Supplementary material

**Electrophosphorescent homo- and heteroleptic copper(I) complexes prepared from various bis-phosphine ligands**

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Figure S1. Absorption spectra of 1 (red) and 4 (blue) in dichloromethane solutions.
**Figure S2.** Emission spectra ($\lambda_{\text{exc}} = 330$ nm, O.D. = 0.2) in dichloromethane rigid matrix (77 K) of 4 (solid line, left window) and 1 (dashed line, right window).
**Figure S3.** Emission spectra ($\lambda_{\text{exc}} = 330$ nm, O.D. = 0.2) in dichloromethane solution (room temperature) of 4 (solid line, left window) and 1 (dashed line, right window)
Figure S4. I-V-B characteristics of the device obtained from 4. Inset: EL spectra of 4 at a concentration of 12.5 wt.-% in a PVK matrix.
**Experimental section**

**General.** All reagents were used as purchased from commercial sources without further purification. All reactions were performed in standard glassware. Evaporation was done using water aspirator and drying *in vacuo* at $10^{-2}$ Torr. UV/Vis spectra ($\lambda_{\text{max}}$ in nm ($\epsilon$)) were measured on a Hitachi U-3000 spectrophotometer. NMR spectra were recorded on a Bruker AV 300 spectrometer. Electrospray (ES) mass spectra in positive mode were acquired on a Perkin Elmer Sciex API-365 spectrometer. Elemental analysis were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France).

**Compound 1.**

![Chemical structure of Compound 1](image)

A mixture of Cu(CNCH$_3$)BF$_4$ (0.08 g, 0.18 mmol) and dppb (0.17 g, 0.37 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred for 1 h under Ar at room temperature. The resulting solution was concentrated to ca. 5 mL. Crystals of 1 were obtained by vapor diffusion of Et$_2$O into this CH$_2$Cl$_2$ solution. Compound 1 was thus obtained in 68% yield as colorless crystals. $^1$H NMR (CDCl$_3$): 6.98 (m, 16 H), 7.09 (m, 16 H), 7.34 (m, 8 H), 7.54 (m, 8 H). $^{31}$P{$^1$H} NMR (CDCl$_3$): 8.12. $^{13}$C{$^{31}$P}{$^1$H} NMR (CDCl$_3$): 129.0, 130.2, 131.2, 131.7, 132.4, 134.0, 141.6. ES-MS: 955.2 ([M – BF$_4$]$^+$, calc. for C$_{60}$H$_{48}$P$_4$Cu: 955.20). Elemental analysis calc. for C$_{60}$H$_{48}$P$_4$CuBF$_4$: C 67.90, H 4.75; found: C 67.85, H 4.40.
Compound 2.

A mixture of Cu(CNCH$_3$)BF$_4$ (0.13 g, 0.35 mmol) and dppm (0.26 g, 0.71 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred for 1 h under Ar at room temperature. The resulting solution was concentrated to ca. 5 mL. Crystals of 2 were obtained by vapor diffusion of Et$_2$O into this CH$_2$Cl$_2$ solution. Compound 2 was thus obtained in 63% yield as colorless crystals. $^1$H NMR (CDCl$_3$): 3.64 (m, 4 H), 7.21 (m, 22 H), 7.34 (m, 18 H). $^{31}$P{${}^1$H} NMR (CDCl$_3$): –7.31. $^{13}$C{${}^{31}$P}{${}^1$H} NMR (CDCl$_3$): 25.3, 129.2, 130.3, 130.9, 132.5. ES-MS: 831.5 ([M – BF$_4$]$^+$, calc. for C$_{50}$H$_{44}$P$_4$Cu: 831.17). Elemental analysis calc. for C$_{50}$H$_{44}$P$_4$CuBF$_4$: C 65.34, H 4.83; found: C 65.16, H 4.75.

Compound 3.

A mixture of Cu(CNCH$_3$)BF$_4$ (0.05 g, 0.16 mmol) and POP (0.08 g, 0.16 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred for 1 h under Ar at room temperature; dppm (0.06 g, 0.16 mmol) was then added and the solution stirred for another 1 h. The resulting solution was concentrated to
ca. 5 mL. Crystals of 3 were obtained by vapor diffusion of Et₂O into this CH₂Cl₂ solution. Compound 3 was thus obtained in 80% yield as colorless crystals. ¹H NMR (CDCl₃): 3.33 (t, J = 8 Hz, 2 H), 6.67 (m, 2 H), 6.99 (m, 26 H), 7.11 (m, 12 H), 7.23 (m, 3 H), 7.30 (m, 3 H), 7.42 (m, 2 H). ³¹P{¹H} NMR (CDCl₃) δ −8.92 (broad), -4.37 (t, J = 40 Hz). ¹³C{³¹P}{¹H} NMR (CDCl₃): 29.3, 120.6, 123.3, 125.3, 128.9, 130.1, 130.3, 130.5, 131.8, 132.5, 133.2, 133.9, 134.50, 134.1, 134.4, 141.2, 158.0. ES-MS: 985.2 ([M − BF₄]⁺, calc. for C₆₁H₅₀P₄OCu: 985.21). Elemental analysis calc. for C₆₁H₅₀P₄OCuBF₄·0.75CH₂Cl₂: C 65.23, H 4.57. found: C 65.68, H 4.35.

**Compound 4.**

![Chemical structure of compound 4](image)

A mixture of Cu(CNCH₃)BF₄ (0.12 g, 0.37 mmol) and POP (0.20 g, 0.37 mmol) in CH₂Cl₂ (20 mL) was stirred for 1 h under Ar at room temperature; dppb (0.17 g, 0.37 mmol) was then added and the solution stirred for another 1 h. The resulting solution was concentrated to ca. 5 mL. Crystals of 4 were obtained by vapor diffusion of Et₂O into this CH₂Cl₂ solution. Compound 4 was thus obtained in 75% yield as colorless crystals. ¹H NMR (CDCl₃): 6.35 (m, 2 H), 6.78 (m, 16 H), 6.97 (m, 20 H), 7.10 (m, 2 H), 7.23 (m, 6 H), 7.39 (m, 2 H), 7.65 (m, 4 H). ³¹P{¹H} NMR (CDCl₃): -7.20, 0.07. ¹³C{³¹P}{¹H} NMR (CDCl₃): 120.9, 124.1, 125.3, 128.6, 128.7, 129.0, 130.0, 130.7, 131.6, 131.8, 132.4, 133.3, 133.6, 134.1, 134.4, 141.2, 158.0. ES-MS: 1047.6 ([M − BF₄]⁺, calc. for C₆₆H₅₂OP₄Cu: 1047.23). Elemental analysis calc. for C₆₆H₅₂OP₄CuBF₄·2H₂O: C 67.67, H 4.82; found: C 67.88, H 4.38.
Compound 5.

A mixture of Cu(CNCH₃)BF₄ (0.05 g, 0.16 mmol) and dppe (0.06 g, 0.16 mmol) in CH₂Cl₂ (20 mL) was stirred for 1 h under Ar at room temperature; dppb (0.07 g, 0.16 mmol) was then added and the solution stirred for another 1 h. The resulting solution was concentrated to ca. 5 mL. Crystals of 5 were obtained by vapor diffusion of Et₂O into this CH₂Cl₂ solution. Compound 5 was thus obtained in 78% yield as colorless crystals. ¹H NMR (CDCl₃): 2.44 (m, 4 H), 6.89 (m, 6 H), 7.01 (m, 12 H), 7.19 (m, 16 H), 7.39 (m, 10 H). ³¹P{¹H} NMR (CDCl₃): 3.76, 8.53. ¹³C{³¹P}{¹H} NMR (CDCl₃): 26.1, 26.7, 128.8, 129.0, 129.1, 129.2, 130.2, 130.4, 130.6, 130.9, 131.2, 131.6, 131.7, 131.9, 132.1, 132.3, 132.4, 132.7, 133.9, 134.0, 141.5. ES-MS: 907.5 ([M – BF₄]⁺, calc. for C₇₆H₄₈P₄Cu: 907.20). Elemental analysis calc. for C₇₆H₄₈P₄CuBF₄·2CH₂Cl₂: C 59.79, H 4.50; found: C 59.53, H 4.16.

Compound 6.

A mixture of Cu(CNCH₃)BF₄ (0.05 g, 0.16 mmol) and dppp (0.06 g, 0.16 mmol) in CH₂Cl₂ (20 mL) was stirred for 1 h under Ar at room temperature; dppb (0.07 g, 0.16 mmol) was then added and the solution stirred for another 1 h. The resulting solution was concentrated to ca. 5
mL. Crystals of 6 were obtained by vapor diffusion of Et$_2$O into this CH$_2$Cl$_2$ solution. Compound 6 was thus obtained in 65% yield as colorless crystals. $^1$H NMR (CDCl$_3$): 1.67 (broad s, 2 H), 2.34 (broad s, 2 H), 2.63 (broad s, 2 H), 6.99 (m, 12 H), 7.08 (m, 12 H), 7.21 (m, 10 H), 7.36 (m, 6 H), 7.53 (m, 2 H), 7.60 (m, 2 H). $^{31}$P{$^1$H} NMR (CDCl$_3$): –9.08, 5.89, 8.38. $^{13}$C{$^{31}$P}{$^1$H} NMR (75 MHz, CDCl$_3$): 17.6, 27.9, 28.1, 128.8, 128.9, 129.0, 130.1, 130.2, 130.3, 131.2, 131.4, 131.45, 131.7, 132.3, 132.4, 132.8, 133.0, 133.9, 133.85, 134.0, 141.3, 141.6. ES-MS: 921.5 ([M – BF$_4$]$^+$, calc. for C$_{57}$H$_{50}$P$_4$Cu: 921.21). Elemental analysis calc. for C$_{57}$H$_{50}$P$_4$CuBF$_4$: C 67.83, H 4.99; found: C 67.13, H 4.89.
Crystal data for 1:
Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et₂O into a CH₂Cl₂ solution of 1. Intensity data for 1 were collected at low temperature on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo Kα radiation source and equipped with an Oxford Cryosystems Cryostream Cooler Device.

\( \text{C}_{60}\text{H}_{48}\text{CuP}_4, \text{BF}_4; M = 1043.29, \) colorless plate crystal, 0.10×0.28×0.50, monoclinic, space group P 2/n, \( a = 13.5721(9), b = 12.5841(8), c = 14.9692(12) \) Å, \( \beta = 100.516(6), V = 2513.7(3) \) Å³, \( Z = 2, T = 180 \) K, \( d = 1.378, \mu(\text{Mo Kα}) = 0.617 \) mm⁻¹. 308 parameters, 11658 reflections measured, 5719 unique \( (R_{int} = 0.04) \), 3534 reflections used in the calculations \( [I > 2.5\sigma] \), \( R = 0.0509, wR = 0.0579 \).

Crystal data for 3:
Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et₂O into a CH₂Cl₂ solution of 3. Data for 3 were collected at a low temperature on an IPDS STOE diffractometer equipped with an Oxford Cryosystem Cryostream Cooler Device.

\( \text{(C}_{61}\text{H}_{50}\text{CuOP}_4), 0.75(\text{CH}_2\text{Cl}_2), (\text{BF}_4); M = 1137.01, \) colorless block crystal, 0.10×0.25×0.37, triclinic, space group P -1, \( a = 14.6080(14), b = 19.213(2), c = 21.0316(17) \) Å, \( \alpha = 80.126(11), \beta = 80.686(11), \gamma = 89.676(12), V = 5737.2(10) \) Å³, \( Z = 4, T = 180 \) K, \( d = 1.316, \mu(\text{Mo Kα}) = 0.615 \) mm⁻¹. 651 parameters, 57446 reflections measured, 20986 unique \( (R_{int} = 0.09) \), 6820 reflections used in the calculations \( [I > 2\sigma] \), \( R = 0.0714, wR = 0.0789 \).

Structures were solved by direct methods using SIR92, and refined by full-matrix least-squares procedures on F using the programs of the PC version of CRYSTALS. Atomic scattering factors were taken from the International tables for X-ray Crystallography. For complex 1, all non-BF4 molecules and non-hydrogen atoms were refined anisotropically. For complex 3, only copper and phosphorus atoms were refined anisotropically, due to the lack of reflexions and high number of parameters. Hydrogen atoms were located in a difference map (those attached to carbon atoms were repositioned geometrically), then refined using a riding model. Absorption corrections were introduced using the program MULTISCAN.

Figure S5. Plot of the structure of the two conformers observed in the crystal lattice of 3. Selected bond lengths and bond angles: Cu(1)-P(1): 2.279(4); Cu(1)-P(2): 2.304(3); Cu(1)-P(3): 2.333(3); Cu(1)-P(4): 2.425(4); P(1)-Cu(1)-P(2): 110.51(13)°; P(1)-Cu(1)-P(3): 124.44(13)°; P(1)-Cu(1)-P(4): 125.43(13)°; P(2)-Cu(1)-P(3): 109.77(13)°; P(2)-Cu(1)-P(4): 108.26(13)°; P(3)-Cu(1)-P(4): 73.28(12)°; Cu(2)-P(101): 2.294(3); Cu(2)-P(102): 2.268(4); Cu(2)-P(103): 2.339(3); Cu(2)-P(104): 2.409(3); P(101)-Cu(2)-P(102): 111.20(12)°; P(101)-Cu(2)-P(103): 109.44(13)°; P(101)-Cu(2)-P(104): 109.51(12)°; P(102)-Cu(2)-P(103): 124.03(13)°; P(102)-Cu(2)-P(104): 123.63(13)°; P(103)-Cu(2)-P(104): 73.86(12)°.
Electrochemistry

The cyclic voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in an homemade airtight three–electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1cm² apparent surface. The working electrode was a Pt microdisk (0.5mm diameter). The supporting electrolyte [nBu₄N][BF₄] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled over CaH₂ prior to use. The solutions used during the electrochemical studies were typically 10⁻³ M in complex compound and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230).