ESI to accompany:

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

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

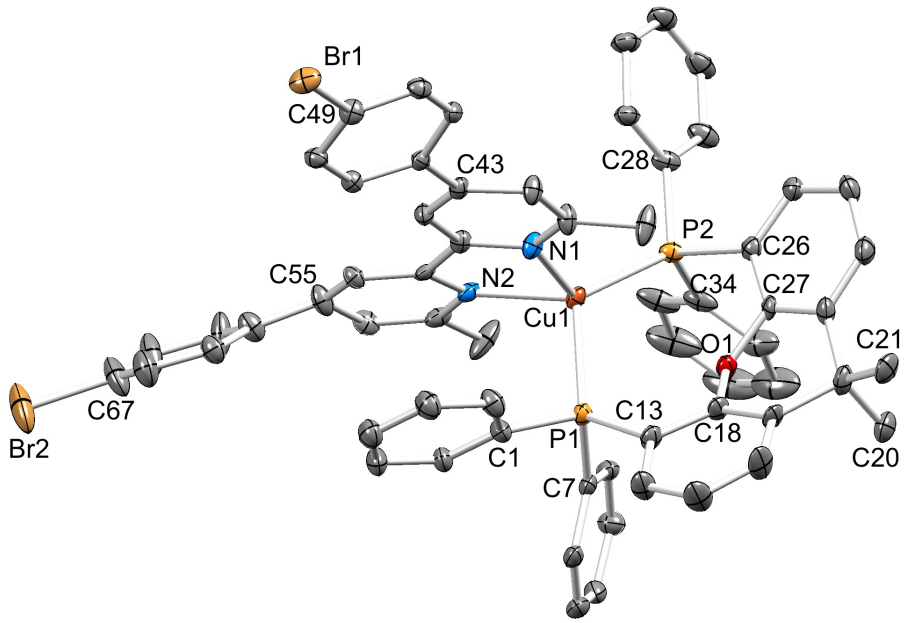

Fig. S1. Structure of the [Cu(**3**)(xantphos)]$^{+}$ cation in [Cu(**3**)(xantphos)][PF_6]·0.5H_2O·Et_2O with ellipsoids plotted at the 30% probability level; H atoms are omitted for clarity. The bromophenyl group containing Br2 is disordered and has been modelled over two sites of equal occupancy which 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)°.

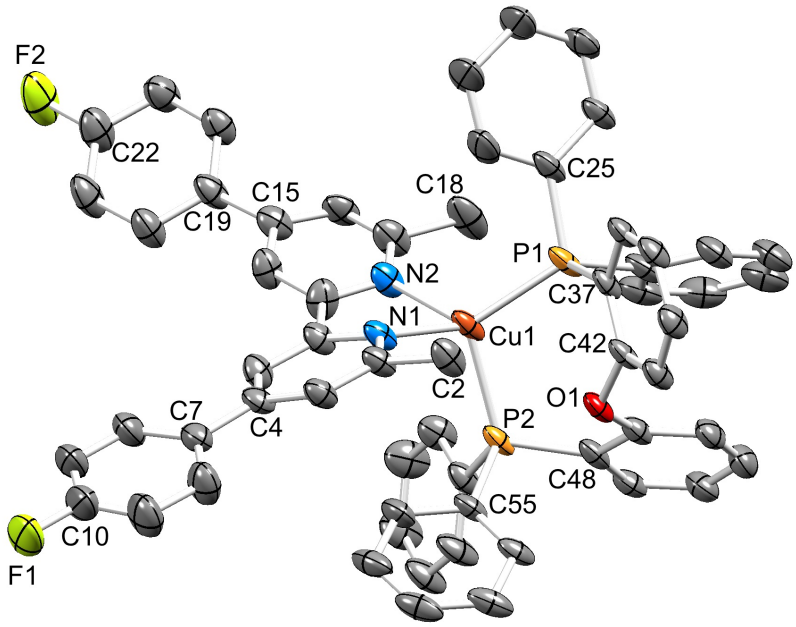

Fig. S2. Structure of the [Cu(**1**)(POP)]$^{+}$ cation in [Cu(**1**)(POP)][PF_6]·0.8H_2O with ellipsoids plotted at the 30% probability level; H atoms are omitted for clarity. The pyridine ring containing N2 and the attached fluorophenyl group containing F2 are disordered and the unit has been modelled 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)°.

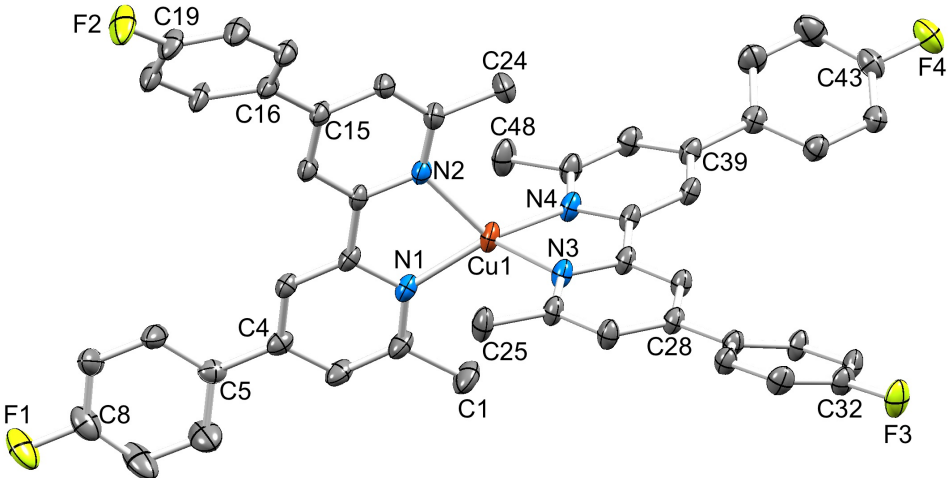

Fig. S3. Structure of the $[Cu(\mathbf{1})_2]^+$ cation in $[Cu(\mathbf{1})_2][PF_6]$ with ellipsoids plotted at the 30% probability level; H atoms are omitted for clarity. Selected bond parameters: Cu1–N2 = 2.044(2), Cu1–N1 = 2.001(2), Cu1–N3 = 2.027(2), Cu1–N4 = 2.000(2) Å; N2–Cu1–N1 = 82.13(9), N2–Cu1–N3 = 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)°.

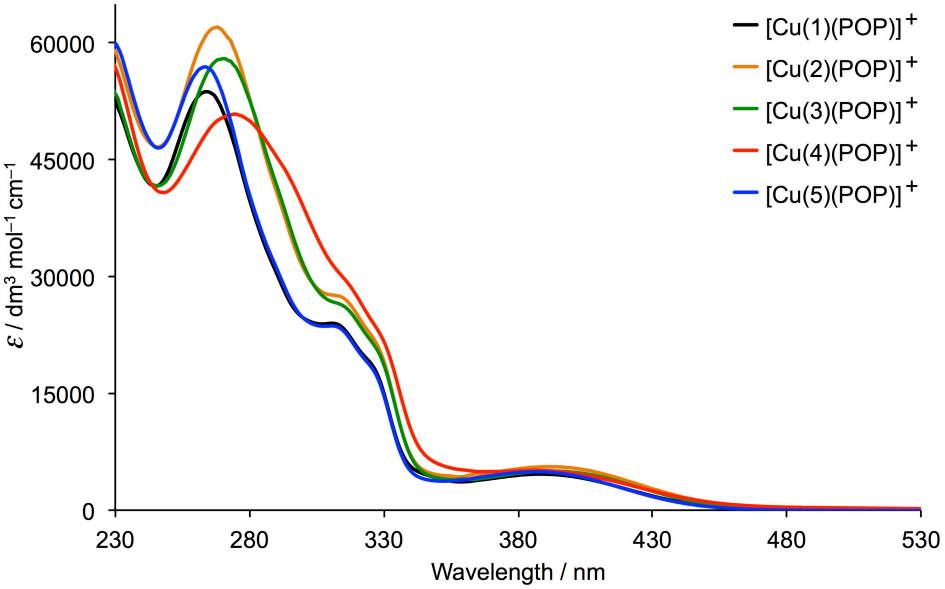

Fig. S4. Solution (CH_2Cl_2, 2.5 x 10^{-5} mol dm^{-3}) absorption spectra of $[Cu(N^N)(POP)][PF_6]$ (N^N = **1–5**) complexes.

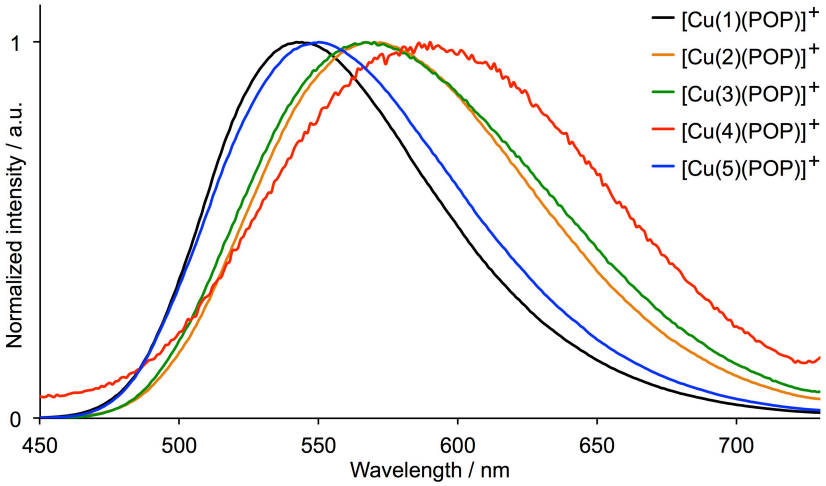

Fig. S5. Normalized solid-state emission spectra of [Cu(N^N)(POP)][PF_6] (N^N = **1–5**). (λ_{exc} = 365 nm).

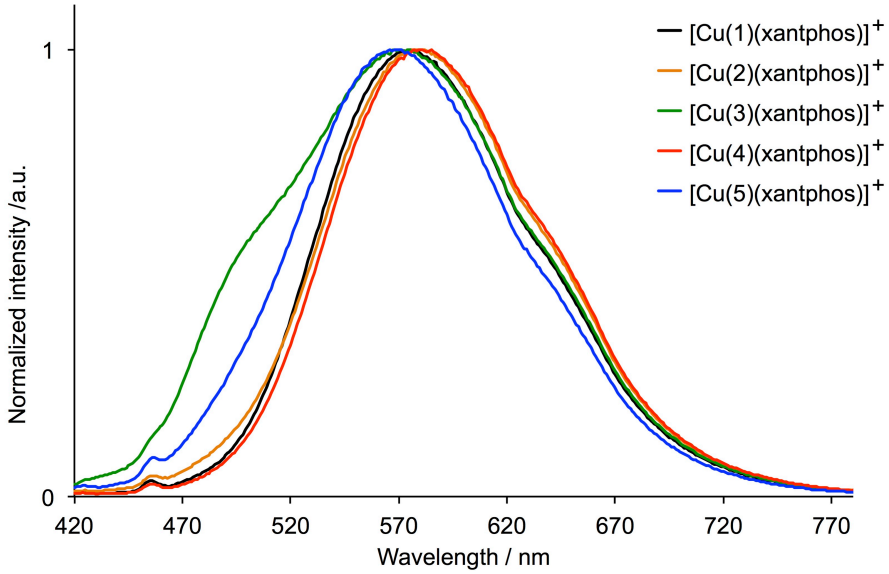

Fig. S6. Normalized solution (CH_2Cl_2, 2.5 x 10^{-5} mol dm^{-3}) emission spectra of [Cu(N^N)(xantphos)][PF_6] (N^N = **1–5**). (λ_{exc} = 400 nm).

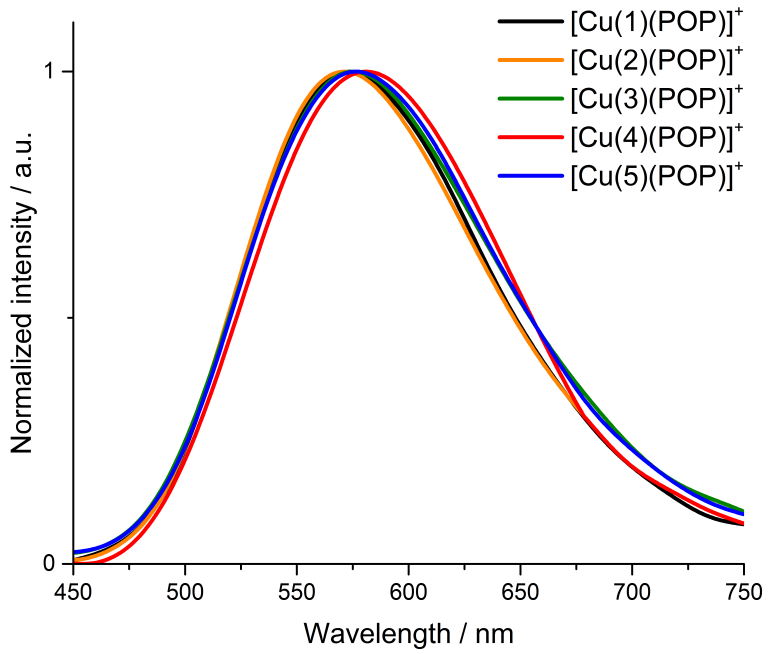

Fig. S7. Normalized thin film emission spectra of [Cu(N^N)(POP)][PF_6] (N^N = **1–5**). (λ_{exc} = 365 nm). The thin film consisted of the complex mixed with the ionic liquid 1-ethyl-3-methylimidazolium hexafluoridophosphate.

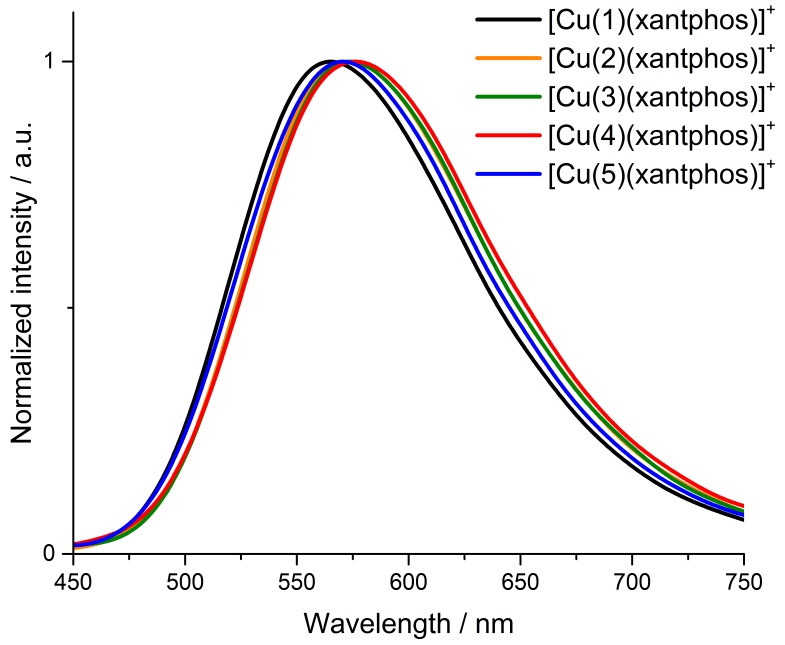

Fig. S8. Normalized thin film emission spectra of [Cu(N^N)(xantphos)][PF_6] (N^N = **1–5**). (λ_{exc} = 365 nm). The thin film consisted of the complex mixed with the ionic liquid 1-ethyl-3-methylimidazolium hexafluoridophosphate.

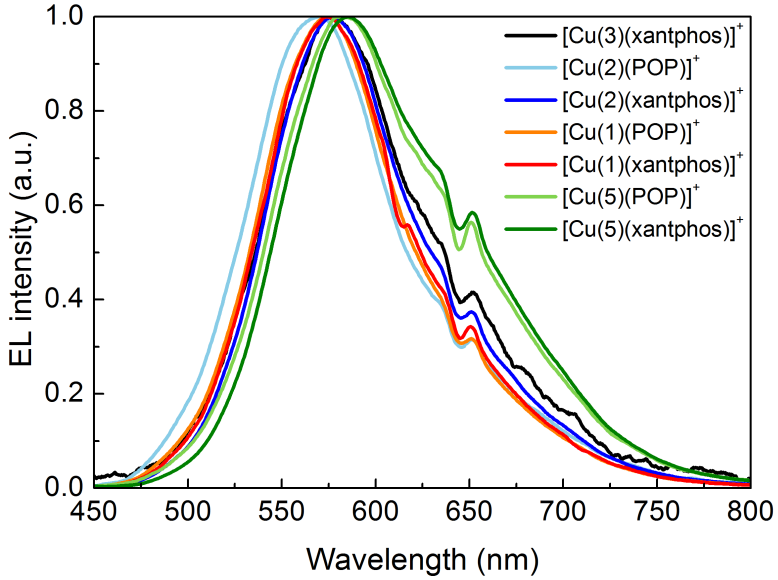

Fig. S9. EL spectra for LECs containing [Cu(**3**)(xantphos)]$^+$, [Cu(**2**)(POP)]$^+$, [Cu(**2**)(xantphos)]$^+$, [Cu(**1**)(POP)]$^+$, [Cu(**1**)(xantphos)]$^+$, [Cu(**5**)(POP)]$^+$ and [Cu(**5**)(xantphos)]$^+$.

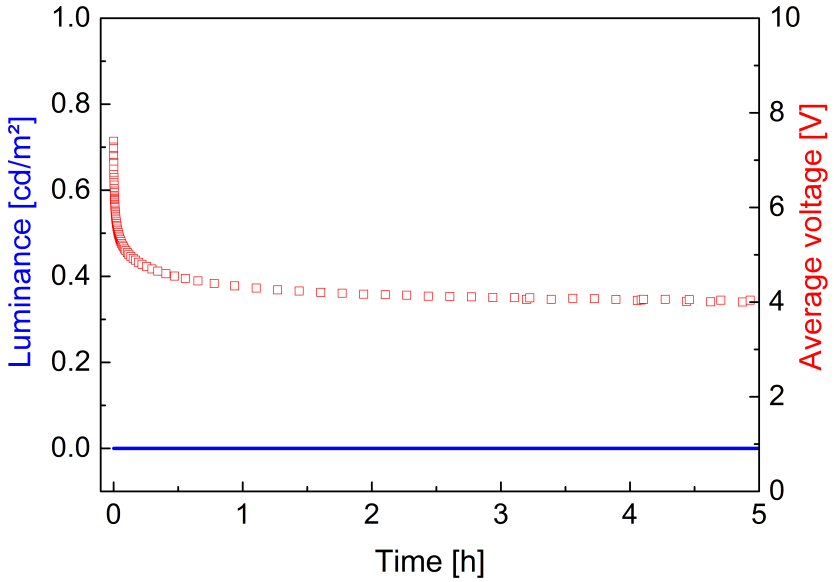

Fig. S10. Luminance (blue line) and average voltage (red symbols) versus time for the LEC with [Cu(**3**)(POP)][PF_6] by applying a block-wave pulsed current of 50 A m^{-2} at a frequency of 1 kHz and a duty cycle of 50%.

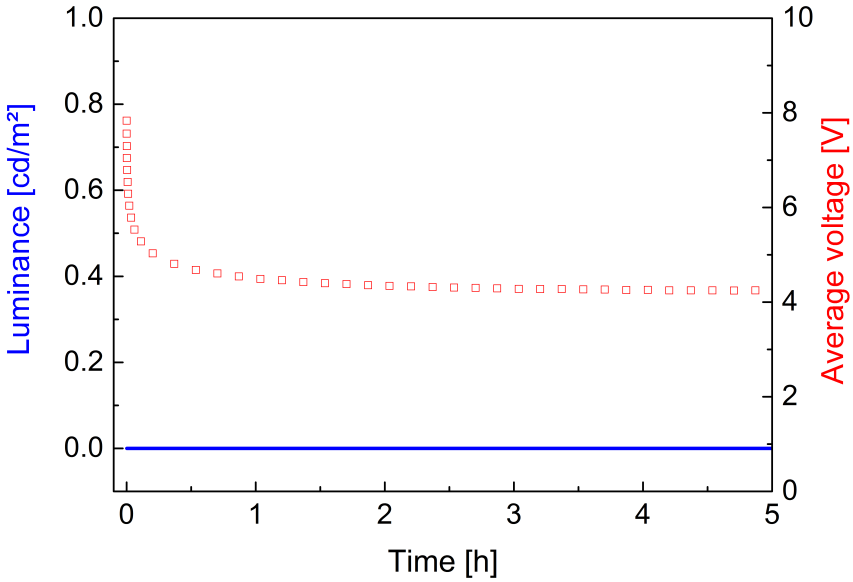

Fig. S11. Luminance (blue line) and average voltage (red symbols) versus time for the LEC with [Cu(**4**)(POP)][PF_6] by applying a block-wave pulsed current of 50 A m^{-2} at a frequency of 1 kHz and a duty cycle of 50%.

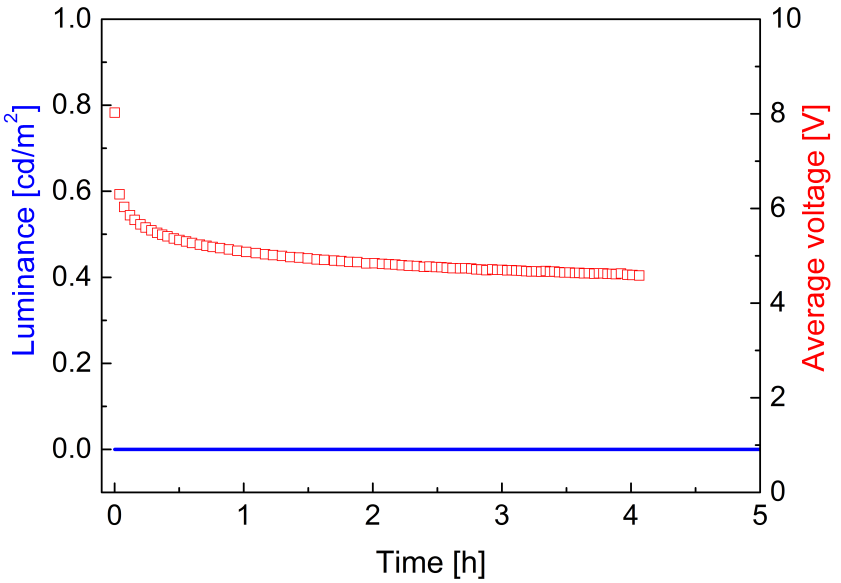

Fig. S12. Luminance (blue line) and average voltage (red symbols) versus time for the LEC with [Cu(**4**)(xantphos)][PF_6] by applying a block-wave pulsed current of 50 A m^{-2} at a frequency of 1 kHz and a duty cycle of 50%.

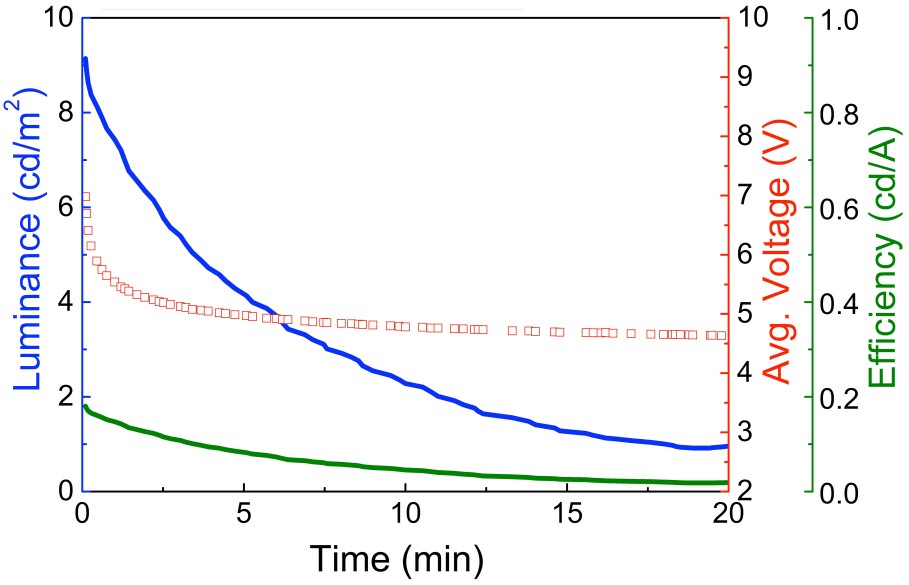

Fig. S13. Luminance (blue line), average voltage (red symbols) and efficiency in cd A^{-1} (green line) versus time for the LEC with [Cu(**3**)(xantphos)][PF_6] by applying a block-wave pulsed current of 50 A m^{-2} at a frequency of 1 kHz and a duty cycle of 50%.

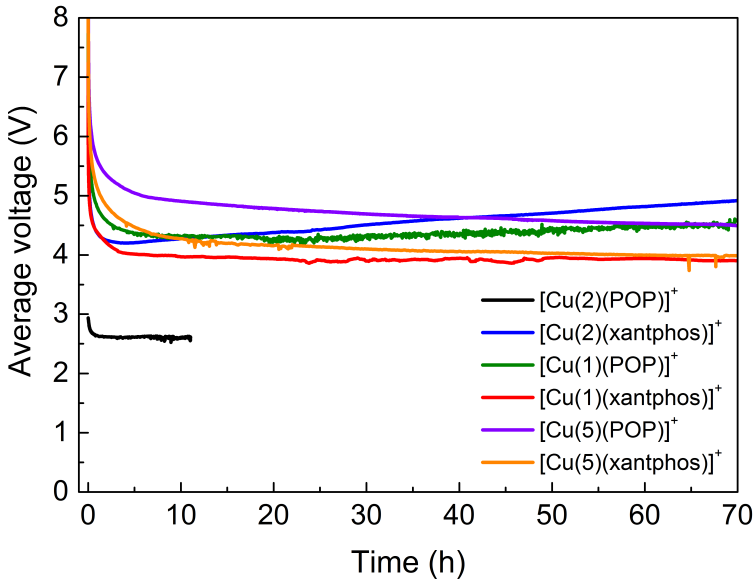

Fig. S14. Average voltage for glass/ITO/PEDOT:PSS/active layer/Al devices measured by applying a block-wave pulsed current of 50 A m^{-2} at a frequency of 1 kHz and a duty cycle of 50%. The active layer consisted of the different [Cu(N^N)(P^P)][PF6] (N^N = 1, 2 and 5) complexes mixed with the ionic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

Table S1. Photoluminescence lifetimes ($\tau_{1/2}$) for [Cu(N^N)(P^P)][PF_6] complexes.

Complex cation	CH_2Cl_2 degassed solution[a,b]					Powder[c]				
	$\tau_{1/2}(1)$ / μs	*A*1	$\tau_{1/2}(2)$ / μs	*A*2	$\tau_{1/2}$(av) / μs	$\tau_{1/2}(1)$ / μs	*A*1	$\tau_{1/2}(2)$ / μs	*A*2	$\tau_{1/2}$(av) / μs
[Cu(**1**)(POP)]$^+$	4.5				4.5	11.7	0.9118	1.5	0.05582	11.1
[Cu(**2**)(POP)]$^+$	4.2				4.2	5.6	0.5335	1.5	0.3531	4.0
[Cu(**3**)(POP)]$^+$	4.4				4.4	7.1	0.3976	1.6	0.4517	4.2
[Cu(**4**)(POP)]$^+$	4.1				4.1	2.3	0.2638	0.6	0.4417	1.2
[Cu(**5**)(POP)]$^+$	4.5	0.4225	1.8	0.504	3.0	11.5	0.8209	1.8	0.1259	10.2
[Cu(**1**)(xantphos)]$^+$	2.5				2.5	7.2	0.6052	0.8	0.1709	5.8
[Cu(**2**)(xantphos)]$^+$	2.8				2.8	7.0	0.5854	1.9	0.3025	5.2
[Cu(**3**)(xantphos)]$^+$	2.8				2.8	8.3	0.5975	1.9	0.3223	6.1
[Cu(**4**)(xantphos)]$^+$	2.6				2.6	4.7	0.4578	1.2	0.4559	3.0
[Cu(**5**)(xantphos)]$^+$	3.7				3.7	7.2	0.6728	1.6	0.2477	5.7