cu(bpy)(diMesbpy)](PF₆) and tripy ligand and c) [Cu(κ²-tripy)(diMesbpy)](PF₆). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed tripy marked with *.
Figure S66 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of \([\text{Cu(bpy)}(\text{diMesbpy})]\)PF$_6$ and tripy.
5.5  \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})](\text{PF}_6) + \text{bpy}\)

Figure S67 - Scheme for the competition study carried out using \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})](\text{PF}_6) + \text{bpy}\), products shown are those observed in the \(^1\text{H} \text{NMR}\) spectrum of the exchange mixture. Also shown is the partial \(^1\text{H} \text{NMR}\) (400 MHz, \(d_6\text{-acetone}, 298 \text{ K}\) stacked spectra a) \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})](\text{PF}_6)\), b) the mixture of \([\text{Cu}(\kappa^2\text{-tripy})(\text{diMesbpy})](\text{PF}_6)\) and bpy ligand and c) \([\text{Cu}(\text{bpy})(\text{diMesbpy})](\text{PF}_6)\). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed tripy marked with *.
Figure S68 - Scheme for the competition study carried out using [Cu(κ²-tripy)(diMesbpy)](PF₆) and bpy, products shown are those observed in the ¹H NMR spectrum of the exchange mixture. Also shown is the partial ¹H NMR (400 MHz, d₆-acetone, 298 K) stacked spectra a) tripy, b) the mixture of [Cu(κ²-tripy)(diMesbpy)](PF₆) and bpy ligand and c) [Cu(bpy)(diMesbpy)](PF₆). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum.
Figure S69 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of $[\text{Cu(κ²-tripy)(diMesbpy)}](\text{PF}_6)$ and bpy.
5.6 \([\text{Cu(pytri)(diMesbpy)}](\text{PF}_6) + \text{terpy}\)

Figure S70 - Scheme for the competition study carried out using \([\text{Cu(pytri)(diMesbpy)}](\text{PF}_6)\) and terpy, products shown are those observed in the \(^1\text{H}\) NMR spectrum of the exchange mixture. Also shown is the partial \(^1\text{H}\) NMR (400 MHz, \(d_6\)-acetone, 298 K) stacked spectra a) \([\text{Cu(pytri)(diMesbpy)}](\text{PF}_6)\), b) the mixture of \([\text{Cu(pytri)(diMesbpy)}](\text{PF}_6)\) and terpy ligand and c) \([\text{Cu}(\kappa^2\text{-terpy})(\text{diMesbpy})](\text{PF}_6)\). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed terpy marked with *, and those for non-complexed pytri marked with *.
Figure S71 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of [Cu(pytri)(diMesbpy)](PF₆) and terpy.
5.7 \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6) + \text{terpy}\)

Figure S72 - Scheme for the competition study carried out using \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6)\) and terpy, products shown are those observed in the \(^1\text{H} \text{NMR}\) spectrum of the exchange mixture. Also shown is the partial \(^1\text{H} \text{NMR}\) (400 MHz, \(d_6\)-acetone, 298 K) stacked spectra a) \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6)\), b) the mixture of \([\text{Cu(bpytri)(diMesbpy)}](\text{PF}_6)\) and terpy ligand and c) \([\text{Cu(κ^2-terpy)(diMesbpy)}](\text{PF}_6)\). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed terpy marked with *, and those for non-complexed pytri marked with **.
Figure S73 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of [Cu(bpytri)(diMesbpy)](PF$_6$) and terpy.
5.8 \([\text{Cu(bpy)(diMesbpy)}](\text{PF}_6) + \text{terpy}\)

Figure S74 - Scheme for the competition study carried out using \([\text{Cu(bpy)(diMesbpy)}](\text{PF}_6)\) and terpy, products shown are those observed in the \(^1\text{H NMR}\) spectrum of the exchange mixture. Also shown is the partial \(^1\text{H NMR}\) (400 MHz, \(d_6\)-acetone, 298 K) stacked spectra a) \([\text{Cu(bpy)(diMesbpy)}](\text{PF}_6)\), b) the mixture of \([\text{Cu(bpy)(diMesbpy)}](\text{PF}_6)\) and terpy ligand and c) \([\text{Cu(κ²-terpy)(diMesbpy)}](\text{PF}_6)\). Dotted lines show that the species in the top and bottom spectra are present in the middle spectrum. Signals for non-complexed tripy marked with *. 
Figure S75 - Pseudo cryospray HRESI-MS (acetone/MeOH) of the Cu(I) competition mixture of [Cu(bpy)(diMesbpy)](PF_6) and terpy.
6 UV-Vis comparison

Figure S76 below shows a comparison of the UV-Vis spectra of the diCu(I) complexes, [Cu₂(L₁)(diMesbpy)₂][PF₆]₂ and [Cu₂(L₂)(diMesbpy)₂][PF₆]₂, to the relevant model Cu(I) complexes.

Figure S76 - UV-Vis spectra of a) the [Cu₂(L₁)(diMesbpy)₂][PF₆]₂ complex and related model Cu(I) complexes, and b) the [Cu₂(L₂)(diMesbpy)₂][PF₆]₂ complex and related model Cu(I) complexes in 2:1 CHCl₃:acetone at 298K.
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