Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary information to accompany:

# Shine bright or live long: substituent effects in $[Cu(N^{\wedge}N)(P^{\wedge}P)]^+$-based light-emitting electrochemical cells where N^N is a 6-substituted 2,2'-bipyridine

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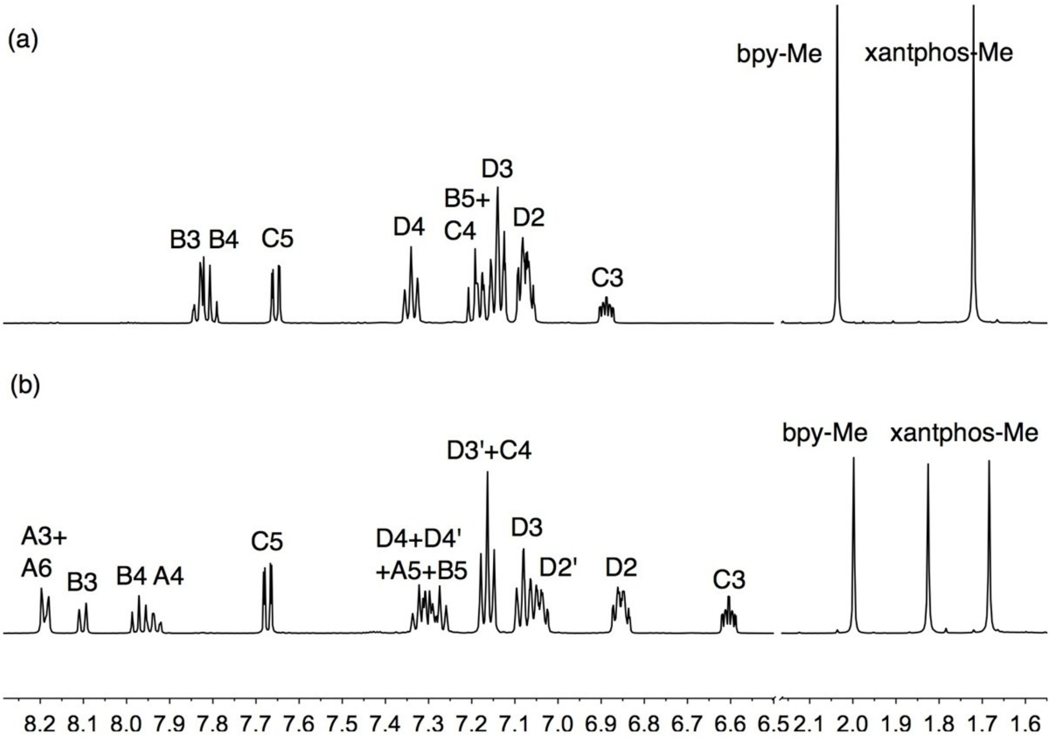


**Fig. S1**. 500 MHz $^1$H NMR spectra of $CD_2Cl_2$ solutions of (a) [Cu(xantphos)($Me_2$bpy)][$PF_6$] and (b) [Cu(xantphos)(Mebpy)][$PF_6$]. See Scheme 2 for atom numbering. Chemical shifts in *δ*/ppm.

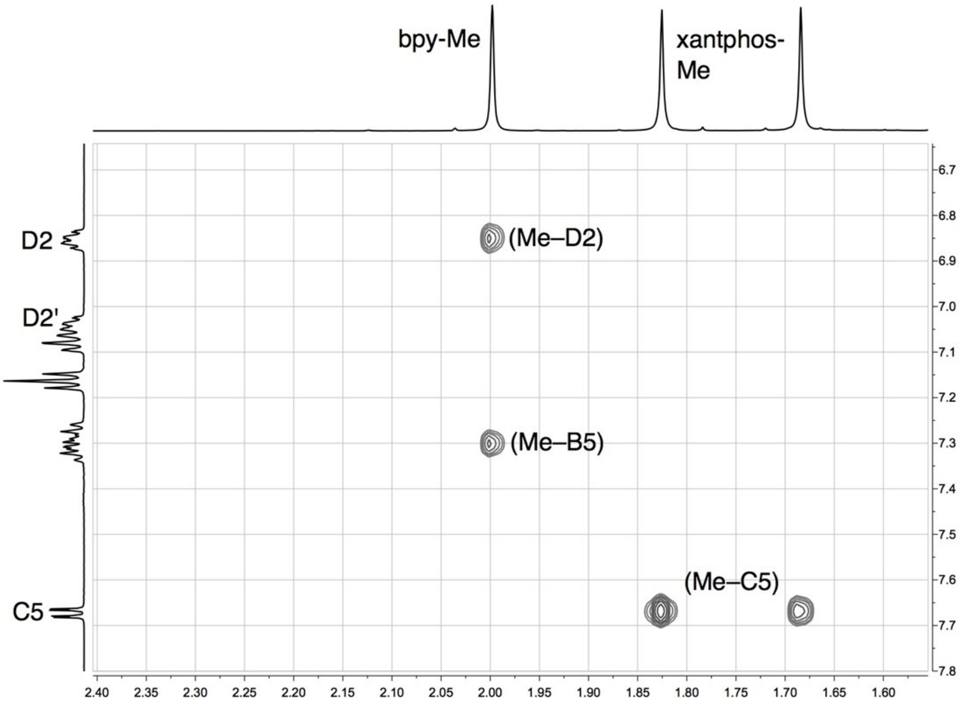


**Fig. S2**. Part of the NOESY spectrum of [Cu(xantphos)(Mebpy)][$PF_6$] (500 MHz, $CD_2Cl_2$); the bpy-Me/D2 cross peak distinguishes D2 from D2' (see Scheme 3).

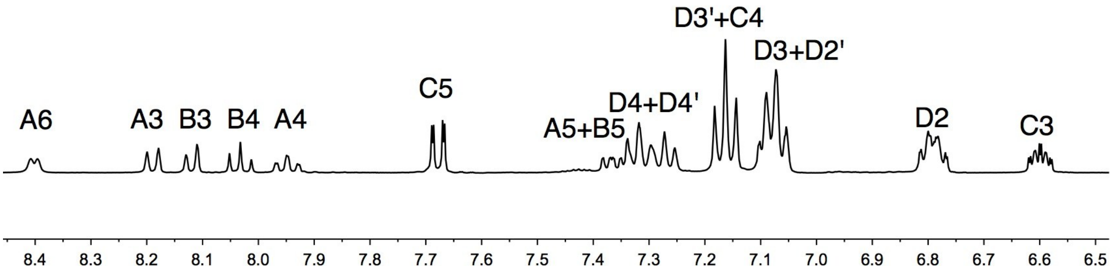


**Fig. S3**. Aromatic region of the 500 MHz $^1$H NMR spectrum of [Cu(xantphos)(Etbpy)][$PF_6$] ($CD_2Cl_2$); see Scheme 2 for atom labelling.

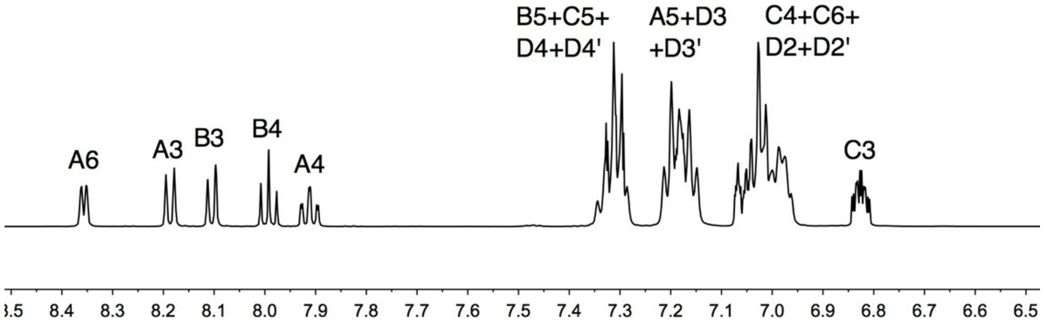


**Fig. S4**. Aromatic region of the 500 MHz $^1$H NMR spectrum of [Cu(POP)(Etbpy)][$PF_6$] ($CD_2Cl_2$); see Scheme 2 for atom labelling.

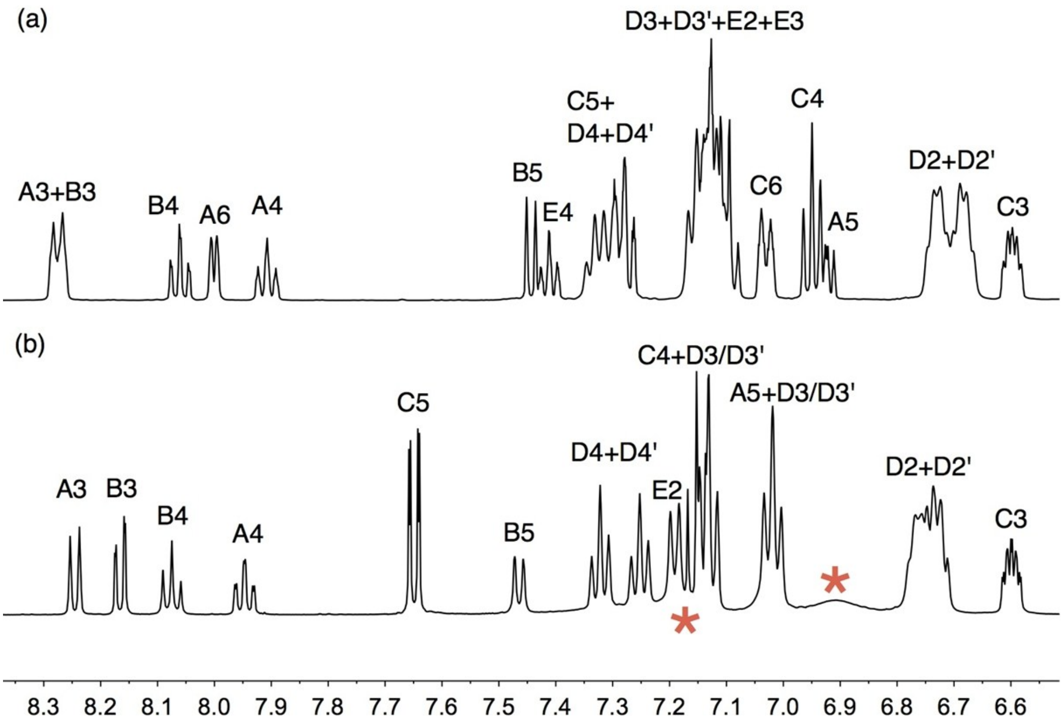


**Fig. S5**. Aromatic region of the 500 MHz $^1$H NMR spectra of $CD_2Cl_2$ solutions of (a) [Cu(POP)(Phbpy)][$PF_6$] and (b) [Cu(xantphos)(Phbpy)][$PF_6$] at 295 K. See Scheme 2 for atom numbering. Chemical shifts in $\delta$/ppm. In (b), broad signals are marked by asterisks (see text).

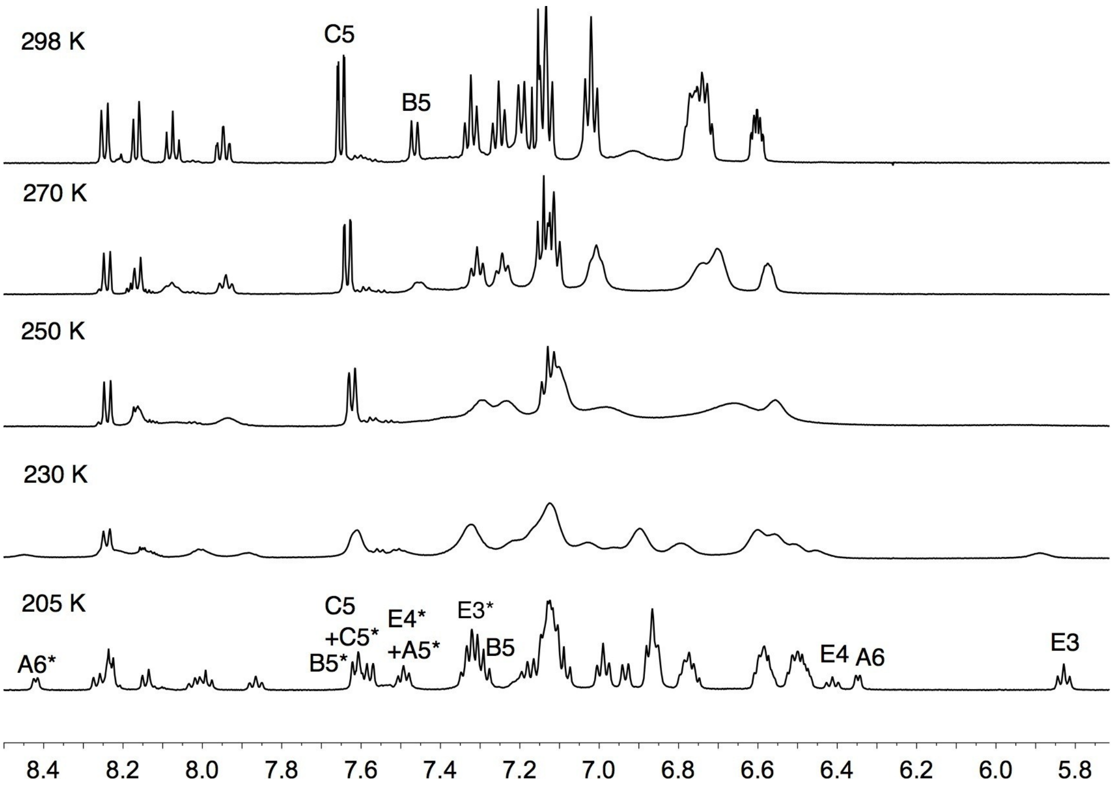


**Fig. S6**. Variable temperature $^1$H NMR spectra of [Cu(xantphos)(Phbpy)][PF$_6$] (500 MHz, CD$_2$Cl$_2$). Complete assignments at 205 K are given in Fig. 1.

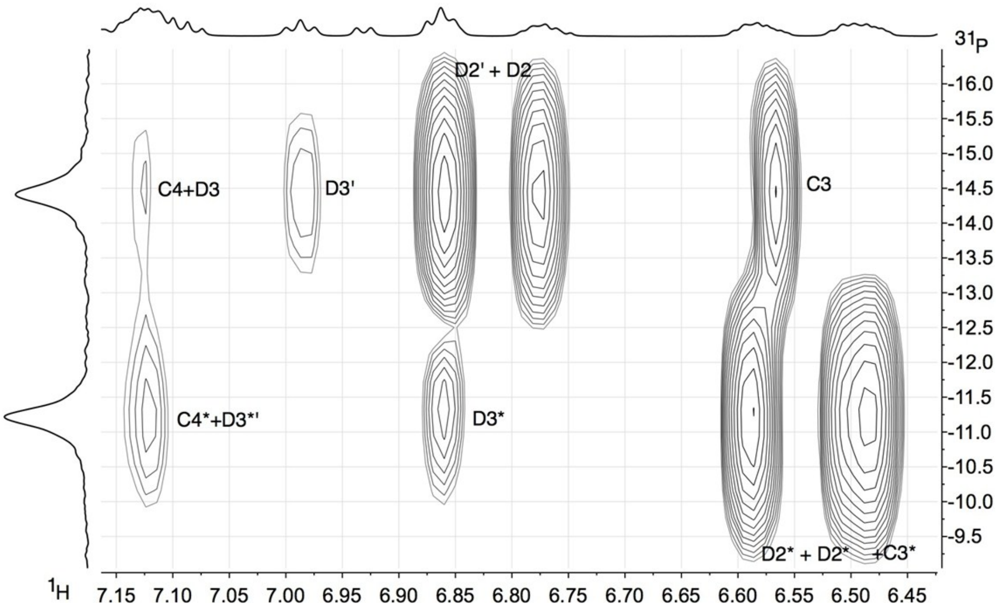


**Fig. S7**. $^{31}$P–$^1$H HMBC spectrum (600 MHz, CD$_2$Cl$_2$) of [Cu(xantphos)(Phbpy)][PF$_6$] at 205 K.

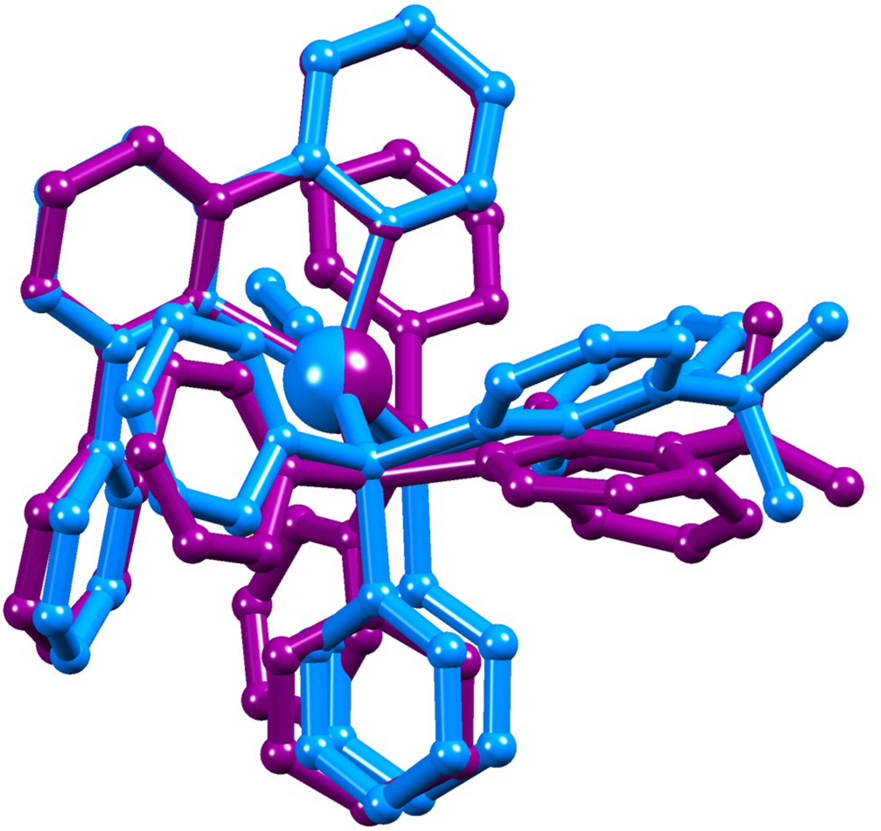


**Fig. S8**. Overlay of the DFT geometry-optimized structures of conformers of $[Cu(xantphos)(Phbpy)]^+$ which are related by inversion of the xanthene unit (right side of figure); for clarity, H atoms are omitted. The Cu atoms and pairs of corresponding N atoms were overlaid. Compare to Fig. 2 in which only the *ipso*-C atoms of $PPh_2$ phenyl rings in front and behind the Cu atoms are shown.

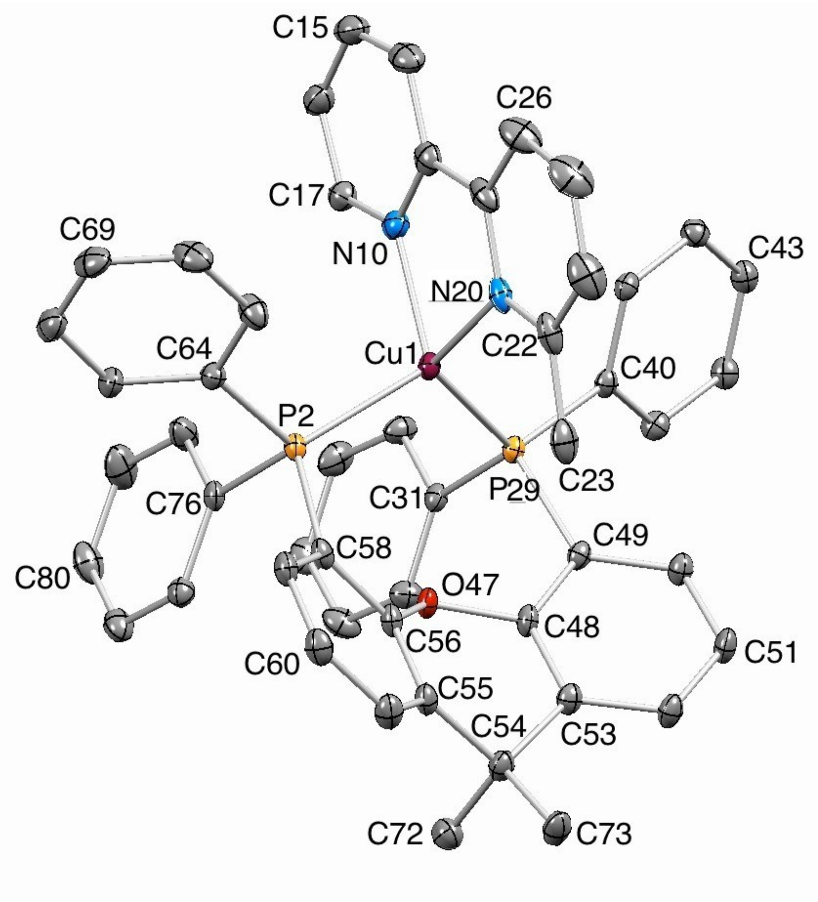


**Fig. S9**. Structure of the $[Cu(xantphos)(Mebpy)]^+$ cation in $[Cu(xantphos)(Mebpy)[PF_6]\cdot CH_2Cl_2\cdot 0.4Et_2O$ with ellipsoids plotted at 30% probability level; H atoms are omitted. Selected bond parameters: Cu1–P2 = 2.2662(9), Cu1–N10 = 2.042(3), Cu1–N20 = 2.073(3), Cu1–P29 = 2.2489(9) Å; P2–Cu1–N10 = 110.97(8), P2–Cu1–N20 = 111.07(8), N10–Cu1–N20 = 80.97(12), P2– Cu1–P29 = 113.38(3), N10–Cu1–P29 = 115.10(8), N20–Cu1–P29 = 121.22(8)°.

Selected theoretical bond parameters (B3LYP-D3//6-31G**/LANL2DZ):
Ground State ($S_0$): Cu1–P2 = 2.3149, Cu1–N10 = 2.1235, Cu1–N20 = 2.1156, Cu1–P29 = 2.3038 Å; P2–Cu1–N10 = 108.49, P2–Cu1–N20 = 118.29, N10–Cu1–N20 = 78.61, P2– Cu1–P29 = 113.34, N10–Cu1–P29 = 117.84, N20–Cu1–P29 = 115.77°.
First Triplet Excited State ($T_1$): Cu1–P2 = 2.391, Cu1–N10 = 1.985, Cu1–N20 = 2.008, Cu1–P29 = 2.413 Å; P2–Cu1–N10 = 129.61, P2–Cu1–N20 = 109.19, N10–Cu1–N20 = 83.04, P2– Cu1–P29 = 105.78, N10–Cu1–P29 = 98.12, N20–Cu1–P29 = 132.90°.

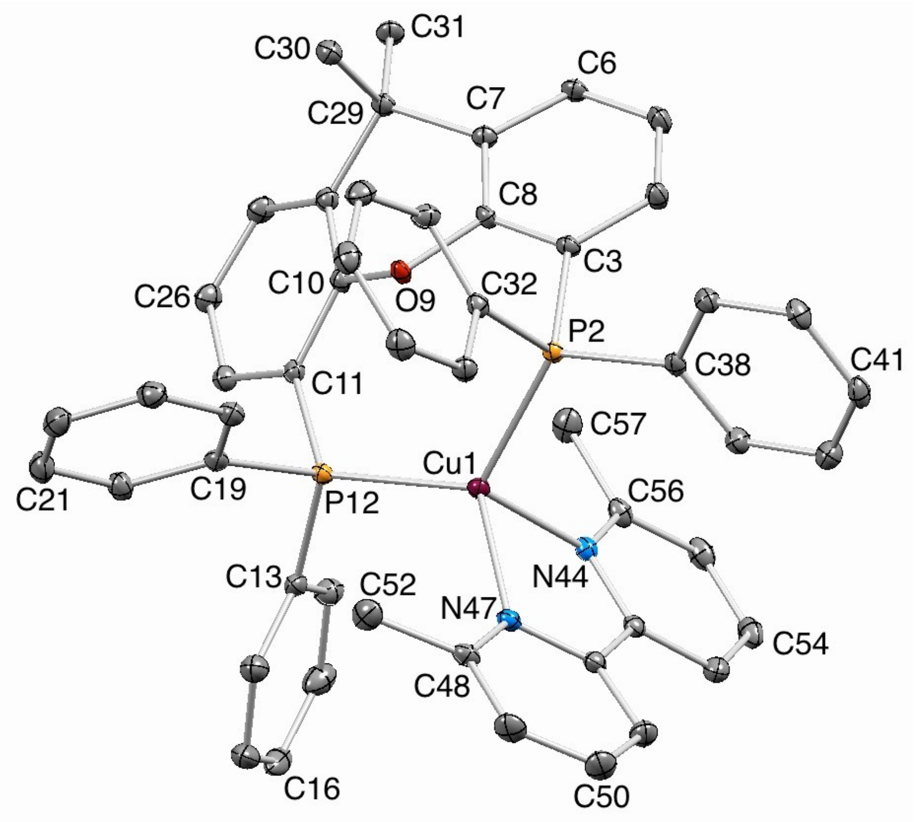


**Fig. S10.** Structure of the [Cu(xantphos)($Me_2$bpy)]$^+$ cation in [Cu(xantphos)($Me_2$bpy)][$PF_6$] with ellipsoids plotted at 30% probability level; H atoms are omitted. Selected bond parameters: Cu1–P2 = 2.3068(7), Cu1–P12 = 2.2774(7), Cu1–N44 = 2.085(2), Cu1–N47 = 2.108(2) Å; P2–Cu1–P12 = 119.47(3), P2–Cu1–N44 = 105.00(6), P12–Cu1–N44 = 118.00(6), P2–Cu1–N47 = 112.36(6), P12–Cu1–N47 = 115.44(6)°, N44–Cu1–N47 = 79.66(9)°. Selected theoretical bond parameters (B3LYP-D3//6-31G**/LANL2DZ): Ground State ($S_0$): Cu1–P2 = 2.3331, Cu1–P12 = 2.3309, Cu1–N44 = 2.1504, Cu1–N47 = 2.1427 Å; P2–Cu1–P12 = 113.15, P2–Cu1–N44 = 118.51, P12–Cu1–N44 = 112.46, P2–Cu1–N47 = 113.49, P12–Cu1–N47 = 116.75, N44–Cu1–N47 = 78.34°. First Triplet Excited State ($T_1$): Cu1–P2 = 2.418, Cu1–P12 = 2.375, Cu1–N44 = 2.072, Cu1–N47 = 1.971 Å; P2–Cu1–P12 = 106.28, P2–Cu1–N44 = 110.35, P12–Cu1–N44 = 117.68, P2–Cu1–N47 = 94.23, P12–Cu1–N47 = 141.76, N44–Cu1–N47 = 82.92°.

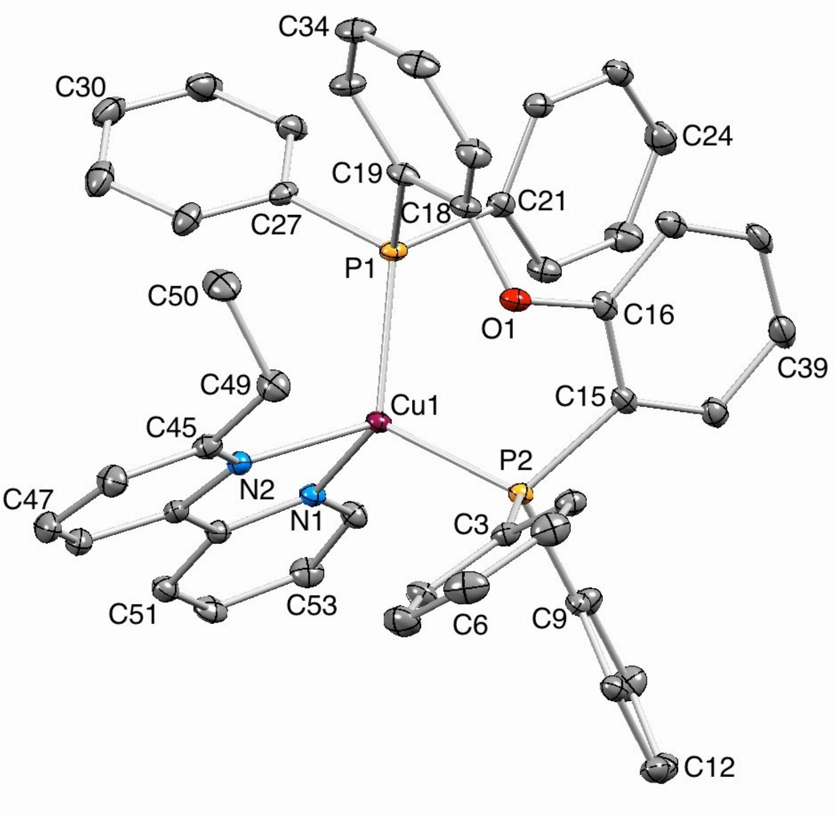


**Fig. S11**. Structure of the $[Cu(POP)(Etbpy)]^+$ cation in $[Cu(POP)(Etbpy)][PF_6]·Et_2O$ with ellipsoids plotted at 40% probability level; H atoms are omitted. Selected bond parameters: Cu1–P1 = 2.2752(7), Cu1–P2 = 2.2654(7), Cu1–N1 = 2.056(2), Cu1–N2 = 2.098(2) Å; P1–Cu1–P2 = 113.08(3), P1–Cu1–N1 = 113.61(6), P2–Cu1–N1 = 116.75(6), P1–Cu1–N2 = 112.48(6), P2–Cu1–N2 = 116.95(6), N1–Cu1–N2 = 80.11(8)°.
Selected theoretical bond parameters (B3LYP-D3//6-31G**/LANL2DZ):
Ground State ($S_0$): Cu1–P1 = 2.3044, Cu1–P2 = 2.3049, Cu1–N1 = 2.1170, Cu1–N2 = 2.1308 Å; P1–Cu1–P2 = 113.04, P1–Cu1–N1 = 111.48, P2–Cu1–N1 = 120.72, P1–Cu1–N2 = 119.09, P2–Cu1–N2 =110.09, N1–Cu1–N2 =78.61°.
First Triplet Excited State ($T_1$): Cu1–P1 = 2.335, Cu1–P2 = 2.427, Cu1–N1 = 2.028, Cu1–N2 = 1.961 Å; P1–Cu1–P2 = 103.57, P1–Cu1–N1 = 104.09, P2–Cu1–N1 = 94.96, P1–Cu1–N2 = 152.01, P2–Cu1–N2 =122.71, N1–Cu1–N2 =82.46°.

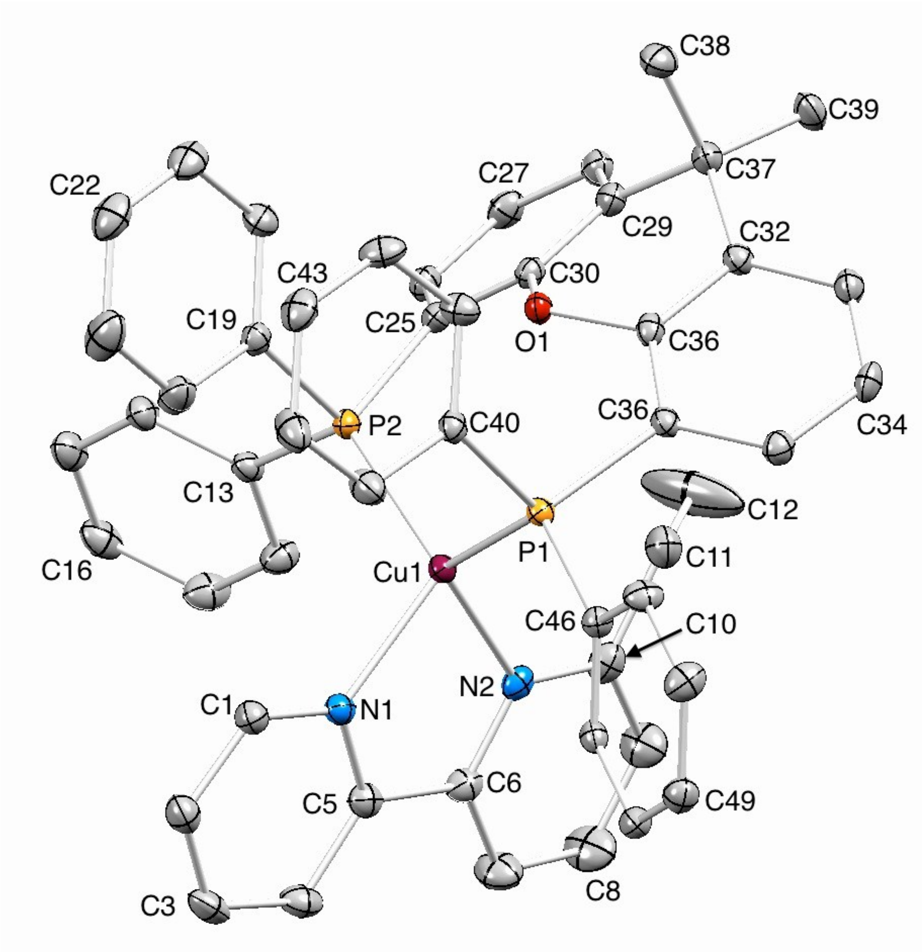


**Fig. S12**. Structure of the [Cu(xantphos)(Etbpy)]$^+$ cation in [Cu(xantphos)(Etbpy)][PF$_6$]$\cdot$CH$_2$Cl$_2\cdot$1.5H$_2$O with ellipsoids plotted at 40% probability level; H atoms are omitted. Selected bond parameters: Cu1–P2 = 2.2665(10), Cu1–P1 = 2.2548(10), Cu1–N2 = 2.080(3), Cu1–N1 = 2.056(3) Å; P2–Cu1–P1 = 113.33(4), P2–Cu1–N2 = 113.26(9), P1–Cu1–N2 = 119.59(8), P2–Cu1–N1 = 112.16(9), P1–Cu1–N1 = 113.96(9), N2–Cu1–N1 = 80.40(12)$^o$.
Selected theoretical bond parameters (B3LYP-D3//6-31G**/LANL2DZ):
Ground State (S$_0$): Cu1–P2 = 2.3099, Cu1–P1 = 2.3103, Cu1–N2 = 2.1209, Cu1–N1 = 2.1248 Å; P2–Cu1–P1 = 113.39, P2–Cu1–N2 = 120.75, P1–Cu1–N2 = 112.97, P2–Cu1–N1 = 110.10, P1–Cu1–N1 = 116.71, N2–Cu1–N1 = 78.58$^o$.
First Triplet Excited State (T$_1$): Cu1–P2 = 2.393, Cu1–P1 = 2.392, Cu1–N2 = 2.004, Cu1–N1 = 1.989 Å; P2–Cu1–P1 = 106.01, P2–Cu1–N2 = 132.09, P1–Cu1–N2 = 109.13, P2–Cu1–N1 = 99.88, P1–Cu1–N1 = 128.33, N2–Cu1–N1 = 82.83$^o$

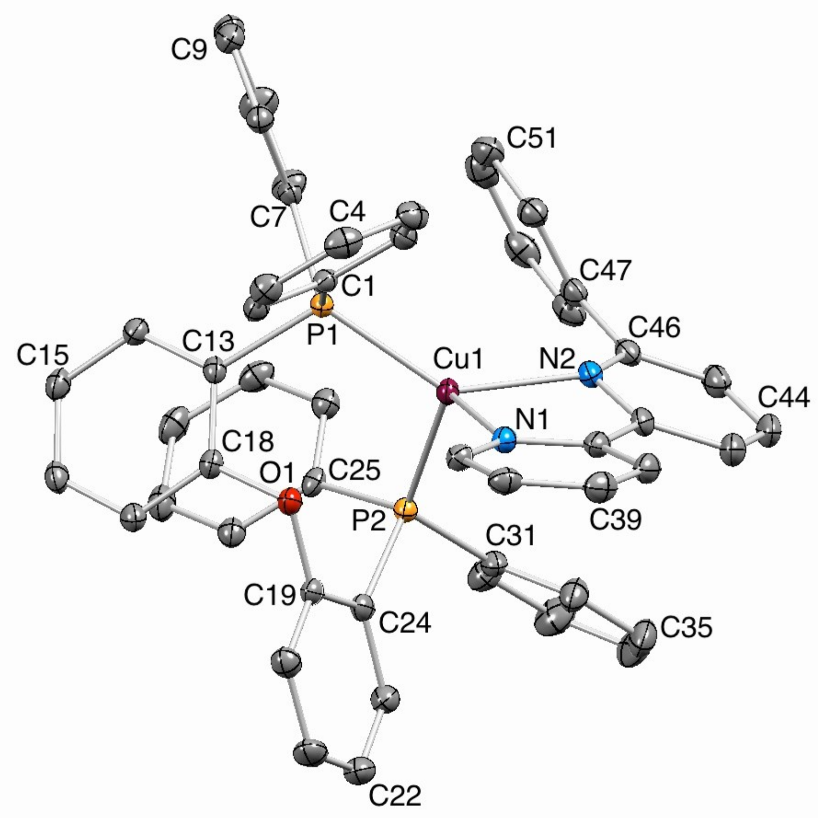


**Fig. S13**. Structure of the $[Cu(POP)(Phbpy)]^+$ cation in $[Cu(POP)(Phbpy)][PF_6]\cdot Et_2O$ with ellipsoids plotted at 40% probability level; H atoms are omitted. Selected bond parameters: Cu1–P2 = 2.2774(5), Cu1–P1 = 2.2707(5), Cu1–N1 = 2.1164(16), Cu1–N2 = 2.1129(16) Å; P2–Cu1–P1 = 109.407(19), P2–Cu1–N1 = 112.07(5), P1–Cu1–N1 = 107.78(5), P2–Cu1–N2 = 104.63(5), P1–Cu1–N2 = 139.15(5), N1–Cu1–N2 = 78.65(6)°.

Selected theoretical bond parameters (B3LYP-D3//6-31G**/LANL2DZ):

Ground State ($S_0$): Cu1–P2 = 2.296, Cu1–P1 = 2.343, Cu1–N1 = 2.131, Cu1–N2 = 2.1154 Å; P2–Cu1–P1 = 113.85, P2–Cu1–N1 = 113.59, P1–Cu1–N1 = 101.38, P2–Cu1–N2 = 131.53, P1–Cu1–N2 = 108.97, N1–Cu1–N2 = 77.86°.

First Triplet Excited State ($T_1$): Cu1–P2 = 2.450, Cu1–P1 = 2.388, Cu1–N1 = 2.035, Cu1–N2 = 1.979 Å; P2–Cu1–P1 = 102.97, P2–Cu1–N1 = 122.95, P1–Cu1–N1 = 102.88, P2–Cu1–N2 = 97.34, P1–Cu1–N2 = 151.25, N1–Cu1–N2 = 82.27°

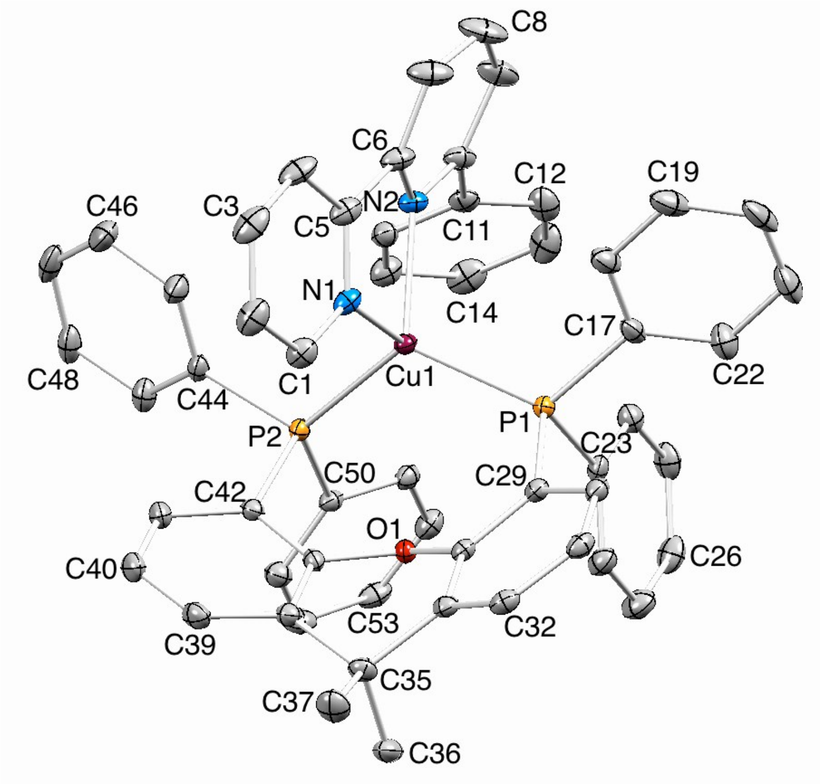


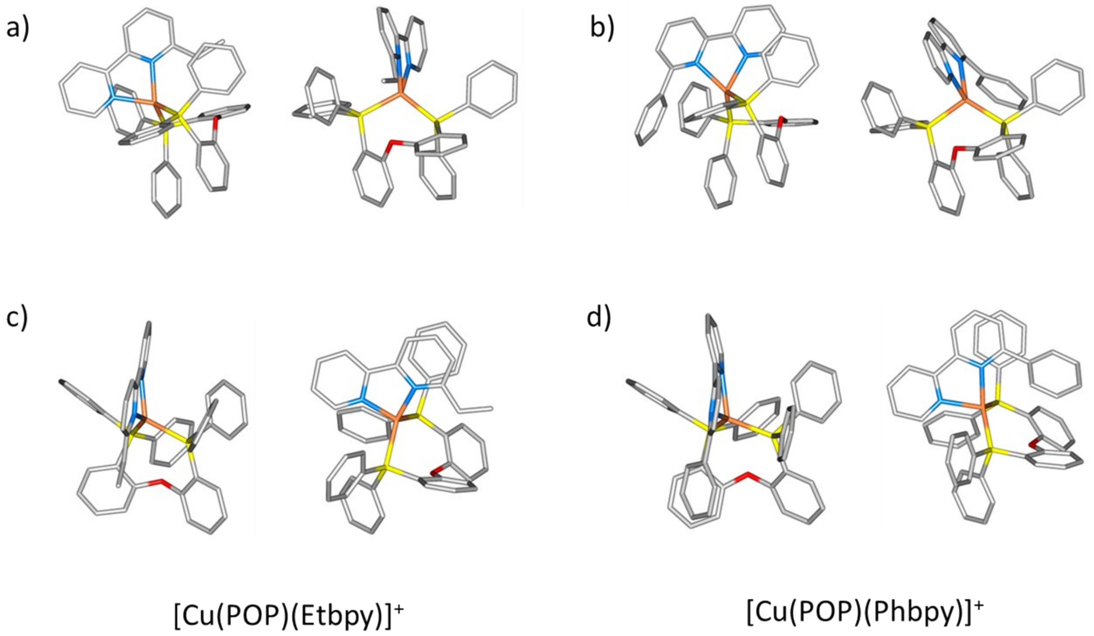
**Fig. S14**. Structure of the [Cu(xantphos)(Phbpy)]$^+$ cation in [Cu(xantphos)(Phbpy)][PF$_6$] with ellipsoids plotted at 40% probability level; H atoms are omitted. Selected bond parameters: Cu1–P2 = 2.2497(11), Cu1–P1 = 2.2672(11), Cu1–N1 = 2.104(3), Cu1–N2 = 2.099(3) Å; P2–Cu1–P1 = 117.10(4), P2–Cu1–N1 = 105.87(10), P1–Cu1–N1 = 111.16(9), P2–Cu1–N2 = 123.69(9), P1–Cu1–N2 = 112.04(10), N1–Cu1–N2 = 79.24(13)°.

Selected theoretical bond parameters (B3LYP-D3//6-31G**/LANL2DZ):

Ground State (S$_0$): Cu1–P2 = 2.3129, Cu1–P1 = 2.3101, Cu1–N1 = 2.1263, Cu1–N2 = 2.1839Å; P2– Cu1–P1 = 112.98, P2–Cu1–N1 = 132.78, P2-Cu1–N2 = 104.35, N1–Cu1–P1 = 107.53, N2–Cu1–P1 = 115.42, N1–Cu1-N2 = 78.08°.

First Triplet Excited State (T$_1$): Cu1–P2 = 2.3800, Cu1–P1 = 2.4354, Cu1–N1 = 1.9793, Cu1–N2 = 2.0456Å; P2– Cu1–P1 = 104.13, P2–Cu1–N1 = 151.28, P2-Cu1–N2 = 102.02, N1–Cu1–P1 = 96.57, N2–Cu1–P1 = 123.92, N1–Cu1-N2 = 81.99°.

Theoretical parameters are those obtained for the blue conformer in Fig. S8.



$[Cu(POP)(Etbpy)]^+$ $[Cu(POP)(Phbpy)]^+$

**Fig. S15**. Two views of the conformers optimized theoretically for $[Cu(POP)(Etbpy)]^+$ (a) and (c), and $[Cu(POP)(Phbpy)]^+$ (b) and (d). The hydrogen atoms are omitted for simplicity. The most stable conformers are (a) and (b), the structures of which closely match those obtained from the single crystal X-ray determinations (Fig. S11 and S13). Notice the intra-cation π-stacking interaction involving one phenyl ring from one $PPh_2$ unit and one of the rings of the diphenyl ether domain. The less stable conformers are (c) and (d). Notice the intra-cation π-stacking interactions between one of the pyridine rings of the bpy ligand and one phenyl ring of one $PPh_2$ unit. The POP domain adopts a “bowl” type structure similar to that adopted by the xanthene unit in $[Cu(xantphos)(Mebpy)]^+$ accommodating the 6-ethyl and 6-phenyl groups of the N^N ligands over it.

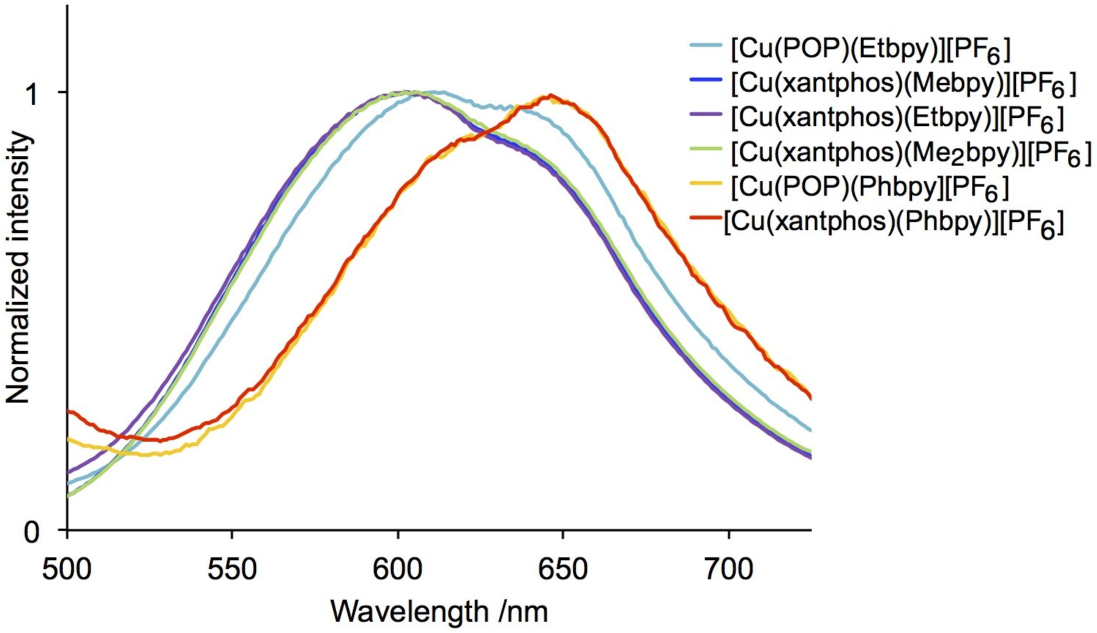


**Fig. S16**. Solution emission spectra of [Cu(P^P)(N^N)][PF$_6$] complexes (CH$_2$Cl$_2$, 2.5 × 10$^{-5}$ mol dm$^{-3}$, non-degassed). See Table 1 for $\lambda_{\text{exc.}}$

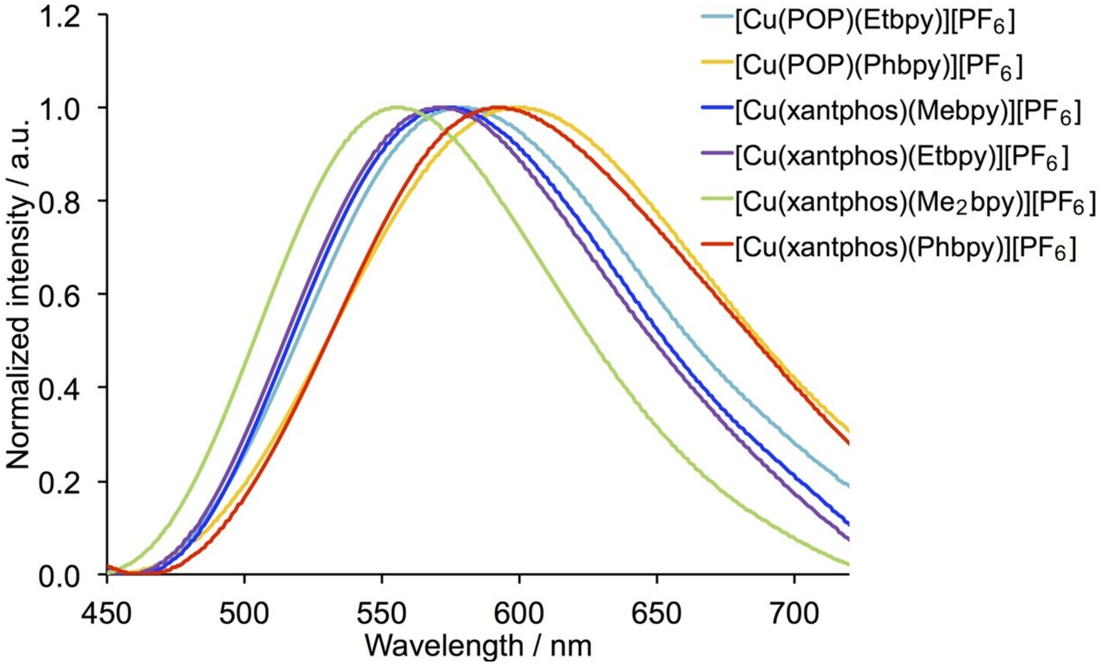


**Fig S17**. Thin film photoluminescence spectra of [Cu(P^P)(N^N)][PF$_6$]:[Emim][PF$_6$] 4:1 molar ratio (device composition). The spectra were recorded exciting the material at 365 nm.

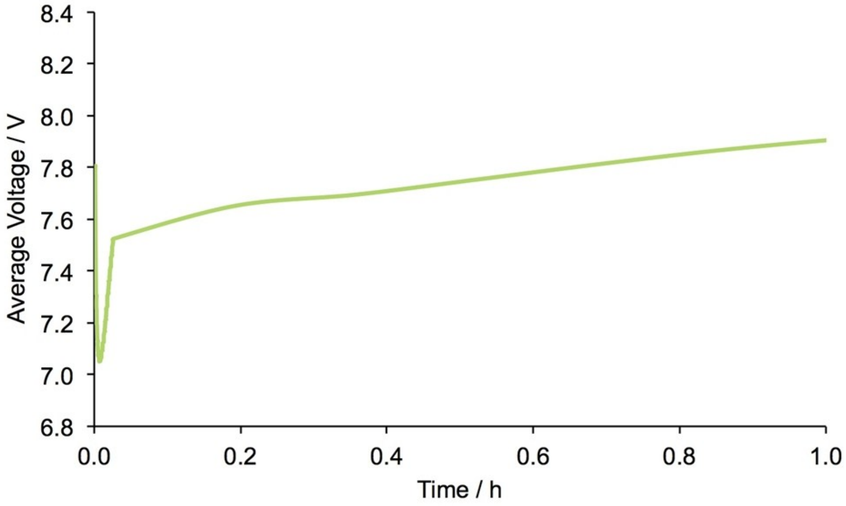


**Fig S18**. Average voltage for ITO/PEDOT:PSS/[Cu(xantphos)(Me$_2$bpy)][PF$_6$]:[Emim][PF$_6$] 1:1 molar ratio/Al under a pulsed current (average current density 50 A m$^{-2}$, 1 kHz, 50% duty cycle, block wave). [Emim][PF$_6$] = 1-ethyl-3-methylimidazolium hexafluoridophosphate.

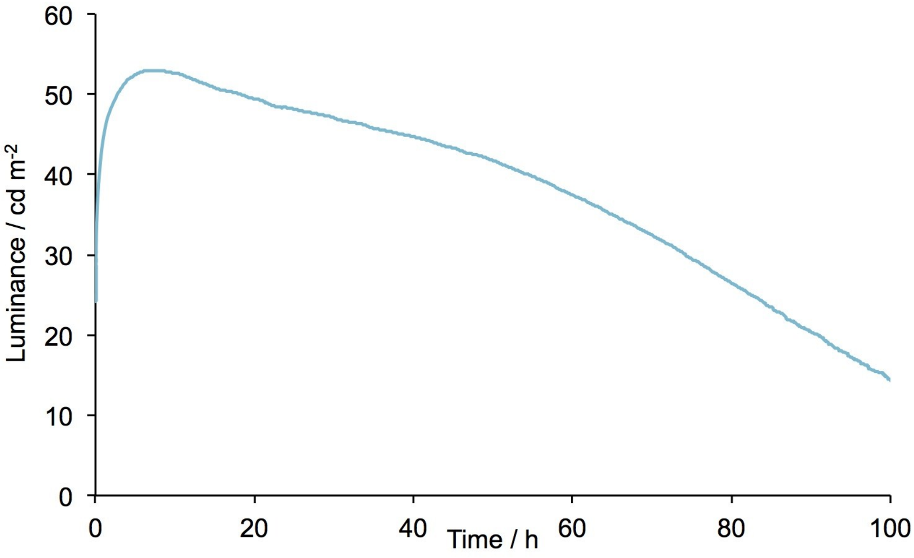


**Fig S19**. Lifetime measurement for ITO/PEDOT:PSS/[Cu(POP)(Etbpy)]:[Emim][PF$_6$] 4:1 molar ratio/Al under a pulsed current (average current density 50 A m$^{-2}$, 1 kHz, 50% duty cycle, block wave). [Emim][PF$_6$] = 1-ethyl-3-methylimidazolium hexafluoridophosphate.

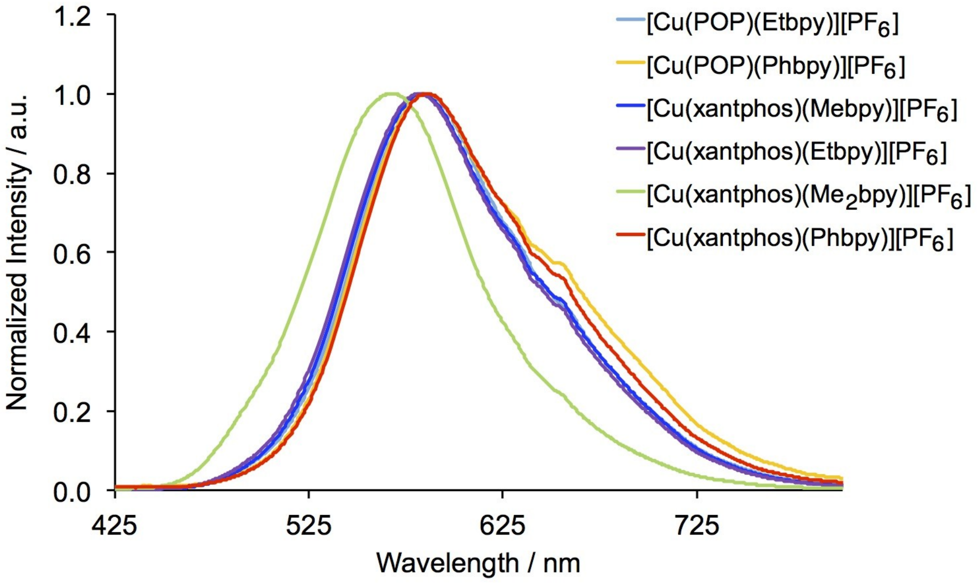


**Fig S20**. Electroluminescence spectra for: ITO/PEDOT:PSS/[Cu(P^P)(N^N)]:[Emim][$PF_6$] 4:1 molar ratio/Al under a pulsed current (average current density 50 A $m^{-2}$, 1 kHz, 50% duty cycle, block wave). [Emim][$PF_6$] = 1-ethyl-3-methylimidazolium hexafluoridophosphate.