Peripheral halo-functionalization in [Cu(N^N)(P^P)]⁺ emitters: their influence on the performances of light-emitting electrochemical cells

Fabian Brunner, Laura Martínez-Sarti, Sarah Keller, Antonio Pertegás, Alessandro Prescimone, Edwin C. Constable, Henk J. Bolink* and Catherine E. Housecroft*

Fig. S1. Structure of the [Cu(3)(xantphos)]⁺ cation.
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Fig. S14. Average voltage for glass/ITO/PEDOT:PSS/active layer/Al devices.

Table S1. Photoluminescence lifetimes (τ₁/₂) for [Cu(N^N)(P^P)][PF₆] complexes.
Fig. S1. Structure of the [Cu(3)(xanthphos)]^+ cation in [Cu(3)(xanthphos)][PF_6]·0.5H_2O·Et_2O with ellipsoids plotted at the 30% probability level; H atoms are omitted for clarity. The bromophenyl group containing Br2 is disordered and has been modelled over two sites of equal occupancy which share atom C55 in common; only one site is shown. Selected bond parameters: Cu1–P1 = 2.317(3), Cu1–P2 = 2.258(3), Cu1–N1 = 2.080(8), Cu1–N2 = 2.121(8) Å; P1–Cu1–P2 = 117.08(11), P1–Cu1–N1 = 104.2(3), P2–Cu1–N1 = 119.6(3), P1–Cu1–N2 = 100.2(2), P2–Cu1–N2 = 129.3(2), N1–Cu1–N2 = 78.8(3)°.

Fig. S2. Structure of the [Cu(1)(POP)]^+ cation in [Cu(1)(POP)][PF_6]·0.8H_2O with ellipsoids plotted at the 30% probability level; H atoms are omitted for clarity. The pyridine ring containing N2 and the attached fluorophenyl group containing F2 are disordered and the unit has been modelled over two sites of 0.65:0.35 fractional occupancies; only the major occupancy site is shown. Selected bond parameters: Cu1–N1 = 2.099(6), Cu1–N2 = 2.097(5), Cu1–P1 = 2.2523(15), Cu1–P2 = 2.297(2) Å; N1–Cu1–N2 = 78.5(2), N1–Cu1–P1 = 123.71(15), N2–Cu1–P1 = 120.00(16), N1–Cu1–P2 = 104.32(15), N2–Cu1–P2 = 116.27(17), P1–Cu1–P2 = 110.37(8)°.
Fig. S3. Structure of the $[\text{Cu(1)}]^{+}$ cation in $[\text{Cu(1)}][\text{PF}_{6}]$ with ellipsoids plotted at the 30% probability level; H atoms are omitted for clarity. Selected bond parameters: Cu1–N2 = 2.044(2), Cu1–N1 = 2.001(2), Cu1–N3 = 2.027(2), Cu1–N4 = 2.000(2) Å; N2–Cu1–N1 = 82.13(9), N2–Cu1–N3 = 117.02(9), N1–Cu1–N3 = 123.42(10), N2–Cu1–N4 = 123.20(10), N1–Cu1–N4 = 133.76(10), N3–Cu1–N4 = 81.89(9)°.

Fig. S4. Solution (CH$_2$Cl$_2$, 2.5 × 10$^{-5}$ mol dm$^{-3}$) absorption spectra of $[\text{Cu(N}^\text{N})(\text{POP})][\text{PF}_{6}]$ ($\text{N}^\text{N} = 1–5$) complexes.
**Fig. S5.** Normalized solid-state emission spectra of $[\text{Cu}(N^N)(\text{POP})][\text{PF}_6]$ ($N^N = 1-5$). ($\lambda_{\text{exc}} = 365$ nm).

**Fig. S6.** Normalized solution (CH$_2$Cl$_2$, $2.5 \times 10^{-5}$ mol dm$^{-3}$) emission spectra of $[\text{Cu}(N^N)(\text{xantphos})][\text{PF}_6]$ ($N^N = 1-5$). ($\lambda_{\text{exc}} = 400$ nm).
**Fig. S7.** Normalized thin film emission spectra of [Cu(N^N)(POP)][PF_6] (N^N = 1–5). (λ_{exc} = 365 nm). The thin film consisted of the complex mixed with the ionic liquid 1-ethyl-3-methylimidazolium hexafluorophosphate.

**Fig. S8.** Normalized thin film emission spectra of [Cu(N^N)(xantphos)][PF_6] (N^N = 1–5). (λ_{exc} = 365 nm). The thin film consisted of the complex mixed with the ionic liquid 1-ethyl-3-methylimidazolium hexafluorophosphate.
**Fig. S9.** EL spectra for LECs containing $\text{[Cu}(3)\text{xantphos}]^+$, $\text{[Cu}(2)\text{POP}]^+$, $\text{[Cu}(2)\text{xantphos}]^+$, $\text{[Cu}(1)\text{POP}]^+$, $\text{[Cu}(1)\text{xantphos}]^+$, $\text{[Cu}(5)\text{POP}]^+$ and $\text{[Cu}(5)\text{xantphos}]^+$.

**Fig. S10.** Luminance (blue line) and average voltage (red symbols) versus time for the LEC with $\text{[Cu}(3)\text{POP}]\text{[PF}_6\text{]}$ by applying a block-wave pulsed current of 50 A m$^{-2}$ at a frequency of 1 kHz and a duty cycle of 50%.
**Fig. S11.** Luminance (blue line) and average voltage (red symbols) versus time for the LEC with [Cu(4)(POP)][PF$_6$] by applying a block-wave pulsed current of 50 A m$^{-2}$ at a frequency of 1 kHz and a duty cycle of 50%.

**Fig. S12.** Luminance (blue line) and average voltage (red symbols) versus time for the LEC with [Cu(4)(xantphos)][PF$_6$] by applying a block-wave pulsed current of 50 A m$^{-2}$ at a frequency of 1 kHz and a duty cycle of 50%.
Fig. S13. Luminance (blue line), average voltage (red symbols) and efficiency in cd A⁻¹ (green line) versus time for the LEC with [Cu(θ)xantphos][PF₆] by applying a block-wave pulsed current of 50 A m⁻² at a frequency of 1 kHz and a duty cycle of 50%.

Fig. S14. Average voltage for glass/ITO/PEDOT:PSS/active layer/Al devices measured by applying a block-wave pulsed current of 50 A m⁻² at a frequency of 1 kHz and a duty cycle of 50%. The active layer consisted of the different [Cu(N²N)(P²P)][PF₆] (N²N = 1, 2 and 5) complexes mixed with the ionic liquid 1-ethyl-3-methylimidazolium hexafluorophosphate.
Table S1. Photoluminescence lifetimes ($\tau_{1/2}$) for [Cu(N^N)(P^P)][PF$_6$] complexes.

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