Supporting information to accompany:

[Cu(P^P)(N^N)][PF_6] compounds with bis(phosphane) and 6-alkoxy, 6-alkylthio, 6-phenyloxy and 6-phenylthio-substituted 2,2'-bipyridine ligands for light-emitting electrochemical cells

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General method for N^N ligand synthesis

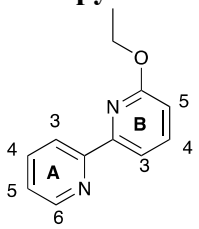
6-Bromo-2,2'-bipyridine (1.0 eq, Table S1) and NaOR or NaSR (R = Me, Et, Ph) (2 eq, Table S1) were dissolved in 2 mL solvent (Table S1) under N_2. The mixture was heated in a microwave reactor under the conditions shown in Table S1, and the product was purified as detailed in Table S1. Each of MeObpy, EtObpy, PhObpy, MeSbpy and EtSbpy was obtained as a colourless oil; PhSbpy was isolated as a white solid (yields are given in Table S1). Spectroscopic data for MeObpy, PhObpy, MeSbpy, EtSbpy and PhSbpy have previously been reported.[1,2,3,4]

Table S1 Reaction conditions and purifications for N^N ligand preparation

Product	Brbpy / mg, mmol	Amount of NaOR or NaSR	Solvent	Microwave conditions	Yield / %
MeObpy	300, 1.28	5.12 mL (0.5 M), 2.56 mmol	DMF	4h, 120 ºC	77[a]
EtObpy	300, 1.28	186 mg (96% assay), 2.62 mmol	DMF	5h, 130 ºC	64[a,b]
PhObpy	104, 0.44	150 mg, 0.88 mmol	NMP	4h, 180 ºC, 1 bar	48[c]
MeSbpy	200, 0.85	126 mg (95% assay), 1.7 mmol	NMP	4h, 180 ºC, 1 bar	64[c]
EtSbpy	100, 0.43	79 mg (90% assay), 0.85 mmol	NMP	4h, 180 ºC, 1 bar	20[d]
PhSbpy	100, 0.43	125 mg (90% assay), 0.85 mmol	NMP	4h, 180 ºC, 1 bar	57[c]

[a]For product purification, the reaction mixture was added to water (25 mL) and extracted with toluene (3 × 25 mL). The combined organic fractions were washed with water (3 × 25 mL) and extracted with aq. H_2SO_4 (20%, 4 × 20 mL). Aqueous NH_3 (16%) was added to the combined aqueous layers until a white precipitate formed. The alkaline solution was extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic fractions were dried over $MgSO_4$. Solvent was evaporated under reduced pressure.
[b]The product was further purified by column chromatography (silica, *n*-pentane:EtOAc 10:1, 10% TEA).
[c]The reaction mixture was added to water (25 mL) and extracted with toluene (3 × 25 mL). The combined organic fractions were washed with water (3 × 25 mL) and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (alumina, *n*-pentane:EtOAc 20:1).
[d]The crude reaction mixture was purified by preparative TLC (silica, n-pentane:EtOAc 1:5) followed by column chromatography (alumina, *n*-pentane:EtOAc 20:1).

EtObpy



^{1}H NMR (500 MHz, CD_2Cl_2) δ/ppm 1.43 (t, J = 7.04 Hz, 3H, H^{Et}), 4.48 (q, J = 7.04 Hz, 2H, H^{Et}), 6.73 (dd, J = 8.21, 0.80 Hz, 1H, H^{B5}), 7.29 (ddd, J = 7.50, 4.79, 1.22 Hz, 1H, H^{A5}), 7.70 (dd, J = 8.21, 7.46 Hz, 1H, H^{B4}), 7.81 (ddd, J = 8.00, 7.50, 1.82 Hz, 1H, H^{A4}), 8.00 (dd, J = 7.46, 0.80 Hz, 1H, H^{B3}), 8.37 (m, 1H, H^{A3}), 8.63 (ddd, J = 4.79, 1.82, 0.95 Hz, 1H, H^{A6}). ^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ/ppm 15.0 (C^{Et}), 62.1 (C^{Et}), 111.7 (C^{B5}), 113.9 (C^{B3}), 121.3 (C^{A3}), 124.1 (C^{A5}), 137.3 (C^{A4}), 139.9 (C^{B4}), 149.6 (C^{A6}), 154.0 (C^{B2}), 156.6 (C^{A2}), 163.9 (C^{B6}). ESI MS: *m/z* 222.96 $[L+Na]^+$ (base peak, calc. 223.08).

Syntheses and characterization of copper complexes

[Cu(POP)(MeObpy)][PF$_6$]. A solution of $[Cu(MeCN)_4][PF_6]$ (93.2 mg, 0.25 mmol) and POP (135 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 30 min. A solution of MeObpy (47 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) was added and the mixture was stirred at room temperature for 1 h. The solution was filtered and the solvent was removed under reduced pressure. The crude product was redissolved in CH_2Cl_2 (2 mL) and layered with Et_2O (10 mL). Yellow crystals were formed and were separated by filtration and washed with *n*-hexane. Solvent residues were removed under reduced pressure. $[Cu(POP)(MeObpy)][PF_6]$ was isolated as a yellow solid (212 mg, 0.23 mmol, 91%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 3.90 (s, 3H, H^{OMe}), 6.77–6.85 (m, 6H, $H^{C3+D2/D2'}$), 7.04–7.09 (m, 2H, H^{C4}), 7.12–7.18 (m, 7H, $H^{B5+C6+D3/D3'}$), 7.26 (ddd, J = 7.6, 5.1, 1.1 Hz, 1H, H^{A5}), 7.30 (t, J = 7.4 Hz, 2H, $H^{D4/D4'}$), 7.34–7.43 (m, 8H, $H^{C5+D4/D4'+D3/D3'}$), 7.46–7.53 (m, 4H, $H^{D2/D2'}$), 8.08 (m, 1H, H^{A4}), 8.14 (m, 1H, H^{B4}), 8.16 (dd, J = 7.7, 1.3 Hz, 1H, H^{B3}), 8.23 (m, 1H, H^{A6}), 8.53 (m, 1H, H^{A3}). ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6): δ/ppm 56.4 (C^{OMe}), 108.5 (C^{B5}), 116.4 (C^{B3}), 121.5 (C^{C6}), 123.5 (C^{A3}), 125.2 (t, J_{PC} = 14

Hz, C^{C2}), 125.9 (t, J_{PC} = 2 Hz, C^{C4}), 126.6 (C^{A5}), 129.4 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.6 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.4 ($C^{D4/D4'}$), 131.2 ($C^{D4/D4'}$), 131.9 ($C^{D1/D1'}$ only from HMBC), 132.7 ($C^{D1/D1'}$ only from HMBC), 132.9 (C^{C5}), 133.1 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.9 (C^{C3}), 135.0 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 139.5 (C^{A4}), 143.1 (C^{B4}), 150.1 (C^{A6}), 151.7 (C^{B2}), 152.7 (C^{A2}), 159.4 (t, J_{PC} = 6 Hz, C^{C1}), 164.7 (C^{B6}). $^{31}P\{^{1}H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –11.4 (br. FWHM = 350 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 787.0 $[M-PF_6]^+$ (base peak, calc. 787.2). Found C 60.44, H 4.56, N 2.90; $C_{47}H_{38}CuF_6N_2O_2P_3$ requires 60.49, H 4.10, N 3.00%.

[Cu(POP)(EtObpy)][PF$_6$]. The method was as for [Cu(POP)(MeObpy)][PF_6] starting with [Cu(MeCN)$_4$][PF_6] (93.2 mg, 0.25 mmol), POP (135 mg, 0.25 mmol) and EtObpy (50 mg, 0.25 mmol). [Cu(POP)(EtObpy)][PF_6] was isolated as a yellow solid (213 mg, 0.23 mmol, 90%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 1.29 (t, J = 7.1 Hz, 3H, H^{OEt}), 4.26 (q, J = 7.1 Hz, 2H, H^{OEt}), 6.77–6.83 (m, 4H, $H^{D2/D2'}$), 6.86 (m, 2H, H^{C3}), 7.06–7.11 (m, 4H, H^{C4+C6}), 7.12–7.16 (m, 5H, $H^{B5+D3/D3'}$), 7.19 (ddd, J = 7.6, 5.2, 1.1 Hz, 1H, H^{A5}), 7.29 (m, 2H, $H^{D4/D4'}$), 7.33-7.38 (m, 6H, $H^{C5+D3/D3'}$), 7.40–7.45 (m, 2H, $H^{D4/D4'}$), 7.55–7.61 (m, 4H, $H^{D2/D2'}$), 8.05 (m, 1H, H^{A4}), 8.11 (m, 1H, H^{B4}), 8.13 (dd, J = 7.7, 1.3 Hz, 1H, H^{B3}), 8.17 (m, 1H, H^{A6}), 8.51 (m, 1H, H^{A3}). $^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6): δ/ppm 14.7 (C^{OEt}), 65.9 (C^{OEt}), 109.2 (C^{B5}), 116.3 (C^{B3}), 121.4 (C^{C6}), 123.4 (C^{A3}), 125.3 (t, J_{PC} = 14 Hz, C^{C2}), 125.9 (t, J_{PC} = 2 Hz, C^{C4}), 126.4 (C^{A5}), 129.4 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.6 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.3 ($C^{D4/D4'}$), 131.4 ($C^{D4/D4'}$), 131.7 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 132.7 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 132.9 (C^{C5}), 133.0 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.8 (C^{C3}), 135.5 (t, J_{PC} = 9 Hz, $C^{D2/D2'}$), 139.4 (C^{A4}), 142.9 (C^{B4}), 149.9 (C^{A6}), 151.9 (C^{B2}), 152.8 (C^{A2}), 159.2 (t, J_{PC} = 6 Hz, C^{C1}), 164.1 (C^{B6}). $^{31}P\{^{1}H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –11.0 (br. FWHM = 310 Hz), –144.2 (sept, J_{PF} = 708 Hz). ESI MS: *m/z* 801.0 $[M-PF_6]^+$ (base peak, calc. 801.2). Found C 59.62, H 4.54, N 3.08; $C_{48}H_{40}CuF_6N_2O_2P_3{\cdot}H_2O$ requires 59.72, H 4.39, N 2.90%.

[Cu(POP)(PhObpy)][PF$_6$]. The method was as for [Cu(POP)(MeObpy)][PF_6] starting with [Cu(MeCN)$_4$][PF_6] (93.2 mg, 0.25 mmol), POP (135 mg, 0.25 mmol) and PhObpy (62 mg, 0.25 mmol). [Cu(POP)(PhObpy)][PF_6] was isolated as a yellow solid (217 mg, 22 mmol, 87%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 6.67–6.74 (m, 5H, $H^{B5+E2+C3}$), 6.83–6.88 (m, 4H, $H^{D2/D2'}$), 7.02 (m, 2H, H^{C4}), 7.11 (m, 2H, H^{C6}), 7.18-7.26 (m, 8H, $H^{D3+D3'}$), 7.27 (ddd,

J = 7.6, 5.1, 1.1 Hz, 1H, H^{A5}), 7.31–7.39 (m, 7H, $H^{E4+C5+D4+D4'}$), 7.45 (m, 2H, H^{E3}), 7.48–7.54 (m, 4H, $H^{D2/D2'}$), 8.12 (m, 2H, H^{A4+B4}), 8.26 (m, 1H, H^{A6}), 8.34 (dd, 1H, J = 7.7, 0.6 Hz, H^{B3}), 8.63 (m, 1H, H^{A3}). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ/ppm 111.6 (C^{B5}), 117.9 (C^{B3}), 121.55 (C^{C6}), 121.6 (C^{E2}), 123.7 (C^{A3}), 124.9 (t, J_{PC} = 15 Hz, C^{C2}), 125.9 (t, J_{PC} = 2 Hz, C^{C4}), 126.8 (C^{A5}), 127.2 (C^{E4}), 129.5 (t, J_{PC} = 4 Hz, $C^{D3/D3'}$), 129.6 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.6 ($C^{D4/D4'}$), 131.3 ($C^{D4/D4'}$), 131.5 (C^{E3}), 131.7 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 132.6 (t, J_{PC} = 18 Hz, $C^{D1/D1'}$), 132.9 (C^{C5}), 133.3 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.9 (C^{C3}), 135.1 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 139.6 (C^{A4}), 143.3 (C^{B4}), 150.2 (C^{A6}), 152.25 (C^{B2}), 152.3 (C^{A2}), 153.7 (C^{E1}), 159.2 (t, J_{PC} = 6 Hz, C^{C1}), 164.3 (C^{B6}). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –11.7 (br. FWHM = 225 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: m/z 849.1 $[M-PF_6]^+$ (base peak, calc. 849.2). Found C 60.46, H 4.65, N 2.93; $C_{52}H_{40}CuF_6N_2O_2P_3{\cdot}2H_2O$ requires C 60.56, H 4.30, N 2.72%.

[Cu(xantphos)(MeObpy)][PF$_6$]. A CH_2Cl_2 (10 mL) solution of $[Cu(MeCN)_4][PF_6]$ (93.2 mg, 0.25 mmol) and a solution of xantphos (145 mg, 0.25 mmol) and MeObpy (47 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) were stirred at ambient temperature for 30 min. The solutions were then combined and the mixture was stirred at room temperature for 1 h. The solution was filtered and the solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 (2 mL) and layered with Et_2O (10 mL). The yellow crystals that formed were removed by filtration and washed with *n*-hexane. Solvent residues were removed under reduced pressure. $[Cu(xantphos)(MeObpy)][PF_6]$ was isolated as a yellow solid (148 mg, 0.15 mmol, 61%). ^1H NMR (500 MHz, acetone-d_6): δ/ppm 1.75 (s, 3H, $H^{a/a'}$), 1.83 (s, 3H, $H^{a/a'}$), 3.40 (s, 3H, H^{OMe}), 6.64 (m, 2H, H^{C3}), 7.02–7.09 (m, 8H, $H^{D2+D2'}$), 7.14–7.24 (m, 9H, $H^{B5+D3+D3'}$), 7.26 (m, 2H, H^{C4}), 7.30–7.37 (m, 4H, $H^{D4+D4'}$), 7.44 (m, 1H, H^{A5}), 7.83 (dd, J = 7.8, 1.5 Hz, 2H, H^{C5}), 8.10 (td, J = 7.9, 1.6 Hz, 1H, H^{A4}), 8.19–8.24 (m, 2H, H^{B3+B4}), 8.36 (ddd, J = 5.1, 1.7, 0.9 Hz, 1H, H^{A6}), 8.54 (dt, J = 8.2, 1.1 Hz, 1H, H^{A3}). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ/ppm 27.7 ($C^{a/a'}$), 29.0 ($C^{a/a'}$), 36.9 ($C^{xantphos\text{-}bridge}$), 56.1 ($C^{OMe}$), 108.6 ($C^{B5}$), 116.4 ($C^{B3}$), 121.5 (t, J_{PC} = 14 Hz, C^{C2}), 123.9 (C^{A3}), 125.9 (t, J_{PC} = 2 Hz, C^{C4}), 127.1 (C^{A5}), 128.2 (C^{C5}), 129.5 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.7 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.75 ($C^{D4/D4'}$), 130.8 ($C^{D4/D4'}$), 131.7 (C^{C3}), 132.8 (t, J_{PC} = 17 Hz, $C^{D1/D1'}$), 133.1 (t, J_{PC} = 17 Hz, $C^{D1/D1'}$), 133.7 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 133.8 (t,

J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.8 (C^{C6}), 139.7 (C^{A4}), 143.4 (C^{B4}), 149.9 (C^{A6}), 151.5 (C^{B2}), 152.7 (C^{A2}), 156.1 (t, J_{PC} = 6 Hz, C^{C1}), 165.1 (C^{B6}). $^{31}P\{^{1}H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –12.6 (br. FWHM = 270 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 827.0 $[M-PF_6]^+$ (base peak, calc. 827.2). Found C 61.92, H 4.81, N 3.17; $C_{50}H_{42}CuF_6N_2O_2P_3$ requires C 61.70, H 4.35, N 2.88%.

[Cu(xantphos)(EtObpy)][PF$_6$]. The method was as for [Cu(xantphos)(MeObpy)][PF_6] starting with [$Cu(MeCN)_4$][PF_6] (93.2 mg, 0.25 mmol), xantphos (145 mg, 0.25 mmol) and EtObpy (50 mg, 0.25 mmol). [Cu(xantphos)(EtObpy)][PF_6] was isolated as a yellow solid (239 mg, 0.24 mmol, 97%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 0.76 (t, J = 7.1 Hz, 3H, H^{OEt}), 1.72 (s, 3H, $H^{a/a'}$), 1.82 (s, 3H, $H^{a/a'}$), 3.84 (q, J = 7.1 Hz, 2H, H^{OEt}), 6.71 (m, 2H, H^{C3}), 7.04–7.14 (m, 8H, $H^{D2+D2'}$), 7.15–7.20 (m, 5H, $H^{B5+D3/D3'}$), 7.23–7.29 (m, 6H, $H^{C4+D3/D3'}$), 7.30–7.34 (m, 4H, $H^{D4+D4'}$), 7.42 (m, 1H, H^{A5}), 7.84 (dd, J = 7.2, 1.4 Hz, 2H, H^{C5}), 8.07 (td, J = 8.0, 1.6 Hz, 1H, H^{A4}), 8.14 (m, 1H, H^{B3}), 8.19 (m, 1H, H^{B4}), 8.31 (m, 1H, H^{A6}), 8.54 (dt, J = 8.2, 1.1 Hz, 1H, H^{A3}). $^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6): δ/ppm 13.9 (C^{OEt}), 27.5 ($C^{a/a'}$), 29.4 ($C^{a/a'}$), 36.9 ($C^{xantphos\text{-}bridge}$), 65.2 ($C^{OEt}$), 109.4 ($C^{B5}$), 116.2 ($C^{B3}$), 121.6 (t, J_{PC} = 14 Hz, C^{C2}), 123.7 (C^{A3}), 125.9 (t, J_{PC} = 2 Hz, C^{C4}), 127.0 (C^{A5}), 128.3 (C^{C5}), 129.5 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.8 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.7 ($C^{D4/D4'}$), 130.9 ($C^{D4/D4'}$), 131.7 (C^{C3}), 132.8 (t, J_{PC} = 17 Hz, $C^{D1/D1'}$), 133.1 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 133.7 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 133.75 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 135.0 (C^{C6}), 139.7 (C^{A4}), 143.2 (C^{B4}), 149.7 (C^{A6}), 151.6 (C^{B2}), 152.8 (C^{A2}), 156.1 (t, J_{PC} = 6 Hz, C^{C1}), 165.2 (C^{B6}). $^{31}P\{^{1}H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –13.0 (br. FWHM = 183 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 841.1 $[M-PF_6]^+$ (base peak, calc. 841.2). Found C 61.91, H 4.98, N 3.19; $C_{51}H_{44}CuF_6N_2O_2P_3$ requires C 62.04, H 4.49, N 2.84%.

[Cu(xantphos)(PhObpy)][PF$_6$]. The method was as for [Cu(xantphos)(MeObpy)][PF_6] starting with [$Cu(MeCN)_4$][PF_6] (93.2 mg, 0.25 mmol), xantphos (145 mg, 0.25 mmol) and PhObpy (62 mg, 0.25 mmol). [Cu(xantphos)(PhObpy)][PF_6] was isolated as a yellow solid (254 mg, 0.25 mmol, 98%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 1.46 (s, 3H, $H^{a/a'}$), 1.48 (s, 3H, $H^{a/a'}$), 6.04 (m, 2H, H^{E2}), 6.58 (dd, J = 8.3, 0.6 Hz, 1H, H^{B5}), 6.68 (m, 2H, H^{C3}), 6.93–6.98 (m, 4H, $H^{D2/D2'}$), 7.10–7.15 (m, 4H, $H^{D3/D3'}$), 7.18–7.25 (m, 9H, $H^{E3+E4+C4+D2/D2'}$), 7.25–7.32 (m, 6H, $H^{D3/D3'+D4/D4'}$), 7.38 (m, 2H, $H^{D4/D4'}$), 7.53 (dd, J = 7.8, 1.5 Hz, 2H, H^{C5}), 7.58 (m, 1H, H^{A5}), 8.13 (m, 1H, H^{A4})

overlapping with 8.15 (m, 1H, H^{B4}), 8.33 (dd, J = 7.8, 0.6 Hz, 1H, H^{B3}), 8.56 (dt, J = 8.2, 1.1 Hz, 1H, H^{A3}), 8.80 (d, J = 5.0 Hz, 1H, H^{A6}). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ/ppm 24.9 ($C^{a/a'}$), 30.9 ($C^{a/a'}$), 36.6 ($C^{xantphos\text{-}bridge}$), 111.4 ($C^{B5}$), 117.7 ($C^{B3}$), 121.3 (t, J_{PC} = 14 Hz, C^{C2}), 121.5 (C^{E2}), 123.9 (C^{A3}), 125.7 (t, J_{PC} = 2 Hz, C^{C4}), 126.9 (C^{E4}), 127.5 (C^{A5}), 128.1 (C^{C5}), 129.6 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.8 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.8 ($C^{D4/D4'}$), 130.8 ($C^{D4/D4'}$), 131.0 (C^{E3}), 131.3 (C^{C3}), 132.9 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 133.0 (t, J_{PC} = 18 Hz, $C^{D1/D1'}$), 133.6 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 133.8 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.8 (C^{C6}), 139.7 (C^{A4}), 143.6 (C^{B4}), 150.3 (C^{A6}), 151.9 (C^{B2}), 152.2 (C^{A2}), 153.1 (C^{E1}), 156.0 (t, J_{PC} = 6 Hz, C^{C1}), 164.8 (C^{B6}). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –12.8 (br. FWHM = 240 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 889.1 $[M-PF_6]^+$ (base peak, calc. 889.2). Found C 63.70, H 4.53, N 2.97; $C_{55}H_{44}CuF_6N_2O_2P_3$ requires C 63.80, H 4.28, N 2.71%.

[Cu(POP)(MeSbpy)][PF$_6$]. The method was as for [Cu(POP)(MeObpy)][PF_6] starting with [Cu(MeCN)$_4$][PF_6] (93.2 mg, 0.25 mmol), POP (135 mg, 0.25 mmol) and MeSbpy (51 mg, 0.25 mmol). [Cu(POP)(MeSbpy)][PF_6] was isolated as a yellow solid (213 mg, 0.23 mmol, 90%). ^1H NMR (500 MHz, acetone-d_6): δ/ppm 2.45 (s, 3H, H^{SMe}), 6.84 (m, 4H, $H^{D2/D2'}$), 6.91 (m, 2H, H^{C3}), 7.08–7.17 (m, 9H, $H^{A5+D3/D3'+C4+C6}$), 7.30 (t, J = 7.5 Hz, 2H, $H^{D4/D4'}$), 7.33–7.45 (overlapping signals, 9H, $H^{D3/D3'+D4/D4'+C5+B5}$), 7.59 (m, 4H, $H^{D2/D2'}$), 8.02–8.08 (overlapping, 2H, H^{A4+B4}), 8.14 (ddt, J = 4.4, 1.7, 0.8 Hz, 1H, H^{A6}), 8.26 (dd, J = 7.9, 0.8 Hz, 1H, H^{B3}), 8.53 (dd, J = 8.2, 1.0 Hz, 1H, H^{A3}). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ/ppm 15.7 (C^{SMe}), 118.9 (C^{B3}), 121.1 (C^{C6}), 122.3 (C^{B5}), 123.5 (C^{A3}), 125.6 (t, J_{PC} = 14 Hz, C^{C2}), 126.0 (t, J_{PC} = 2 Hz, C^{C4}), 126.5 (C^{A5}), 129.3 (t, J_{PC} = 4 Hz, $C^{D3/D3'}$), 129.6 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.3 ($C^{D4/D4'}$), 131.3 ($C^{D4/D4'}$), 131.6 ($C^{D1/D1'}$ from HMBC), 132.4 ($C^{D1/D1'}$ from HMBC), 133.0 (C^{C5}), 133.1 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.8 (C^{C3}), 135.5 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 139.5 (C^{A4}), 140.0 (C^{B4}), 149.9 (C^{A6}), 152.7 ($C^{A2/B2}$), 152.75 ($C^{A2/B2}$), 158.8 (t, J_{PC} = 6 Hz, C^{C1}), 163.6(C^{B6}). $^{31}P\{^1H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –11.2 (br. FWHM = 260 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 803.0 $[M-PF_6]^+$ (base peak, calc. 803.2). Found C 59.07, H 4.25, N 2.83; $C_{47}H_{38}CuF_6N_2OP_3S$ requires C 59.46, H 4.03, N 2.95%.

[Cu(POP)(EtSbpy)][PF$_6$]. The method was as for [Cu(POP)(MeObpy)][PF_6] starting with [Cu(MeCN)$_4$][PF_6] (93.2 mg, 0.25 mmol), POP (135 mg, 0.25 mmol) and EtSbpy (54 mg, 0.25 mmol). [Cu(POP)(EtSbpy)][PF_6] was

isolated as a yellow solid (190 mg, 0.20 mmol, 79%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 1.13 (t, J = 7.4 Hz, 3H, H^{SEt}), 2.98 (q, J = 7.4 Hz, 2H, H^{SEt}), 6.77-6.91 (overlapping m, 6H, $H^{D2/D2'+C3}$), 7.09–7.17 (overlapping m, 9H, $H^{C4+C6+D3/D3'+A5}$), 7.27–7.43 (m, 9H, $H^{C5+B5+D3/D3'+D4+D4'}$), 7.56 (m, 4H, $H^{D2/D2'}$), 8.00–8.07 (overlapping m, 2H, H^{A4+B4}), 8.17 (ddd, J = 5.2, 1.7, 0.9 Hz, 1H, H^{A6}), 8.26 (dd, J = 8.0, 0.8 Hz, 1H, H^{B3}), 8.51 (m, 1H, H^{A3}). ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6): δ/ppm 13.5 (C^{SEt}), 27.1 (C^{SEt}), 118.9 (C^{B3}), 120.9 (C^{C6}), 122.7 (C^{B5}), 123.5 (C^{A3}), 125.4 (t, J_{PC} = 14 Hz, C^{C2}), 126.0 (C^{C4}), 126.4 (C^{A5}), 129.3 (t, J_{PC} = 4 Hz, $C^{D3/D3'}$), 129.5 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.4 ($C^{D4/D4'}$), 131.3 ($C^{D4/D4'}$), 131.7 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 132.4 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 133.0 (C^{C5}), 133.2 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.9 (C^{C3}), 135.4 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 139.5 (C^{A4}), 139.7 (C^{B4}), 149.9 (C^{A6}), 152.7 ($C^{A2/B2}$), 152.9 ($C^{A2/B2}$), 158.8 (t, J_{PC} = 6.0 Hz, C^{C1}), 162.7 (C^{B6}). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6): δ /ppm –11.4 (br. FWHM = 280 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 817.0 $[M-PF_6]^+$ (base peak, calc. 817.2). Found C 59.15, H 4.40, N 3.02; $C_{48}H_{40}CuF_6N_2OP_3S{\cdot}H_2O$ requires 58.75, H 4.31, N 2.85%.

[Cu(POP)(PhSbpy)][PF$_6$]. The method was as for [Cu(POP)(MeObpy)][PF_6] starting with [Cu(MeCN)$_4$][PF_6] (93.2 mg, 0.25 mmol), POP (135 mg, 0.25 mmol) and PhSbpy (66 mg, 0.25 mmol). [Cu(POP)(PhSbpy)][PF_6] was isolated as a yellow solid (192 mg, 0.19 mmol, 76%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 6.75 (dd, J = 8.1, 0.8 Hz, 1H, H^{B5}), 6.88–6.92 (m, 6H, $H^{C3+D2/D2'}$), 7.12 (m, 4H, H^{C4+C6}), 7.17–7.22 (overlapping m, 7H, $H^{A5+E2+D3/D3'}$), 7.32–7.38 (m, 8H, $H^{C5+D3/D3'+D4/D4'}$), 7.41 (m, 2H, $H^{D4/D4'}$), 7.49 (m, 2H, H^{E3}), 7.55 (m, 1H, H^{E4}), 7.63 (m, 4H, $H^{D2/D2'}$), 7.90 (m, 1H, H^{B4}), 8.06 (m, 1H, H^{A4}), 8.20 (m, 1H, H^{A6}), 8.30 (dd, 1H, J = 7.9, 0.8 Hz, H^{B3}), 8.54 (m, 1H, H^{A3}). ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6): δ/ppm 119.5 (C^{B3}), 121.2 (C^{C6}), 123.4 (C^{B5}), 123.7 (C^{A3}), 125.5 (t, J_{PC} = 15 Hz, C^{C2}), 126.1 (t, J_{PC} = 2 Hz, C^{C4}), 126.6 (C^{A5}), 129.5 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.7 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.8 (C^{E1}), 130.5 (C^{C5}), 131.3 (C^{E3}), 131.4 ($C^{D4/D4'}$), 131.45 (C^{E4}), 131.5 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 132.4 (t, J_{PC} = 18 Hz, $C^{D1/D1'}$), 133.1 ($C^{D4/D4'}$), 133.3 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.9 (C^{C3}), 135.5 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 136.0 (C^{E2}), 139.6 (C^{A4}), 140.1 (C^{B4}), 150.0 (C^{A6}), 152.5 (C^{A2}), 153.1 (C^{B2}), 158.8 (t, J_{PC} = 6 Hz, C^{C1}), 163.9 (C^{B6}). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6): δ/ppm –11.6 (br. FWHM = 194 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 865.1 $[M-PF_6]^+$ (base peak, calc. 865.2).

Found C 61.35, H 4.66, N 2.99; $C_{52}H_{40}CuF_6N_2OP_3S{\cdot}H_2O$ requires C 60.67, H 4.11, N 2.72%.

[Cu(xantphos)(MeSbpy)][PF$_6$]. The method was as for [Cu(xantphos)(MeObpy)][PF_6] starting with [$Cu(MeCN)_4$][PF_6] (93.2 mg, 0.25 mmol), xantphos (145 mg, 0.25 mmol) and MeSbpy (51 mg, 0.25 mmol). [Cu(xantphos)(MeSbpy)][PF_6] was isolated as a yellow solid (198 mg, 0.20 mmol, 80%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 1.71 (s, 3H, $H^{a/a'}$), 1.86 (s, 3H, $H^{a/a'}$), 2.17 (s, 3H, H^{SMe}), 6.68 (m, 2H, H^{C3}), 7.02–7.07 (m, 4H, $H^{D2/D2'}$), 7.13–7.19 (m, 8H, $H^{D2/D2'+D3/D3'}$), 7.23–7.28 (m, 6H, $H^{C4+D3/D3'}$), 7.31 (m, 2H, $H^{D4/D4'}$), 7.40 (m, 2H, $H^{D4/D4'}$), 7.44 (m, 1H, H^{A5}), 7.50 (dd, J = 8.2, 0.7 Hz, 1H, H^{B5}), 7.83 (dd, J = 7.8, 1.4 Hz, 2H, H^{C5}), 8.07 (ddd, J = 8.1, 7.5, 1.7 Hz, 1H, H^{A4}), 8.13 (m, 1H, H^{B4}), 8.26 (m, 1H, H^{B3}), 8.33 (m, 1H, H^{A6}), 8.48 (dt, J = 8.1, 1.0 Hz, 1H, H^{A3}). ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6): δ/ppm 15.2 (C^{SMe}), 27.3 ($C^{a/a'}$), 30.0 ($C^{a/a'}$), 36.8 ($C^{xantphos\text{-}bridge}$), 118.8 ($C^{B3}$), 121.9 (t, J_{PC} = 15 Hz, C^{C2}), 122.1 (C^{B5}), 123.9 (C^{A3}), 125.9 (t, J_{PC} = 2 Hz, C^{C4}), 127.1 (C^{A5}), 128.3 (C^{C5}), 129.3 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.8 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.8 ($C^{D4/D4'}$), 130.9 ($C^{D4/D4'}$), 131.6 (C^{C3}), 132.6 (t, J_{PC} = 17 Hz, $C^{D1/D1'}$), 133.0 (t, J_{PC} = 17 Hz, $C^{D1/D1'}$), 133.7 and 133.8 (overlapping t, J_{PC} = 8 Hz, $C^{D2+D2'}$), 134.5 (C^{C6}), 139.8 (C^{A4}), 140.1 (C^{B4}), 149.8 (C^{A6}), 152.3 (C^{A2}), 152.6 (C^{B2}), 156.1 (t, J_{PC} = 6 Hz, C^{C1}), 164.2 (C^{B6}). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6): δ/ppm –11.8 (br. FWHM = 250 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 843.0 $[M{-}PF_6]^+$ (base peak, calc. 843.2). Found C 59.90, H 4.54, N 3.12; $C_{50}H_{42}CuF_6N_2OP_3S{\cdot}H_2O$ requires C 59.61, H 4.40, N 2.78%.

[Cu(xantphos)(EtSbpy)][PF$_6$]. The method was as for [Cu(xantphos)(MeObpy)][PF_6] starting with [$Cu(MeCN)_4$][PF_6] (93.2 mg, 0.25 mmol), xantphos (145 mg, 0.25 mmol) and EtSbpy (54 mg, 0.25 mmol). [Cu(xantphos)(EtSbpy)][PF_6] was isolated as a yellow solid (163 mg, 0.16 mmol, 65%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 0.76 (t, J = 7.4 Hz, 3H, H^{SEt}), 1.63 (s, 3H, $H^{a/a'}$), 1.90 (s, 3H, $H^{a/a'}$), 2.73 (q, J = 7.4 Hz, 2H, H^{SEt}), 6.75 (m, 2H, H^{C3}), 7.00 (m, 4H, $H^{D2/D2'}$), 7.13 (m, 4H, $H^{D3/D3'}$), 7.21–7.34 (overlapping m, 12H, $H^{C4+D2/D2'+D3/D3'+D4/D4'}$), 7.51 (overlapping m, 2H, H^{A5+B5}), 7.82 (dd, J = 7.8, 1.4 Hz, 2H, H^{C5}), 8.07 (m, 1H, H^{A4}) overlapping with 8.10 (m, 1H, H^{B4}), 8.21 (dd, J = 8.0, 0.8 Hz, 1H, H^{B3}), 8.43 (ddd, J = 8.3, 1.0, 1.0 Hz, 1H, H^{A3}), 8.54 (br, 1H, H^{A6}). ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6): δ/ppm 13.1 (C^{SEt}), 26.0 ($C^{a/a'}$), 26.5 ($C^{a/a'}$), 36.8 ($C^{xantphos\text{-}bridge}$), 118.7 ($C^{B3}$), 122.1 (t,

J_{PC} = 14 Hz, C^{C2}), 122.5 (C^{B5}), 123.7 (C^{A3}), 125.8 (t, J_{PC} = 2 Hz, C^{C4}), 127.1 (C^{A5}), 128.2 (C^{C5}), 129.5 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.9 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.8 ($C^{D4/D4'}$), 130.9 ($C^{D4/D4'}$), 131.5 (C^{C3}), 132.6 (t, J_{PC} = 17 Hz, $C^{D1/D1'}$), 133.0 (t, J_{PC} = 16 Hz, $C^{D1/D1'}$), 133.75 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 133.8 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.6 (C^{C6}), 139.5 (C^{A4}), 139.9 (C^{B4}), 150.0 (C^{A6}), 152.4 (C^{A2}), 152.6 (C^{B2}), 156.2 (t, J_{PC} = 6 Hz, C^{C1}), 163.2 (C^{B6}). $^{31}P\{^{1}H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –12.1 (br. FWHM = 210 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 857.0 $[M-PF_6]^+$ (base peak, calc. 857.2). Found C 60.64, H 4.73, N 3.13; $C_{51}H_{44}CuF_6N_2OP_3S$ requires C 61.05, H 4.42, N 2.79%.

[Cu(xantphos)(PhSbpy)][PF$_6$]. The method was as for [Cu(xantphos)(MeObpy)][PF_6] starting with [$Cu(MeCN)_4$][PF_6] (93.2 mg, 0.25 mmol), xantphos (145 mg, 0.25 mmol) and PhSbpy (66 mg, 0.25 mmol). [Cu(xantphos)(PhSbpy)][PF_6] was isolated as a yellow solid (179 mg, 0.17 mmol, 68%). ^{1}H NMR (500 MHz, acetone-d_6): δ/ppm 1.58 (s, 3H, $H^{a/a'}$), 1.59 (s, 3H, $H^{a/a'}$), 6.76 (m, 2H, H^{C3}), 6.85 (m, 2H, H^{E2}), 6.91 (dd, *J* = 8.2, 0.8 Hz, 1H, H^{B5}), 7.02 (m, 4H, $H^{D2/D2'}$), 7.16 (m, 4H, $H^{D3/D3'}$), 7.22–7.39 (overlapping m, 14H, $H^{E3+C4+D2/D2'+D3/D3'+D4/D4'}$), 7.41 (m, 2H, $H^{D4/D4'}$), 7.47 (m, 1H, H^{E4}), 7.56 (ddd, *J* = 7.6, 5.1, 1.1 Hz, 1H, H^{A5}), 7.67 (dd, *J* = 7.8, 1.4 Hz, 2H, H^{C5}), 8.00 (m, 1H, H^{B4}), 8.10 (m, 1H, H^{A4}), 8.27 (dd, *J* = 8.0, 0.8 Hz, 1H, H^{B3}), 8.47 (dt, *J* = 8.3, 1.1 Hz, 1H, H^{A3}), 8.67 (br, 1H, H^{A6}). $^{13}C\{^{1}H\}$ NMR (126 MHz, acetone-d_6): δ/ppm 25.9 ($C^{a/a'}$), 31.5 ($C^{a/a'}$), 36.7 ($C^{xantphos\text{-}bridge}$), 119.5 ($C^{B3}$), 121.9 (t, J_{PC} = 14 Hz, C^{C2}), 123.4 (C^{B5}), 123.9 (C^{A3}), 125.8 (t, J_{PC} = 3 Hz, C^{C4}), 127.4 (C^{A5}), 128.5 (C^{C5}), 129.5 (C^{E1}), 129.6 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 129.9 (t, J_{PC} = 5 Hz, $C^{D3/D3'}$), 130.9 (C^{E3}), 130.9 ($C^{D4+D4'}$), 131.1 (C^{E4}), 131.7 (C^{C3}), 132.7 (t, J_{PC} = 17 Hz, $C^{D1/D1'}$), 132.8 (t, J_{PC} = 18 Hz, $C^{D1/D1'}$), 133.7 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 133.9 (t, J_{PC} = 8 Hz, $C^{D2/D2'}$), 134.3 (C^{C6}), 135.4 (C^{E2}), 139.8 (C^{A4}), 140.4 (C^{B4}), 150.2 (C^{A6}), 152.5 (C^{A2}), 152.7 (C^{B2}), 156.0 (t, J_{PC} = 6 Hz, C^{C1}), 164.4 (C^{B6}). $^{31}P\{^{1}H\}$ NMR (162 MHz, acetone-d_6): δ/ppm –11.7 (br. FWHM = 175 Hz), –144.2 (sept, J_{PF} = 707 Hz). ESI MS: *m/z* 905.0 $[M-PF_6]^+$ (base peak, calc. 905.2). Found C 61.56, H 4.61, N 2.75; $C_{55}H_{44}CuF_6N_2OP_3S{\cdot}H_2O$ requires C 61.77, H 4.34, N 2.62%.

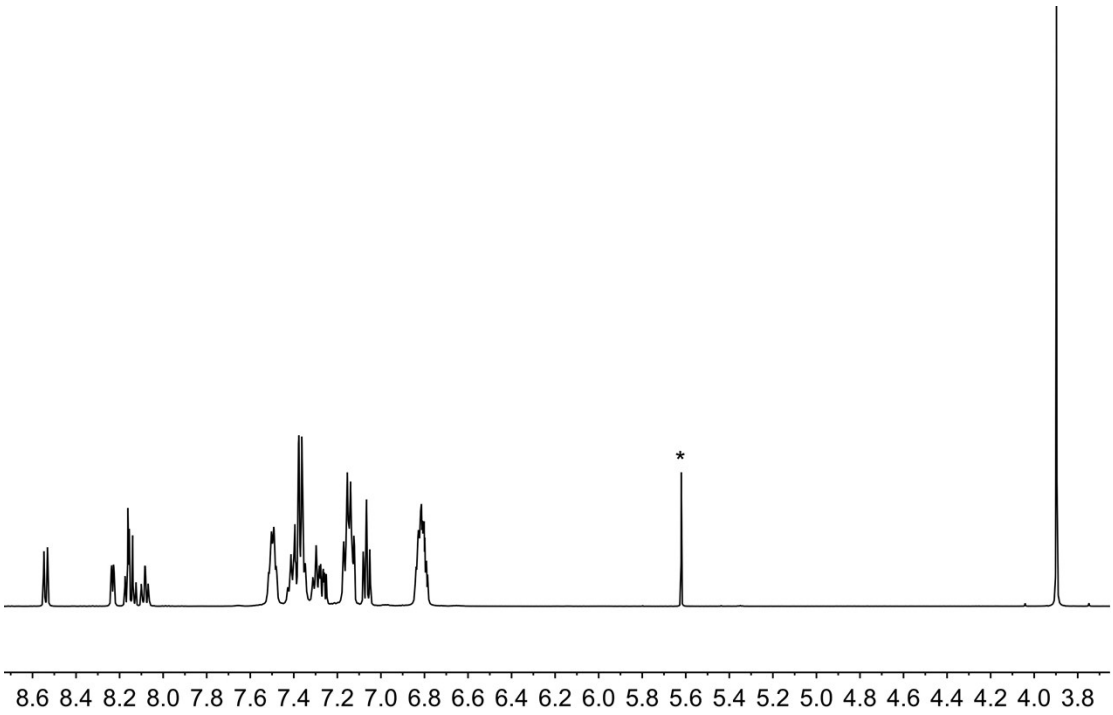


Fig. S1 500 MHz ^{1}H NMR spectrum of [Cu(POP)(MeObpy)][PF_6] in acetone-d_6. See also Fig. 1 in the manuscript. * = residual $CD_3C(O)CD_2H$. Chemical shifts in δ/ppm.

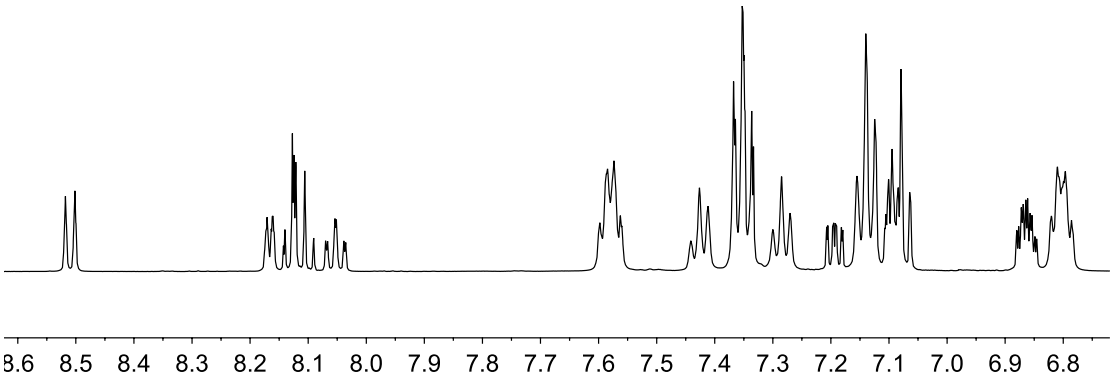


Fig. S2 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(POP)(EtObpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

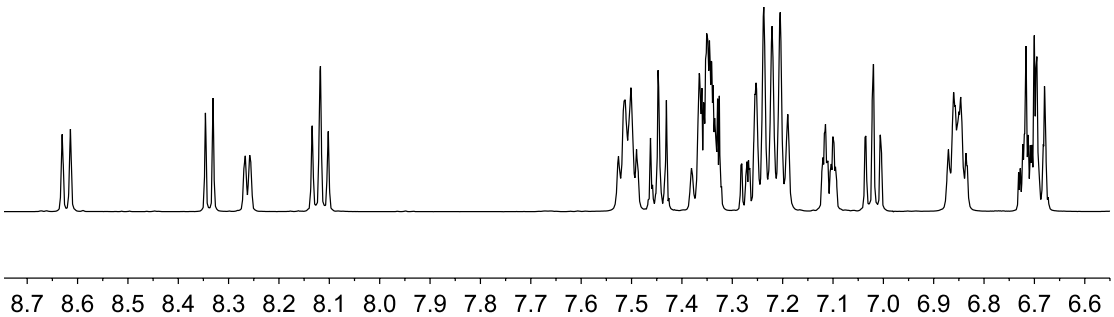


Fig. S3 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(POP)(PhObpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

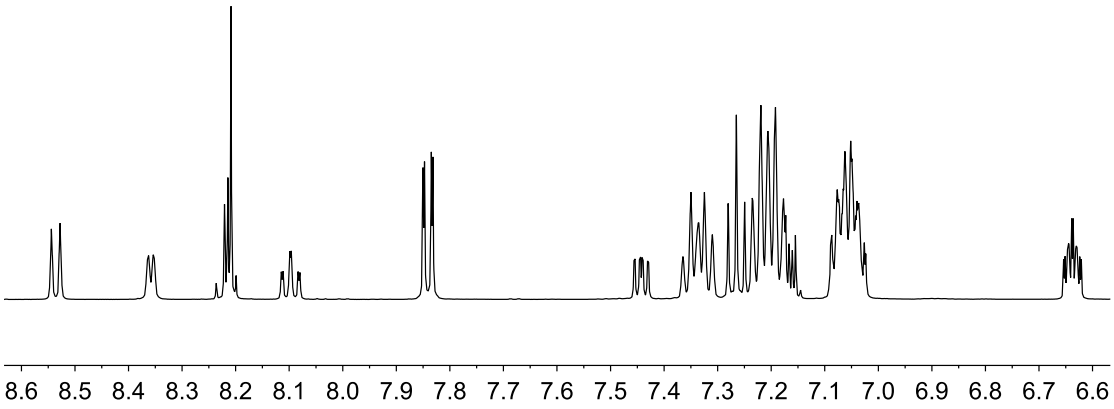


Fig. S4 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(xantphos)(MeObpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

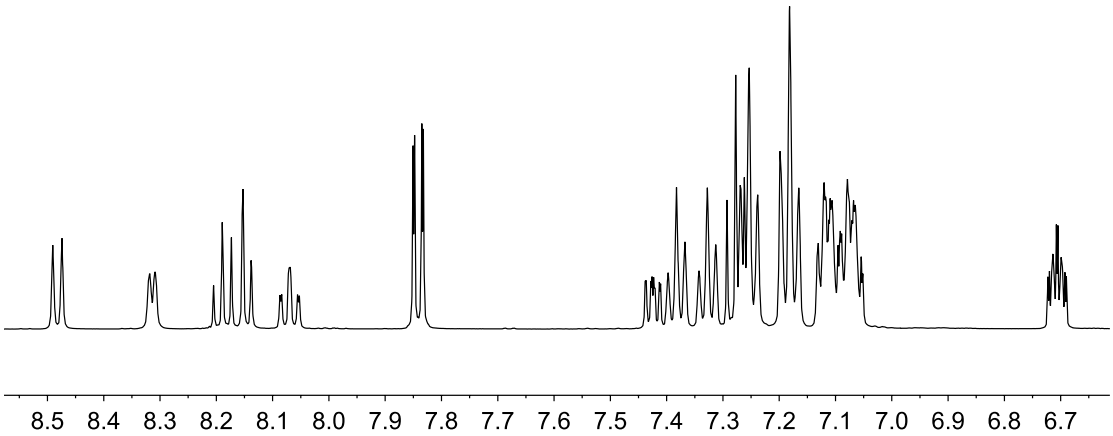


Fig. S5 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(xantphos)(EtObpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

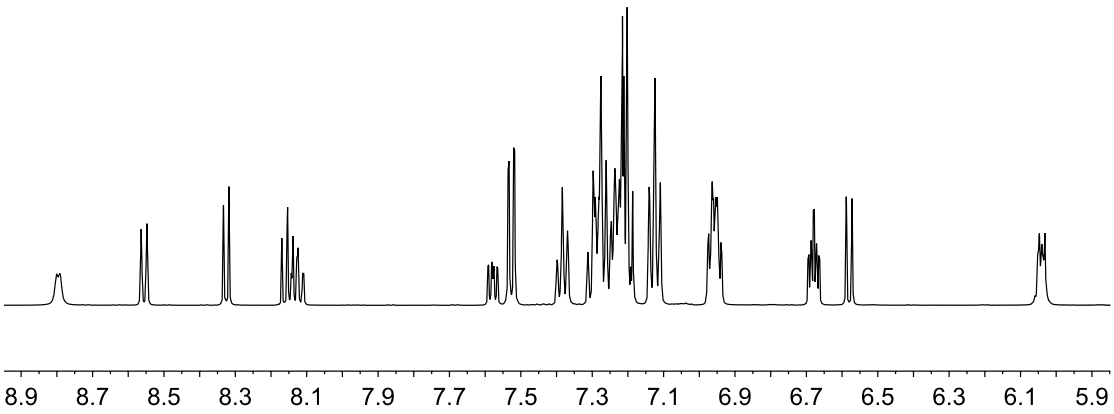


Fig. S6 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(xantphos)(PhObpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

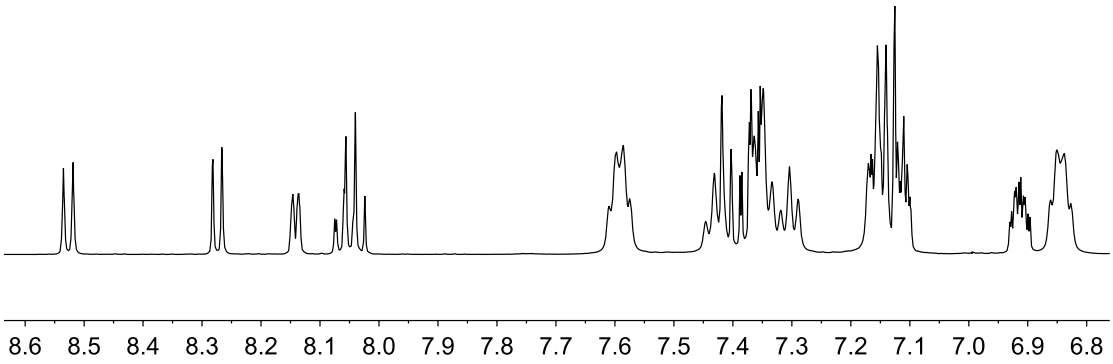


Fig. S7 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(POP)(MeSbpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

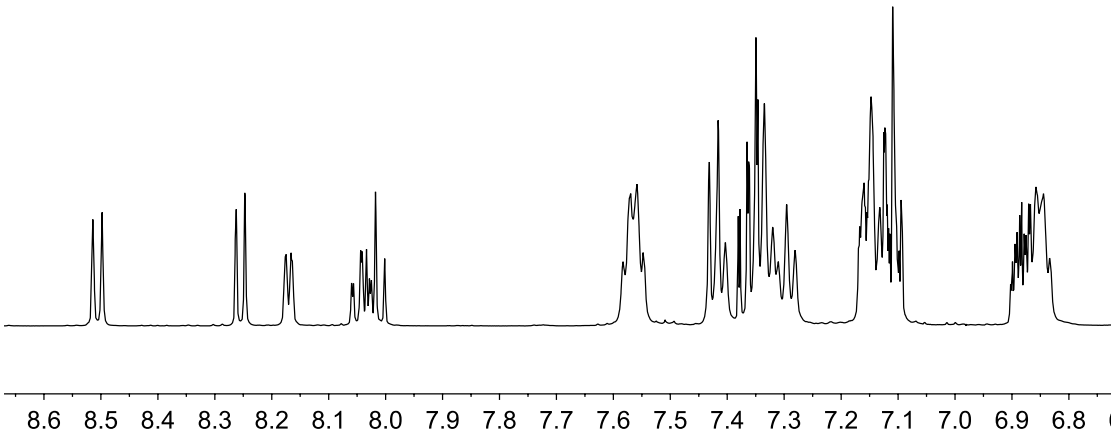


Fig. S8 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(POP)(EtSbpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

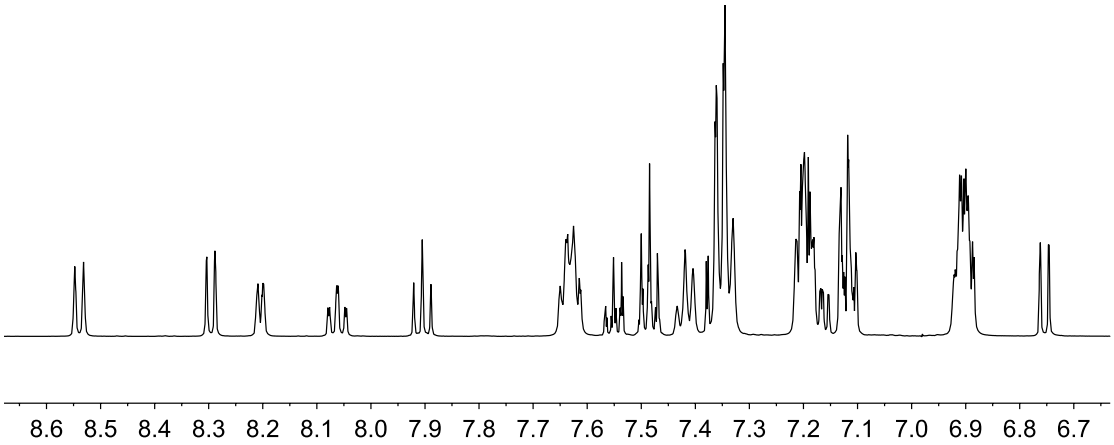


Fig. S9 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(POP)(PhSbpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

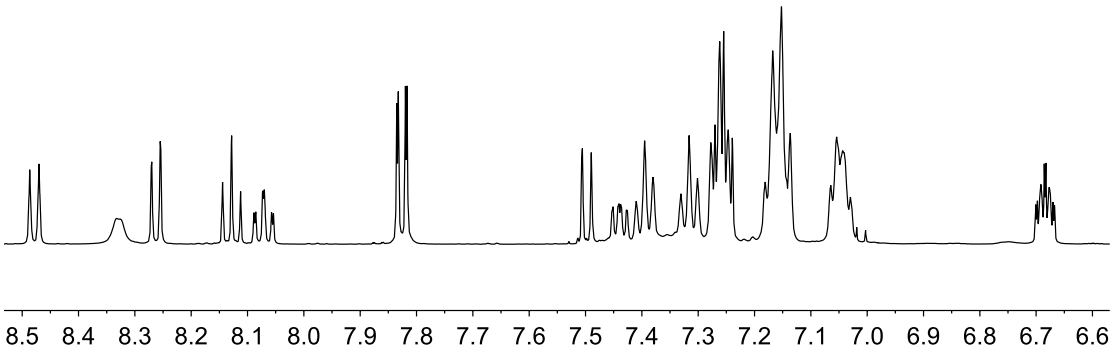


Fig. S10 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(xantphos)(MeSbpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

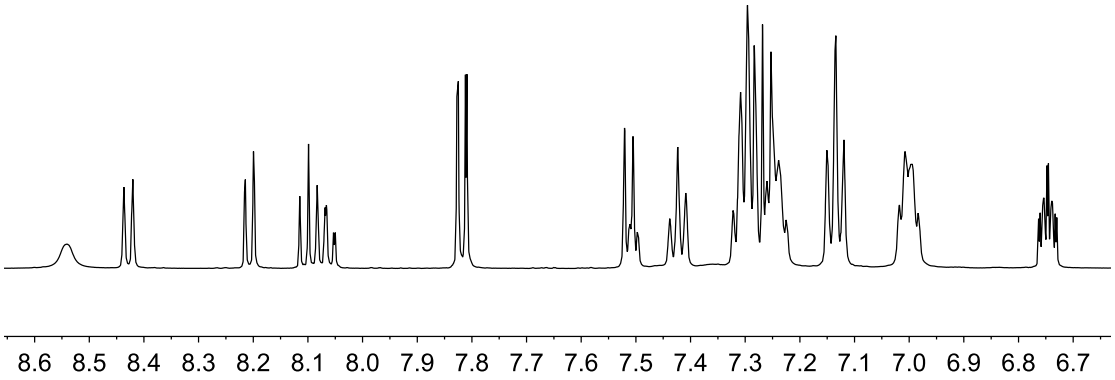


Fig. S11 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(xantphos)(EtSbpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

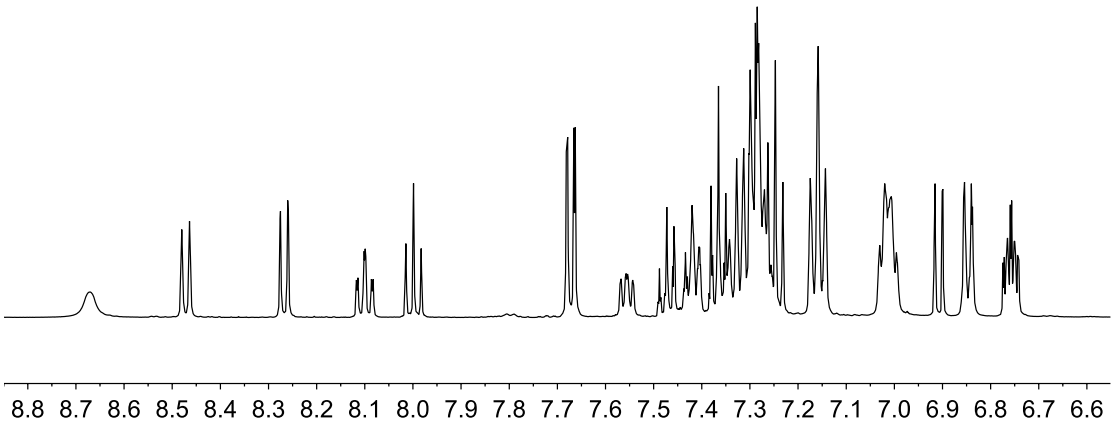


Fig. S12 Aromatic region of the 500 MHz ^{1}H NMR spectrum of [Cu(xantphos)(PhSbpy)][PF_6] in acetone-d_6. Chemical shifts in δ/ppm.

Table S2 Crystallographic data for the copper(I) complexes

Compound	[Cu(POP)(MeObpy)][PF$_6$]	[Cu(POP)(EtObpy)][PF$_6$]	2{[Cu(POP)(PhObpy)][PF$_6$]} ·1.5CH_2Cl_2	[Cu(POP)(MeSbpy)][PF$_6$]
Formula	$C_{47}H_{38}CuF_6N_2O_2P_3$	$C_{48}H_{40}CuF_6N_2O_2P_3$	$C_{105.50}H_{83}Cl_3Cu_2F_{12}N_4O_4P_6$	$C_{47}H_{38}CuF_6N_2OP_3S$
Formula weight	933.29	947.31	2118.11	949.35
Crystal colour; habit	yellow block	yellow block	yellow block	yellow block
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1/c$	$Pbca$	P–1	P–1
a, b, c / Å	10.7304(8) 43.541(3) 9.6702(7)	16.3593(10) 20.1565(12) 26.5917(17)	14.4382(9) 17.1970(11) 21.5959(14)	9.9139(9) 14.2468(13) 15.7717(14)
α,β,γ/ °	90 108.260(4) 90	90 90 90	107.797(3) 104.175(3) 94.745(3)	82.112(3) 84.629(3) 71.123(3)
U / Å^3	4290.5(5)	8768.5(9)	4877.4(6)	2085.0(3)
D_c / Mg m^{-3}	1.445	1.435	1.44	1.512
Z	4	8	2	2
μ (Cu-Kα) / mm^{-1}	2.359	2.317	2.885	2.875
T / K	123	123	123	123
Refln. collected (R_{int})	28076 (0.030)	31282 (0.042)	64272 (0.033)	27895 (0.025)
Unique refln.	7688	8014	17894	7564
Refln. for refinement	7266	7093	16525	7524
Parameters	583	559	1216	550
Threshold	I >2σ(I)	I >2σ(I)	I >2σ(I)	I >2σ(I)
$R1$ ($R1$ all data)	0.0951(0.0977)	0.0397 (0.0453)	0.0547 (0.0582)	0.0453 (0.0454)
$wR2$ ($wR2$ all data)	0.2331 (0.2338)	0.0964 (0.0991)	0.1435 (0.1445)	0.0847 (0.0847)
Goodness of fit	1.0713	0.9818	0.9889	0.9337
CCDC	1562408	1562410	1562412	1562449

Compound	[Cu(POP)(EtSbpy)][PF$_6$] ·Et_2O	[Cu(POP)(PhSbpy)][PF$_6$]	[Cu(xantphos)(MeObpy)][PF$_6$] ·CH_2Cl_2·0.5Et_2O	[Cu(xantphos)(EtObpy)][PF$_6$] ·0.5CH_2Cl_2·0.5H_2O
Formula	$C_{52}H_{50}CuF_6N_2O_2P_3S$	$C_{52}H_{40}CuF_6N_2OP_3S$	$C_{53}H_{49}Cl_2CuF_6N_2O_{2.50}P_3$	$C_{51.50}H_{46}ClCuF_6N_2O_{2.50}P_3$
Formula weight	1037.50	1011.42	1095.34	1038.85
Crystal colour; habit	yellow block	yellow block	yellow block	yellow block
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P2_1/n$	P–1	P–1
a, b, c / Å	31.7468(14) 15.6233(7) 19.5833(9)	9.8131(14) 28.886(4) 16.433(3)	10.9394(9) 15.1458(11) 18.1780(14)	10.8766(6) 15.2866(9) 18.4018(10)
α,β,γ/ °	90 101.338(3) 90	90 103.040(6) 90	109.391(4) 98.101(4) 108.096(4)	106.817(4) 102.402(3) 107.943(4)
U / Å^3	9523.6(7)	4538.0(12)	2598.5(4)	2626.6(3)
D_c / Mg m^{-3}	1.45	1.480	1.400	1.313
Z	8	4	2	2
μ (Cu-Kα) / mm^{-1}	2.581	2.681	2.962	2.445
T / K	123	123	123	123
Refln. collected (R_{int})	30655 (0.105)	30102 (0.036)	29615 (0.043)	34275 (0.052)
Unique refln.	8549	8311	9390	9596
Refln. for refinement	4643	8050	8070	6647
Parameters	559	595	649	622
Threshold	I >2σ(I)	I >2σ(I)	I >2σ(I)	I >2σ(I)
$R1$ ($R1$ all data)	0.0716 (0.1221)	0.0377 (0.0386)	0.0789 (0.0870)	0.0874 (0.1131)
$wR2$ ($wR2$ all data)	0.1918 (0.2423)	0.0859 (0.0861)	0.2020 (0.2060)	0.2180 (0.2367)
Goodness of fit	1.0159	0.9970	1.0785	1.1211
CCDC	1562407	1562453	1562409	1562411

Compound	[Cu(xantphos)(PhObpy)][PF$_6$] ·3CH_2Cl_2	[Cu(xantphos)(MeSbpy)][PF$_6$] ·0.5CH_2Cl_2·0.5Et_2O	[Cu(xantphos)(EtSbpy)][PF$_6$] ·1.5Et_2O	[Cu(xantphos)(PhSbpy)][PF$_6$] ·0.5CH_2Cl_2
Formula	$C_{58}H_{50}Cl_6CuF_6N_2O_2P_3$	$C_{52.50}H_{48}ClCuF_6N_2O_{1.50}P_3S$	$C_{57}H_{59}CuF_6N_2O_{2.50}P_3S$	$C_{55.5}H_{45}ClCuF_6N_2OP_3S$
Formula weight	1290.22	1068.95	1114.63	1093.95
Crystal colour; habit	yellow block	yellow block	yellow block	yellow block
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P–1	P–1	P–1	P–1
a, b, c / Å	13.3823(8) 14.0597(8) 17.5669(10)	10.9688(6) 15.3886(8) 18.2399(10)	10.9194(5) 15.3624(8) 16.8151(9)	10.9025(7) 13.2292(9) 17.8354(12)
α,β,γ/ °	103.548(3) 112.186(3) 98.856(3)	110.2998(17) 97.3701(19) 108.6020(18)	95.111(3) 93.760(3 107.807(3)	80.615(3) 84.731(3) 83.868(3
U / Å^3	2865.4(3)	2636.0(3)	2662.0(2)	2516.2(3)
D_c / Mg m^{-3}	1.495	1.347	1.39	1.44
Z	2	2	2	2
μ (Cu-Kα) / mm^{-1}	4.449	2.797	2.354	2.939
T / K	123	123	123	123
Refln. collected (R_{int})	37703 (0.033)	34770 (0.023)	31869 (0.039)	32882 (0.032)
Unique refln.	10515	9618	9530	9230
Refln. for refinement	9124	9024	8534	9178
Parameters	703	649	631	622
Threshold	I >2σ(I)	I >2σ(I)	I >2σ(I)	I >2σ(I)
$R1$ ($R1$ all data)	0.0697 (0.0771)	0.0613 (0.0634)	0.0597 (0.0654)	0.0470 (0.0525)
$wR2$ ($wR2$ all data)	0.1821 (0.1855)	0.1715 (0.1727)	0.1461 (0.1481)	0.1233 (0.1258)
Goodness of fit	1.0491	0.9810	1.0908	1.0152
CCDC	1562457	15624458	15624460	1562448

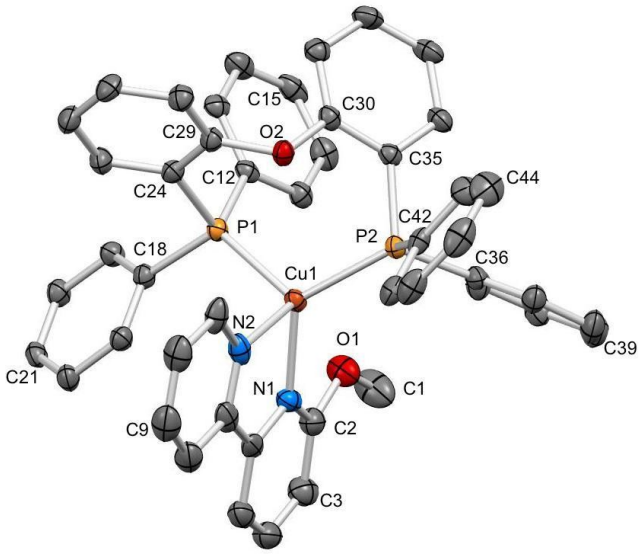


Fig. S13 Structure of the $[Cu(POP)(MeObpy)]^+$ cation in $[Cu(POP)(MeObpy)][PF_6]$. H atoms are omitted and ellipsoids are plotted at 40% probability level. Selected bond parameters: Cu1–P1 = 2.2711(12), Cu1–P2 = 2.2387(12), Cu1–N1 = 2.045(4), Cu1–N2 = 2.096(4), O1–C1 = 1.443(7), O1–C2 = 1.330(7), O2–C29 = 1.398(5), O2–C30 = 1.400(5) Å; P1–Cu1–P2 = 113.83(5), P1–Cu1–N1 = 110.44(11), P2–Cu1–N1 = 124.55(12), P1–Cu–N2 = 105.71(12), P2–Cu1–N2 = 117.08(11), N1–Cu1–N2 = 79.49(17), C1–O1–C2 = 118.3(5), C29–O2–C30 = 118.7(3)°.

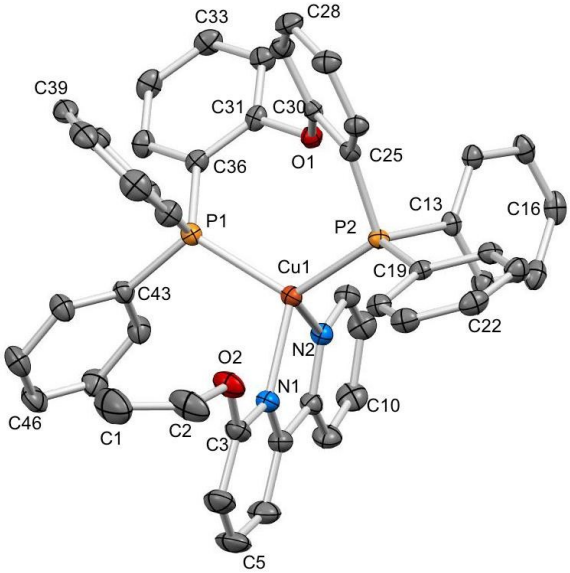


Fig. S14 Structure of the $[Cu(POP)(EtObpy)]^+$ cation in $[Cu(POP)(EtObpy)][PF_6]$. H atoms are omitted and ellipsoids are plotted at 40% probability level. Selected bond parameters: Cu1–P1 = 2.2712(6), Cu1–P2 = 2.2259(6), Cu1–N1 = 2.0589(18), Cu1–N2 = 2.0737(17), O1–C30 = 1.392(2), O1–C31 = 1.397(2), O2–C2 = 1.454(3), O2–C3 = 1.348(3) Å; P1–Cu1–P2 = 116.48(2), P1–Cu1–N1 = 109.75(5), P2–Cu1–N1 = 126.11(5), P1–Cu1–N2 = 105.49(5), P2–Cu1–N2 = 111.46(5), N1–Cu1–N2 = 79.65(7), C30–O1–C31 = 118.88(15), C2–O2–C3 = 119.52(19)°.

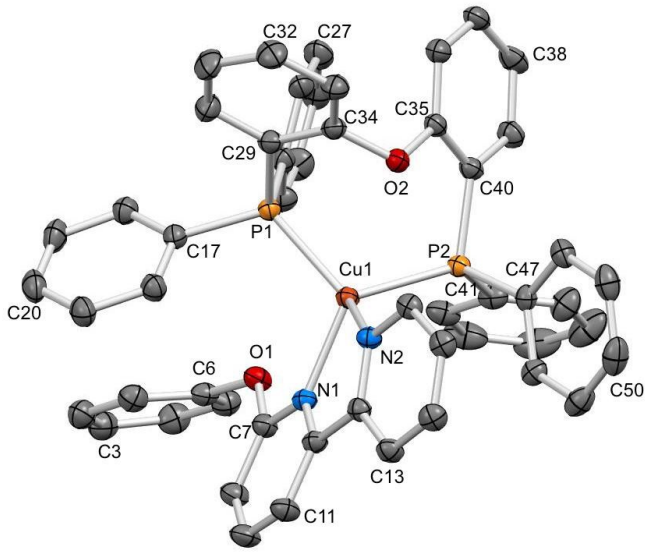


Fig. S15 Structure of one of the two crystallographically independent $[Cu(POP)(PhObpy)]^+$ cations in $2\{[Cu(POP)(PhObpy)][PF_6]\}\cdot 1.5CH_2Cl_2$. Solvent molecules and H atoms are omitted and ellipsoids are plotted at 40% probability level. Selected bond parameters: Cu1–P1 = 2.2391(7), Cu1–P2 = 2.2599(7), Cu1–N1 = 2.076(2), Cu1–N2 = 2.094(2), O1–C6 = 1.409(3), O1–C7 = 1.365(3), O2–C34 = 1.403(3), O2–C35 = 1.395(3) Å; P1–Cu1–P2 = 110.83(3), P1–Cu1–N1 = 114.23(6), P2–Cu1–N1 = 125.02(6), P1–Cu1–N2 = 123.33(6), P2–Cu1–N2 = 100.71(6), N1–Cu1–N2 = 79.43(8), C6–O1–C7 = 117.17(19), C34–O2–C35 = 116.64(18)°.

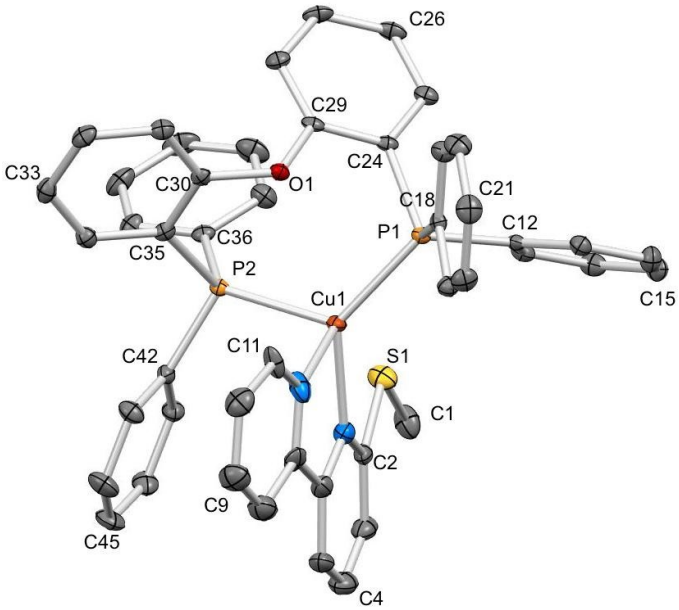


Fig. S16 Structure of the $[Cu(POP)(MeSbpy)]^+$ cation in $[Cu(POP)(MeSbpy)][PF_6]$. H atoms are omitted and ellipsoids are plotted at 40% probability level. Selected bond parameters: Cu1–P1 = 2.2281(7), Cu1–P2 = 2.2913(7), Cu1–N1 = 2.069(2), Cu1–N2 = 2.138(2), S1–C1 = 1.790(3), S1–C2 = 1.769(3), O1–C29 = 1.387(3), O1–C30 = 1.393(3) Å; P1–Cu1–P2 = 118.99(3), P1–Cu1–N1 = 133.70(6), P2–Cu1–N1 = 102.37(6), P1–Cu1–N2 = 113.71(6), P2–Cu1–N2 = 97.21(7), N–Cu1–N2 = 78.09(9), C1–S1–C2 = 103.63(13), C29–O1–C30 = 118.78(17)°.

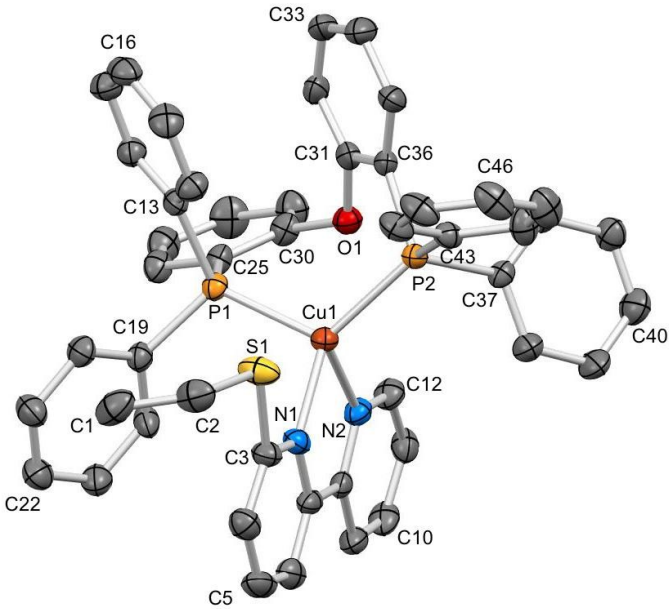


Fig. S17 Structure of the $[Cu(POP)(EtSbpy)]^+$ cation in $[Cu(POP)(EtSbpy)][PF_6]\cdot Et_2O$. H atoms are omitted and ellipsoids are plotted at 30% probability level; solvent molecule was not refined (see text). Selected bond parameters: Cu1–P1 = 2.2756(18), Cu1–P2 = 2.2328(17), Cu1–N1 = 2.059(5), Cu1–N2 = 2.101(5), S1–C2 = 1.798(8), S1–C3 = 1.770(7), O1–C30 = 1.412(8), O1–C31 = 1.404(8) Å; P1–Cu1–P2 = 113.86(7), P1–Cu1–N1 = 106.57(16), P2–Cu1–N1 = 132.61(15), P1–Cu1–N2 = 105.48(15), P2–Cu1–N2 = 110.70(16), N1–Cu1–N2 = 79.8(2), C2–S1–C3 = 104.0(4), C30–O1–C31 = 116.5(5)°.

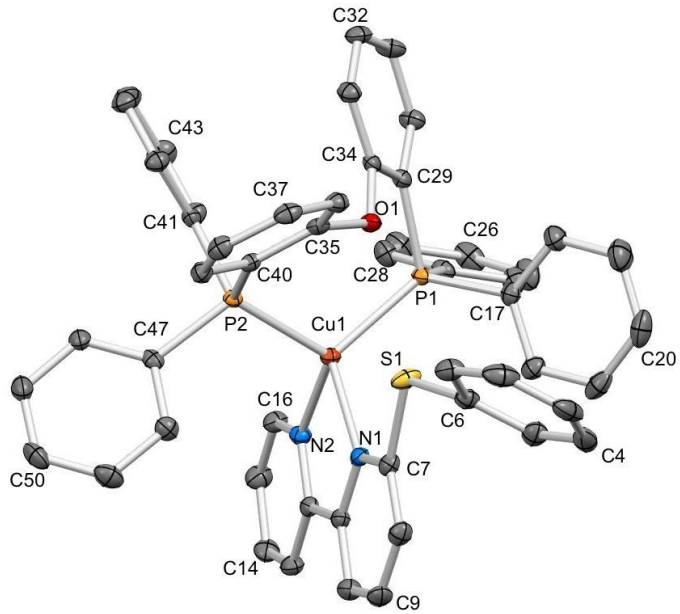


Fig. S18 Structure of the $[Cu(POP)(PhSbpy)]^+$ cation in $[Cu(POP)(PhSbpy)][PF_6]$. H atoms are omitted and ellipsoids are plotted at 40% probability level. Selected bond parameters: Cu1–P2–2.2818(6), Cu1–P1 = 2.2699(6), Cu1–N2 = 2.0725(17), Cu1–N1 = 2.1239(16), C6–S1 = 1.776(2), C7–S1 = 1.752(2), C34–O1 = 1.383(2), C35–O1 = 1.388(2) Å; P2–Cu1–P1 = 112.49(2), P2–Cu1–N2 = 114.48(5), P1–Cu1–N2 = 116.08(5), P2–Cu–N1 = 111.72(5), P1–Cu1–N1 = 119.34(5), N–Cu–N1 = 78.86(7)°.

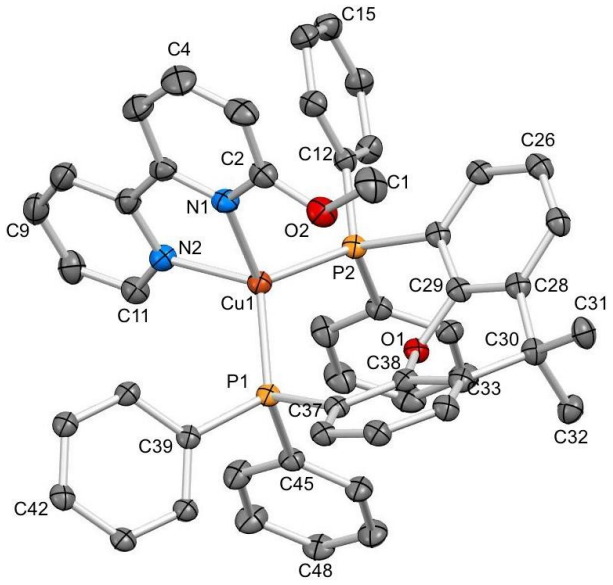


Fig. S19 Structure of the $[Cu(xantphos)(MeObpy)]^+$ cation in $[Cu(xantphos)(MeObpy)][PF_6]\cdot CH_2Cl_2\cdot 0.5Et_2O$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 30% probability level. Selected bond parameters: Cu1–P1 = 2.2376(10), Cu1–P2 = 2.2569(10), Cu1–N1 = 2.046(3), Cu1–N2 = 2.071(3), O1–C29 = 1.386(4), O1–C38 = 1.393(4), O2–C1 = 1.440(5), O2–C2 = 1.325(5) Å; P1–Cu1–P2 = 114.42(4), P1–Cu1–N1 = 121.10(9), P2–Cu1–N1 = 109.89(9), P1–Cu1–N2 = 115.42(9), P2–Cu1–N2 = 111.62(9), N1–Cu–N2 = 79.67(13)°.

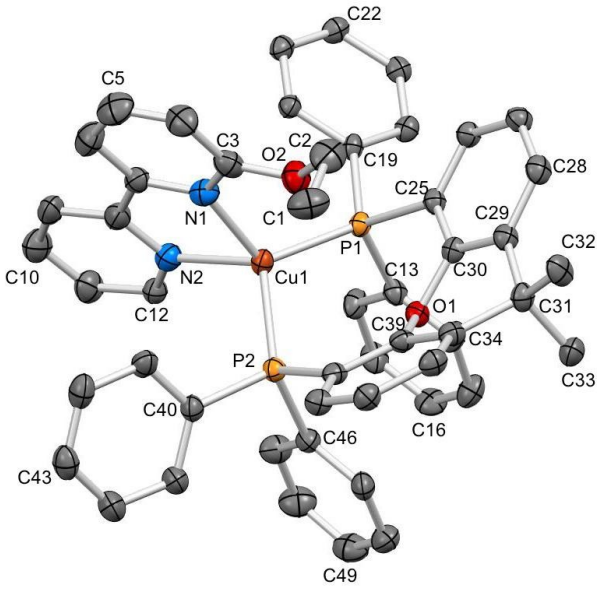


Fig. S20 Structure of the $[Cu(xantphos)(EtObpy)]^+$ cation in $[Cu(xantphos)(EtObpy)][PF_6]\cdot 0.5CH_2Cl_2\cdot 0.5H_2O$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 30% probability level. Selected bond parameters: Cu1–P1 = 2.2363(11), Cu1–P2 = 2.2524(12), Cu1–N1 = 2.026(4), Cu1–N2 = 2.094(4), O1–C30 = 1.376(5), O1–C39 = 1.387(5), O2–C2 = 1.435(7), O2–C3 = 1.316(6) Å; P1–Cu1–P2 = 114.15(4), P1–Cu1–N1 = 119.87(12), P2–Cu1–N1 = 112.97(11), P1–Cu1–N2 = 114.22(12), P2–Cu1–N2 = 111.02(12), N1–Cu1–N2 = 79.91(17), C30–O1–C39 = 114.5(3), C2–O2–C3 = 122.4(5)°.

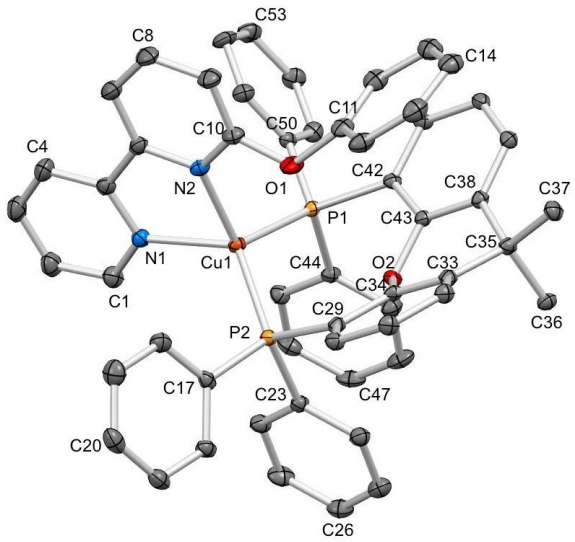


Fig. S21 Structure of the $[Cu(xantphos)(PhObpy)]^+$ cation in $[Cu(xantphos)(PhObpy)][PF_6]\cdot 3CH_2Cl_2$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 30% probability level. Selected bond parameters: Cu1–P1 = 2.2767(9), Cu1–P2 = 2.2422(9), Cu1–N1 = 2.087(3), Cu1–N2 = 2.068(3), O1–C10 = 1.357(5), O1–C11 = 1.405(4), O2–C34 = 1.391(4), O2–C43 = 1.390(4) Å; P1–Cu1–P2 = 113.29(3), P1–Cu1–N1 = 111.01(8), P2–Cu1–N1 = 119.20(8), P1–Cu1–N2 = 111.65(8), P2–Cu1–N2 = 118.52(8), N1–Cu1–N2 = 78.76(11), C10–O1–C11 = 119.4(3), C34–O2–C43 = 113.8(2)°.

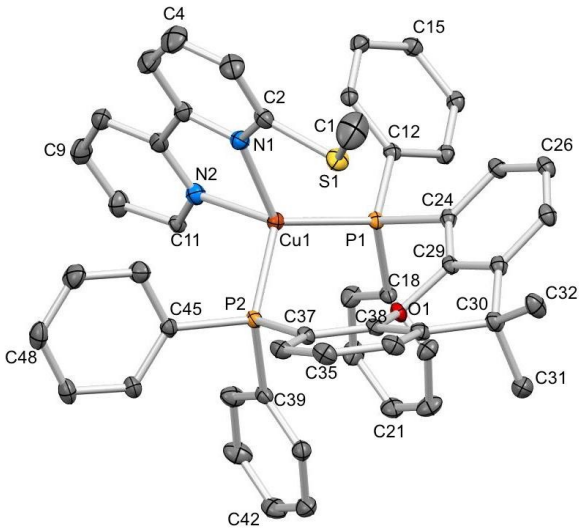


Fig. S22 Structure of the $[Cu(xantphos)(MeSbpy)]^+$ cation in $[Cu(xantphos)(MeSbpy)][PF_6]\cdot 0.5CH_2Cl_2\cdot 0.5Et_2O$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 30% probability level. Selected bond parameters: Cu1–P2 = 2.2666(8), Cu1–P1 = 2.2463(8), Cu1–N2 = 2.079(3), Cu1–N1 = 2.049(3), C1–S1 = 1.783(4), C2–S1 = 1.744(3), C29–O1 = 1.396(3), C38–O1 = 1.384(3) Å; P2–Cu1–P1 = 113.33(3), P2–Cu1–N2 = 111.24(8), P1–Cu1–N2 = 114.12(8), P2–Cu1–N1 = 111.71(8), P1–Cu1–N1 = 122.20(7), N2–Cu1–N1 = 79.70(11), C1–S1–C2 = 104.2(2), C29–O1–C38 = 114.2(2)°.

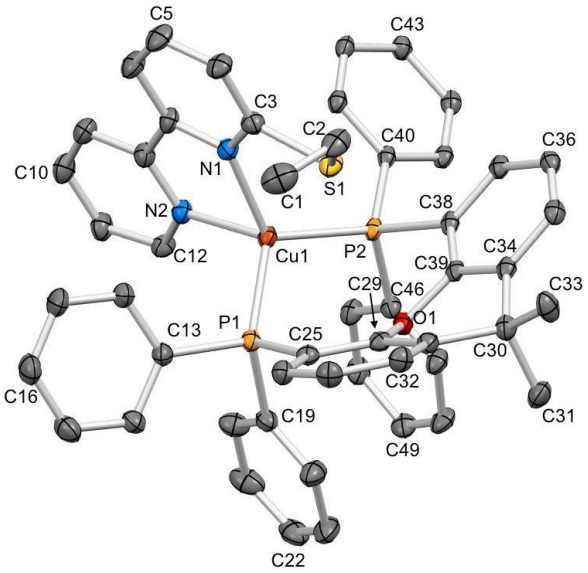


Fig. S23 Structure of the $[Cu(xantphos)(EtSbpy)]^+$ cation in $[Cu(xantphos)(EtSbpy)][PF_6]\cdot 1.5Et_2O$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 30% probability level. Selected bond parameters: Cu1–P1 = 2.2680(8), Cu1–P2 = 2.2534(7), Cu1–N1 = 2.062(2), Cu1–N2 = 2.084(2), S1–C2 = 1.822(3), S1–C3 = 1.753(3), O1–C29 = 1.386(3), O1–C39 = 1.396(3) Å; P1–Cu1–P2 = 113.65(3), P1–Cu1–N1 = 114.37(7), P2–Cu1–N1 = 118.96(7), P1–Cu1–N2 = 112.49(7), P2–Cu1–N2 = 113.39(6), N1–Cu1–N2 = 79.48(9), C2–S1–C3 = 103.77(14), C29–O1–C39 = 114.56(19)º.

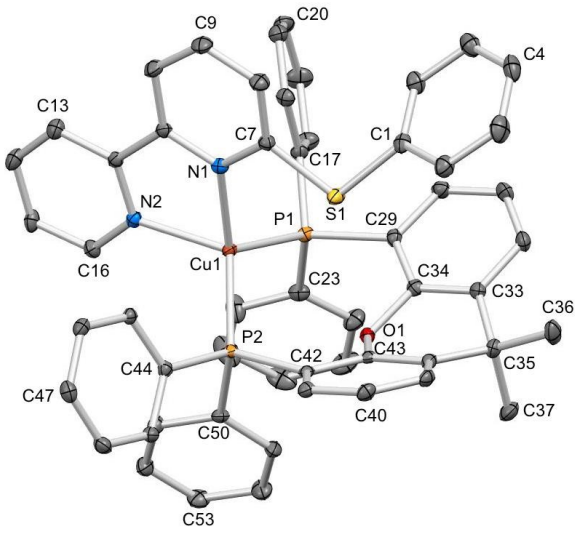


Fig. S24 Structure of the $[Cu(xantphos)(PhSbpy)]^+$ cation in $[Cu(xantphos)(PhSbpy)][PF_6]\cdot 0.5CH_2Cl_2$. H atoms are omitted and ellipsoids are plotted at 40% probability level. The solvent molecule was not refined (see text). Selected bond parameters: Cu1–P1 = 2.2717(7), Cu1–P2 = 2.2466(7), Cu1–N1 = 2.066(2), Cu1–N2 = 2.079(2), S1–C1 = 1.774(3), S1–C7 = 1.764(2), O1–C34 = 1.388(3), O1–C43 = 1.386(3) Å; P1–Cu1–P2 = 115.71(2), P1–Cu1–N1 = 111.38(6), P2–Cu1–N1 = 119.48(6), P1–Cu1–N2 = 112.79(6), P2–Cu1–N2 = 112.84(6), N1–Cu1–N2 = 79.40(8), C1–S1–C7 = 103.84(12), C34–O1–C43 = 114.85(18)º.

Table S3 Selected structural parameters calculated at the B3LYP-D3/(def2svp+ def2tzvp) level in CH_2Cl_2 solution for $[Cu(P\hat{}P)(N\hat{}N)]^+$ complexes in their electronic ground state S_0 and in their first triplet excited state T_1.

Cation	Cu–P distance /Å (Cu1–P1, Cu1–P2)	Cu–N distance /Å (Cu1–N1, Cu1–N2)	P–Cu–P chelating angle /°	N–Cu–N chelating angle /°	Angle formed by P–Cu–P and N–Cu–N planes /°	N–C–C–N torsion angle /°
Ground state ($\mathbf{S_0}$)						
[Cu(POP)(bpy)]$^+$ [a]	2.246, 2.284	2.096, 2.069	113.84	80.09	80.37	14.29
[Cu(POP)(6-MeObpy)]$^+$	2.256, 2.281	2.104, 2.082	113.04	79.08	81.05	14.24
[Cu(POP)(6-EtObpy)]$^+$	2.268, 2.271	2.103, 2.081	113.70	78.17	82.60	9.69
[Cu(POP)(6-PhObpy)]$^+$	2.262, 2.282	2.106, 2.081	113.36	78.60	86.02	5.69
[Cu(POP)(6-MeSbpy)]$^+$	2.271, 2.286	2.098, 2.097	113.84	79.10	81.97	9.78
[Cu(POP)(6-EtSbpy)]$^+$	2.275, 2.282	2.097, 2.095	113.86	79.14	82.34	9.82
[Cu(POP)(6-PhSbpy)]$^+$	2.302, 2.271	2.107, 2.106	113.09	78.40	84.42	9.33
[Cu(xantphos)(bpy)]$^+$ [a]	2.269, 2.270	2.104, 2.068	114.40	79.75	86.94	3.23
[Cu(xantphos)(6-MeObpy)]$^+$	2.268, 2.276	2.099, 2.083	114.20	78.94	87.84	3.73
[Cu(xantphos)(6-EtObpy)]$^+$	2.274, 2.275	2.107, 2.079	114.15	78.74	88.76	2.51
[Cu(xantphos)(6-PhObpy)]$^+$	2.276, 2.274	2.107, 2.081	114.36	78.56	89.67	2.02
[Cu(xantphos)(6-MeSbpy)]$^+$	2.257, 2.300	2.100, 2.096	114.40	78.95	86.61	5.95
[Cu(xantphos)(6-EtSbpy)]$^+$	2.274, 2.289	2.105, 2.091	113.53	78.84	88.02	2.81
[Cu(xantphos)(6-PhSbpy)]$^+$	2.313, 2.255	2.115, 2.097	115.48	78.53	89.37	5.85
Triplet excited state ($\mathbf{T_1}$)						
[Cu(POP)(bpy)]$^+$ [a]	2.365, 2.334	1.982, 1.981	102.90	83.46	59.69	2.83
[Cu(POP)(6-MeObpy)]$^+$	2.364, 2.333	2.003, 1.951	103.50	82.49	60.67	3.29
[Cu(POP)(6-EtObpy)]$^+$	2.365, 2.329	2.000, 1.952	103.85	82.43	60.79	3.53
[Cu(POP)(6-PhObpy)]$^+$	2.353, 2.340	1.988, 1.965	105.26	82.40	63.75	4.24
[Cu(POP)(6-MeSbpy)]$^+$	2.386, 2.310	2.016, 1.953	104.00	82.33	62.11	3.73
[Cu(POP)(6-EtSbpy)]$^+$	2.387, 2.307	2.018, 1.948	104.30	82.02	62.81	3.35
[Cu(POP)(6-PhSbpy)]$^+$	2.396, 2.314	2.019, 1.949	103.73	81.79	65.32	3.57
[Cu(xantphos)(bpy)]$^+$ [a]	2.399, 2.350	1.997, 1.981	105.92	83.06	57.53	1.99
[Cu(xantphos)(6-MeObpy)]$^+$	2.378, 2.362	1.981, 1.979	105.72	82.63	61.01	2.64
[Cu(xantphos)(6-EtObpy)]$^+$	2.378, 2.361	1.979, 1.979	106.75	82.66	65.01	4.04
[Cu(xantphos)(6-PhObpy)]$^+$	2.378, 2.350	1.985, 1.981	106.96	82.41	65.58	5.07
[Cu(xantphos)(6-MeSbpy)]$^+$	2.399, 2.342	1.990, 1.970	105.93	82.50	64.05	1.12
[Cu(xantphos)(6-EtSbpy)]$^+$	2.397, 2.342	1.988, 1.972	105.74	82.47	64.98	1.67
[Cu(xantphos)(6-PhSbpy)]$^+$	2.391, 2.340	2.000, 1.959	107.50	82.33	69.42	2.22

[a] Values from ref. 5.

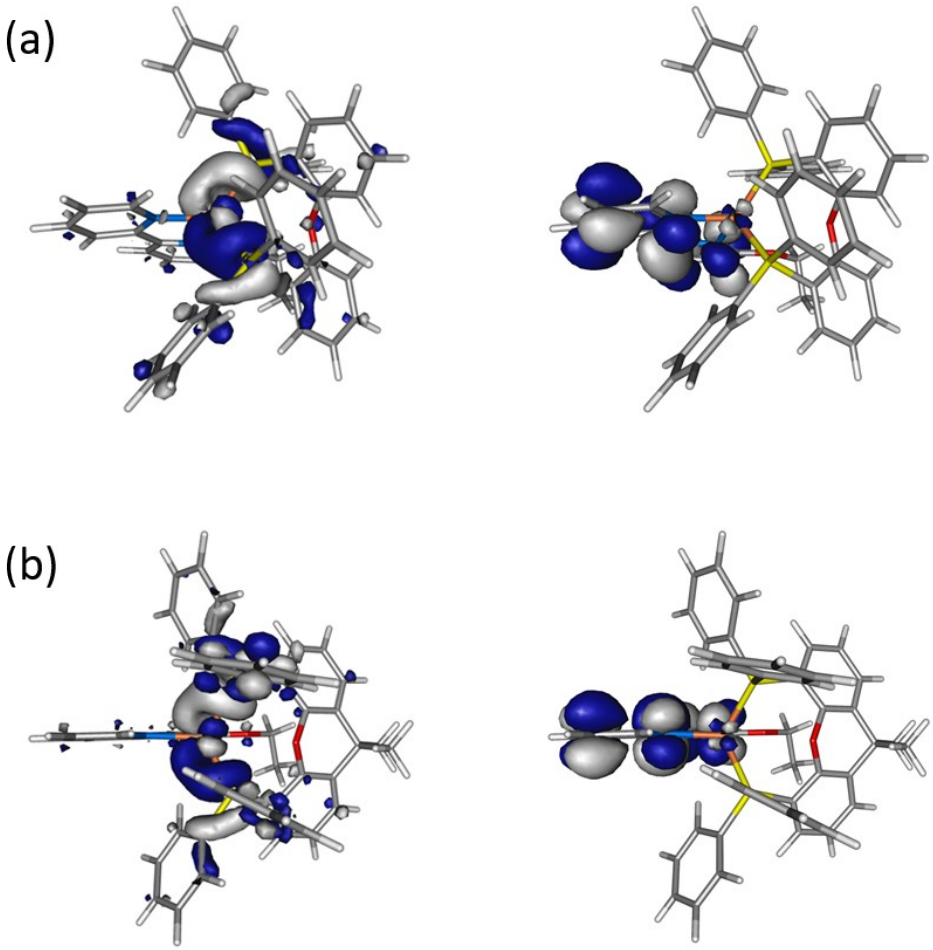


Fig. S25 Isovalue contour plots (±0.03 a.u.) for the HOMO (left) and LUMO (right) of complexes $[Cu(POP)(6\text{-}EtObpy)]^+$ (a) and $[Cu(Xanthpos)(6\text{-}EtObpy)]^+$ (b).

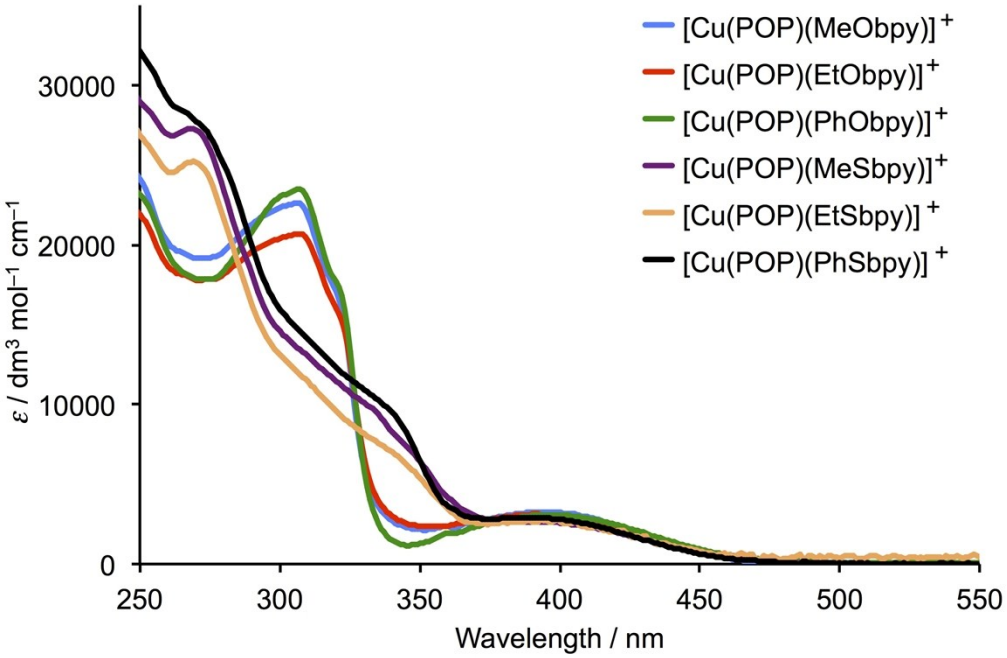


Fig. S26 Absorption spectra of CH_2Cl_2 solutions of $[Cu(POP)(N\text{^}N)][PF_6]$ complexes (concentration = 2.5×10^{-5} mol dm^{-3}).

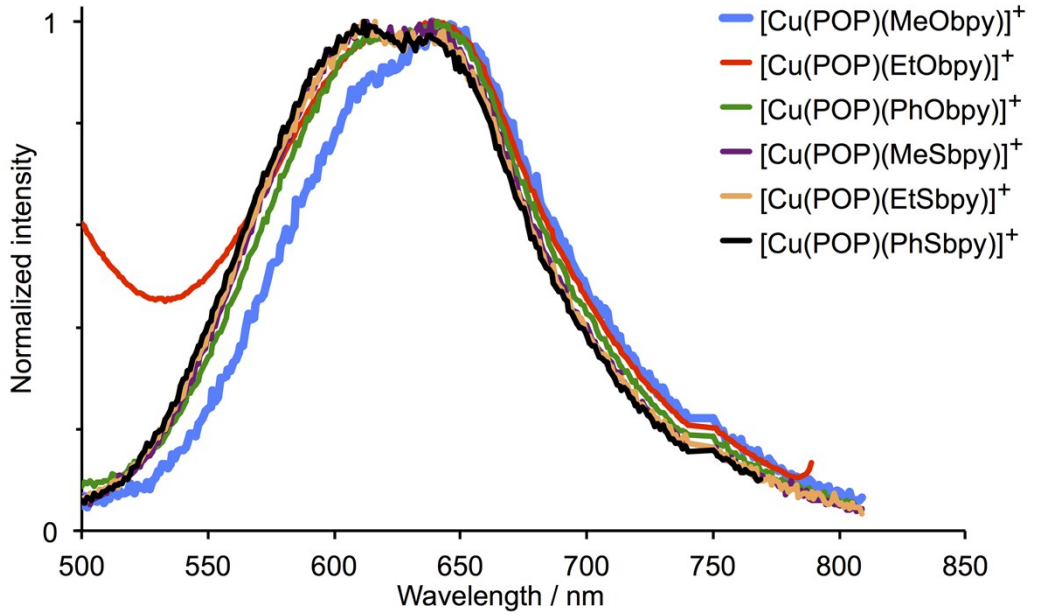


Fig. S27 Emission spectra of solutions (CH_2Cl_2, 2.5 × 10^{-5} mol dm^{-3}) of [Cu(POP)(N^N)][PF_6] complexes (see Table 3 for λ_{exc}).

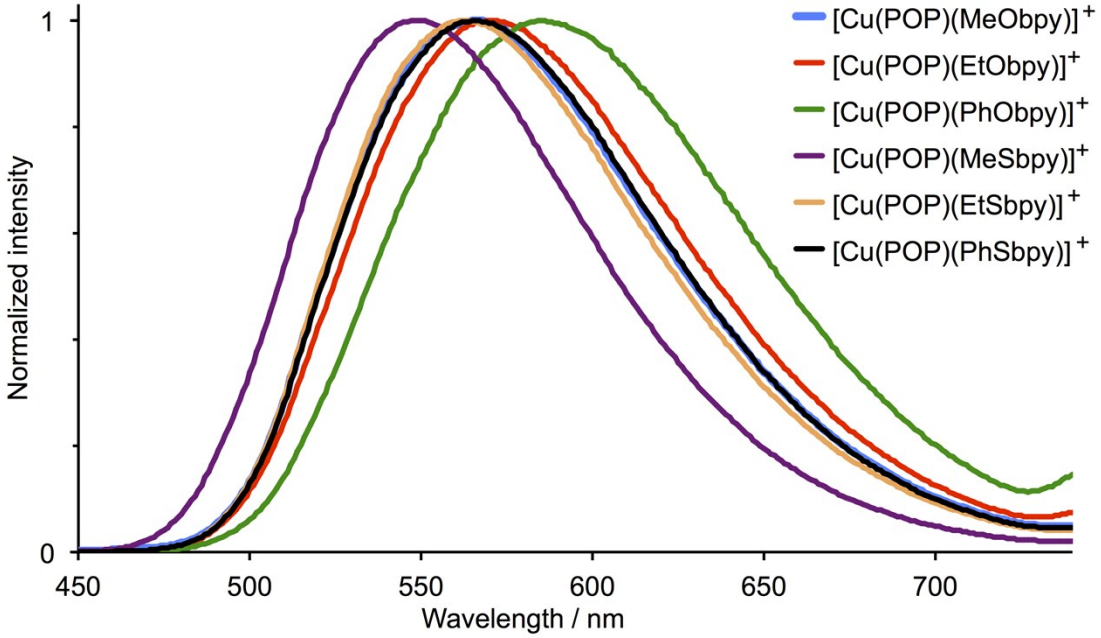


Fig. S28 Emission spectra of powder samples of [Cu(POP)(N^N)][PF_6] complexes (λ_{exc} = 365 nm).

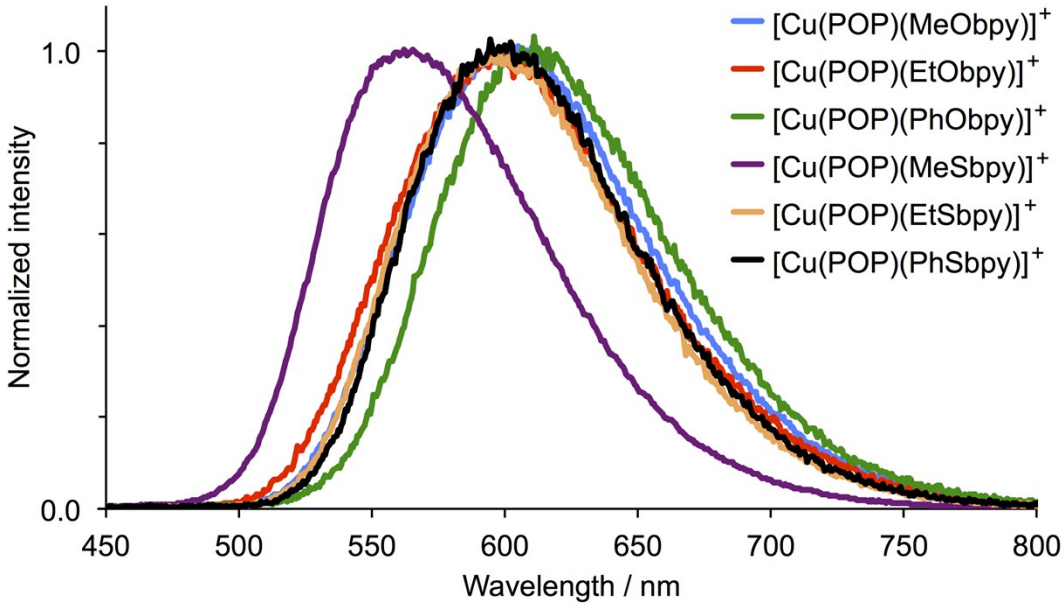


Fig. S29 Emission spectra of [Cu(POP)(N^N)][PF_6] complexes in frozen Me-THF (λ_{exc} = 410 nm).

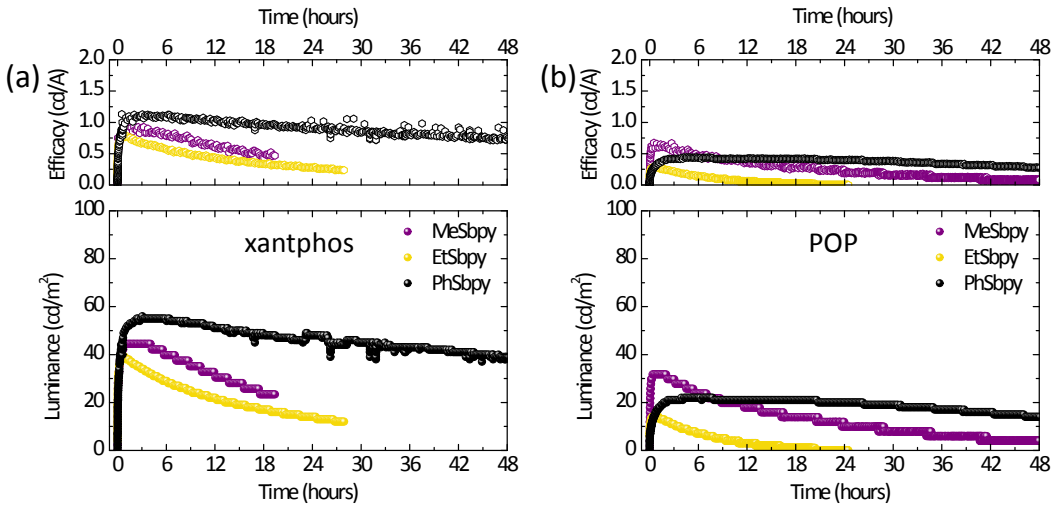


Fig. S30 Efficacy (top) and luminance (bottom) *vs.* time for LECs employing RSbpy ligands and either (a) xantphos or (b) POP as bisphosphane ligands. LECs were driven with pulsed current density at 50 A/m^2 (1 kHz, 50% duty cycle, square wave).

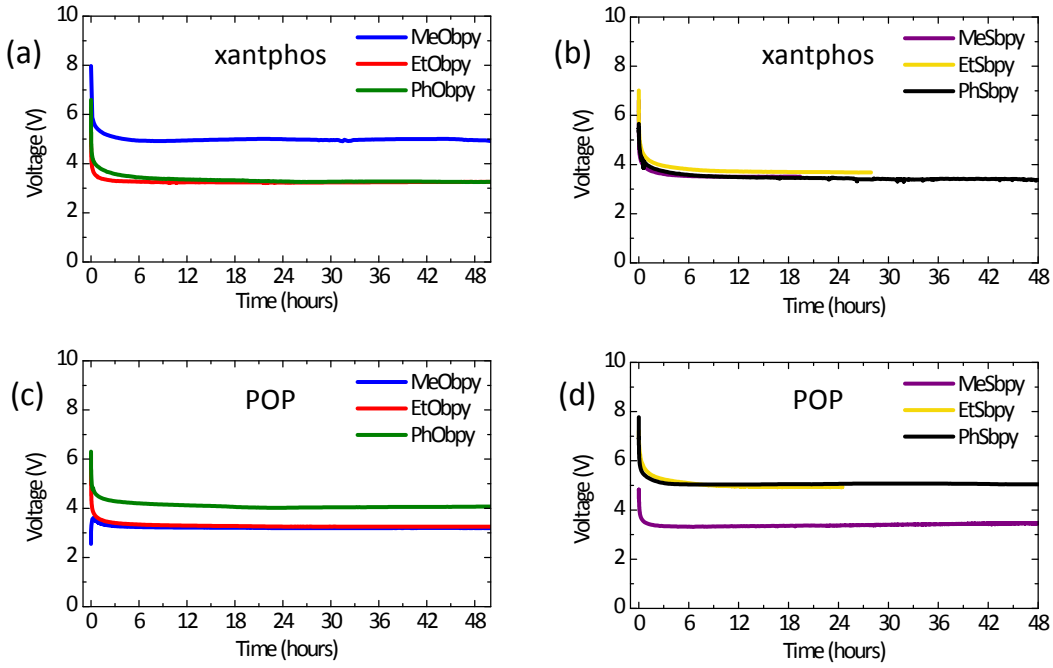


Fig. S31 Time evolution of the voltage for LECs based on (a) [Cu(xantphos)(RObpy)][PF_6], (b) [Cu(xantphos)(RSbpy)][PF_6], (c) [Cu(POP)(RObpy)][PF_6] and (d) [Cu(POP)(RSbpy)][PF_6] complexes. LECs were driven with pulsed current density at 50 A/m^2 (1 kHz, 50% duty cycle, square wave).

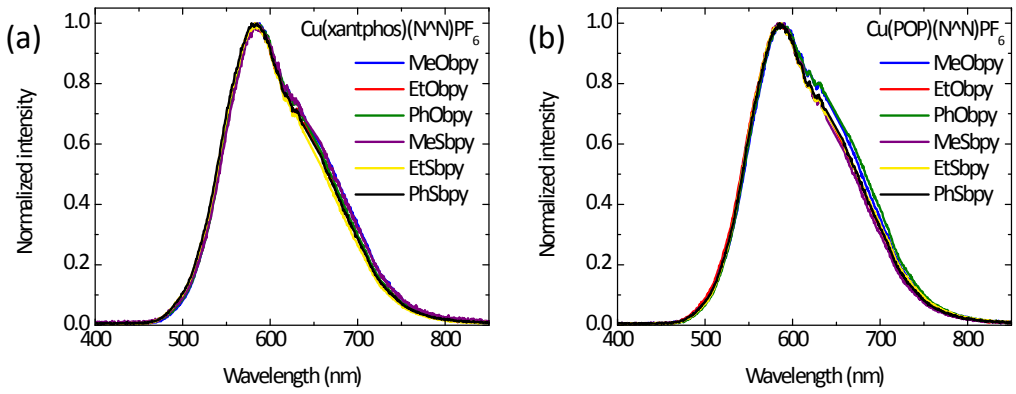


Fig. S32 Electroluminescence spectra of LECs employing [Cu(P^P)(RXbpy)][PF_6] complexes (X = O, S) with (a) xantphos or (b) POP ligands. LECs were driven with pulsed current density at 50 A/m^2 (1 kHz, 50% duty cycle, square wave).

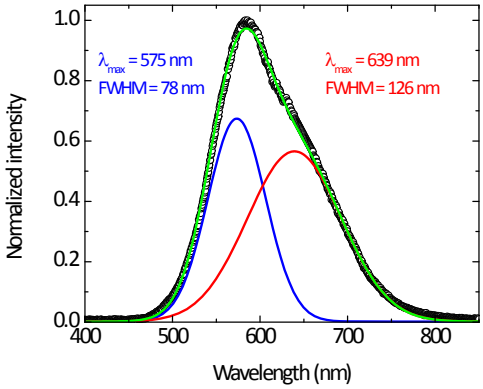


Fig. S33 Fit of the electroluminescence spectra for the complex [Cu(xantphos)(PhObpy)][PF_6] with the sum of two Gaussian functions. The centre and full width at half maximum of the two components are reported in the corresponding colour.

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