Electronic Supplementary Material (ESI) for Dalton Transactions.

ESI to accompany:

$[Cu(bpy)(P^\wedge P)]^+$ containing light-emitting electrochemical cells: improving performance through simple substitution

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Experimental Section

General

A Bruker Avance III-500 NMR spectrometer was used to record ^1H and ^{13}C and ^{31}P NMR spectra at 295 K. ^1H and ^{13}C chemical shifts were referenced to residual solvent peaks with respect to ∂(TMS) = 0 ppm and ^{31}P with respect to ∂(85% aqueous H_3PO_4) = 0 ppm. Absorption spectra were recorded with an Agilent 8453 spectrophotometer and fluorescence spectra with a Shimadzu RF-5301PC spectrofluorometer.

Electrospray ionization (ESI) mass spectra were recorded on a Bruker esquire 3000plus instrument. Electrochemical measurements were made using a CH Instruments 900B potentiostat with glassy carbon, platinum wire and silver wire as the working, counter and reference electrodes, respectively. Substrates were dissolved in HPLC grade CH_2Cl_2 (ca. 10^{-4} to 10^{-5} mol dm^{-3}) containing 0.1 mol dm^{-3} $[^nBu_4N][PF_6]$ as the supporting electrolyte; all solutions were degassed with argon. Cp_2Fe was used as internal reference.

Quantum yields were measured with a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus-QY (solution, PMMA film and powder) or a Hamamatsu absolute quantum yield C9920 (device film). Lifetimes were measured using a Hamamatsu Compact Fluorescence lifetime Spectrometer C11367 Quantaurus-Tau; an LED light source with excitation wavelength of 365 nm was used.

The thin films for quantum yield and lifetime measurements were prepared according to the following procedure:

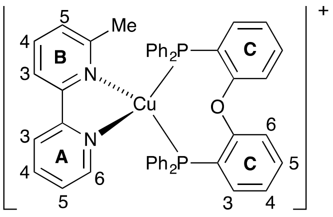
PMMA films: About 0.3 mL of a solution of [Cu(POP)(6-Mebpy)][PF_6] (5 × 10^{-3} mol dm^{-3}) and PMMA (poly(methyl methacrylate), 20 mg cm^{-3}) were applied to a square quartz glass plate (1 cm^2). Immediately, the plate was spin-coated for 16 s at 130 rpm with spin coating module SAWATEC SM-180-BT.

Device films: A CH_2Cl_2 20mg/mL of each iTMC mixed with 1-ethyl-3-methylimidazolium hexafluoridophosphate in 1:1 molar ratio was spin-coated at 2000 rpm for 20 s on a quartz plate (1 cm^2).

Abbreviations: POP = bis(2-diphenylphosphinophenyl)ether; 6-Mebpy = 6-methyl-2,2'-bipyridine; 6,6'-Me_2bpy = 6,6'-dimethyl-2,2'-bipyridine.

The complex [Cu(MeCN)$_4$][PF_6] was prepared as reported in literature.[1] The ligand 6-Mebpy was prepared adapting literature methods,[2] and the NMR spectroscopic data matched those reported.[3]

[Cu(POP)(6-Mebpy)][PF$_6$]

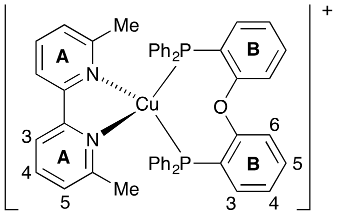


PPh$_2$ phenyl ring = **D** (see text discussion)

The colourless solution of [Cu(MeCN)$_4$][PF_6] (93 mg, 0.25 mmol) and POP (134 mg, 0.25 mmol) in CH_2Cl_2 (40 mL) was stirred for 2 h. Then 6-Mebpy (43 mg, 0.25 mmol) was added and the yellow solution was stirred for another 4 h. Solvent was removed in vacuo, and the yellow residue was redissolved in CH_2Cl_2 (4 mL), transferred to a tube and the solution layered with Et_2O. This gave [Cu(POP)(6-Mebpy)][PF_6] as yellow crystals in good yield (220 mg, 0.24 mmol, 96 %). ^1H NMR (500 MHz, CD_2Cl_2) ∂ /ppm 8.31 (d, J = 5.1 Hz, 1H, H^{A6}), 8.17 (d, J = 8.2 Hz, 1H, H^{A3}), 8.07 (d, J = 7.9 Hz, 1H, H^{B3}), 7.91 (overlapping m, 2H, H^{A4+B4}), 7.36 – 7.28 (m, 6H, $H^{C5+D4+D4'}$), 7.25 (d, J = 7.7 Hz, 1H, H^{B5}), 7.21 (t, J = 7.5 Hz, 4H, $H^{D3/D3'}$), 7.17 (m, 5H, $H^{A5+D3/D3'}$), 7.07 (m, 4H, $H^{D2/D2'}$), 7.05 (m, 4H, H^{C6+C4}), 6.96

(m, 4H, H$^{D2/D2'}$), 6.87 (m, 2H, H^{C3}), 2.35 (s, 3H, H^{Me}).^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) ∂/ppm 159.5 (C^{B6}), 158.4 (m, C$^{C1+C1'}$), 152.9 (C^{A2}), 152.0 (C^{B2}), 149.5 (C^{A6}), 139.3 (C^{B4}), 138.9 (C^{A4}), 134.7 (C^{C3}), 133.6 (t, J_{PC} = 7.9 Hz, C$^{D2/D2'}$), 133.4 (t, J_{PC} = 7.9 Hz, C$^{D2/D2'}$), 132.6 (C^{C5}), 131.5 (t, J = 17.1 Hz, C$^{D1+D1'}$), 130.7 (C$^{D4/D4'}$), 130.5 (C$^{D4/D4'}$), 129.3 (t, J = 4.6 Hz, C$^{D3/D3'}$), 129.2 (t, J = 4.6 Hz, C$^{D3/D3'}$), 126.5 (C^{B5}), 126.0 (C^{A5}), 125.7 (t, J = 2.0 Hz, C^{C4}), 124.7 (t, J = 14.5 Hz, C^{C2}), 122.8 (C^{A3}), 120.7 (C^{C6}), 120.1 (C^{B3}), 26.7 (C^{Me}). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2). ∂ / ppm –12.4 (broad, FWHM = 500 Hz, POP), –144.5 (septet, J_{PF} = 710 Hz, $[PF_6]^-$). UV-Vis (CH_2Cl_2, 2.5 × 10^{-5} mol dm^{-3}): λ / nm (ε / dm^{3} mol^{-1} cm^{-1}) 247sh (26500), 290 (21300), 313sh (14800), 380 (2200). Emission: Solution (CH_2Cl_2, 2.5 × 10^{-5} mol dm^{-3}, λ_{exc} = 378 nm): λ_{max}^{em} = 610, 639 nm, film (CH_2Cl_2, 5 × 10^{-3} mol dm^{-3}, 20 mg × mL^{-1} PMMA , λ_{exc} = 365 nm): λ_{max}^{em} = 550 nm, powder (λ_{exc} = 365 nm): λ_{max}^{em} = 567 nm. ESI MS: *m/z* 771.5 $[M–PF_6]^+$ (base peak, calc. 771.2). Found C 60.95, H 4.55, N 3.33; [Cu(POP)(6-Mebpy)]$[PF_6]$ · 0.5 H_2O requires C 60.94, H 4.24, N 3.02.

[Cu(POP)(6,6'-Me$_2$bpy)][PF$_6$]



PPh$_2$ phenyl ring = **C**

A colourless solution of $[Cu(MeCN)_4][PF_6]$ (131 mg, 0.35 mmol) and POP (226 mg, 0.42 mmol) in CH_2Cl_2 (40 mL) was stirred for 2 h. Then 6,6'-Me$_2$bpy (65 mg, 0.35 mmol) was added. The yellow solution was stirred for another 2 h. Solvent was then removed in vacuo. The yellow residue was redissolved in CH_2Cl_2 (4 mL), transferred to a tube and layered with Et_2O. This resulted in a mixture of yellow crystals and yellow oil. The mother liquor was removed and hexane was added to all three phases, upon which a pale yellow solid was obtained. This was washed with hexane to yield [Cu(POP)(6,6'-Me$_2$bpy)][PF$_6$] as a pale yellow powder (320 mg, 0.34 mmol, 98%). ^{1}H NMR (500 MHz, CD_2Cl_2) ∂ /ppm 7.89 (d, J = 7.3 Hz, 2H, H^{A3}), 7.85 (t, J = 7.8 Hz, 2H, H^{A4}), 7.32 (m, 2H, H^{B5}), 7.28 (m, 4H, H^{C4}), 7.23 (dd, J = 7.4, 0.8 Hz, 2H, H^{A5}), 7.21–7.16 (overlapping m, 4H, H^{B3+B4}), 7.12 (m, 8H, H^{C3}), 7.01 (m, 8H, H^{C2}), 6.93 (m, 2H, H^{B6}), 2.22 (s, 6H, H^{Me}). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) ∂/ppm 159.3 (C^{A6}), 158.7 (m, C^{B1}), 152.9 (C^{A2}), 139.2 (C^{A4}), 134.3 (C^{B3}), 133.5 (t, J_{PC} = 8.1 Hz, C^{C2}), 132.7 (C^{B5}), 132.2 (t, J = 16.5 Hz, C^{C1}), 130.4 (C^{C4}), 129.2 (t, J = 5.1 Hz, C^{C3}), 126.6 (C^{A5}), 125.7 (C^{B4}), 120.6 (t, J = 2.0 Hz, C^{B6}), 120.2 (C^{A3}), 26.9 (C^{Me}). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2). ∂ / ppm –13.5 (broad, FWHM = 380 Hz, POP), –144.5 (septet, J_{PF} = 710 Hz, $[PF_6]^-$). UV-Vis (CH_2Cl_2, 2.5×10^{-5} mol dm^{-3}): λ / nm (ε / dm^3 mol^{-1} cm^{-1}) 230 sh (49500), 283 (24300), 319sh (14400), 371 (3000). Emission: solution (CH_2Cl_2, 2.5×10^{-5} mol dm^{-3}, λ_{exc} = 372 nm): $\lambda_{max}{}^{em}$ = 565, 645 nm; film (CH_2Cl_2, 5×10^{-3} mol dm^{-3}, 20 mg × mL^{-1} PMMA , λ_{exc} = 365 nm): $\lambda_{max}{}^{em}$ = 529 nm; powder (λ_{exc} = 365 nm): $\lambda_{max}{}^{em}$ = 535 nm. ESI MS: *m/z* 785.5 $[M–PF_6]^+$ (base peak, calc. 785.2). Found C 63.07, H 4.71, N 3.05; $[Cu(POP)(6,6'\text{-}Me_2bpy)][PF_6] \cdot 0.5$ hexane requires C 62.86, H 4.86, N 2.87

Single crystal X-ray determination of $[Cu(POP)(6\text{-}Mebpy)][PF_6]$

After SQUEEZE: $C_{49}H_{60}ClCuF_6N_2OP_3$, M = 917.29, yellow needle, monoclinic, space group $P2_1/n$, a = 9.7056(4), b = 16.3421(7), c = 29.3522(14) Å, β = 96.439(2)°, U = 4626.2(4) Å^3, Z = 4, D_c = 1.317 Mg m^{-3}, μ(Cu-Kα) = 2.161 mm^{-1}, T = 123 K. Total 51874 reflections, 8423 unique, R_{int} = 0.028. Refinement of 8278 reflections (659 parameters) with $I > 3\sigma(I)$ converged at final R_1 = 0.0394 (R_1 all data = 0.0398), wR_2 = 0.0392 (wR_2 all data = 0.0396), gof = 1.0728. CCDC 996509.

Single crystal X-ray determination of $[Cu(POP)(6,6'\text{-}Me_2bpy)][PF_6]\cdot 2H_2O\cdot 0.5CH_2Cl_2$

$C_{48.5}H_{45}ClCuF_6N_2O_3P_3$, M = 1009.81, orange block, monoclinic, space group $P2_1/c$, a = 16.3230(8), b = 15.5884(9), c = 20.3378(11) Å, β = 105.944(3)°, U = 4975.9(3) Å^3, Z = 4, D_c = 1.348 Mg m^{-3}, μ(Cu-Kα) = 2.571 mm^{-1}, T = 123 K. Total 40330 reflections, 8670 unique, R_{int} = 0.084. Refinement of 8631 reflections (570 parameters) with $I > 3\sigma(I)$ converged at final R_1 = 0.1341 (R_1 all data = 0.1342), wR_2 = 0.3231 (wR_2 all data = 0.3235), gof = 0.9898. CCDC 1009455.

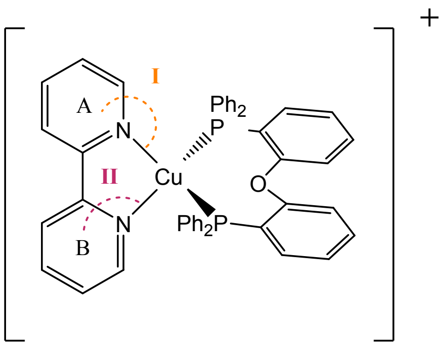
LEC preparation

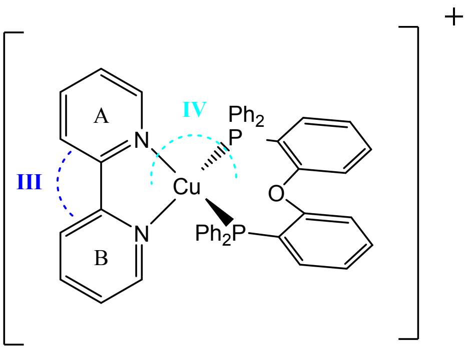
The electroluminescence devices were made as follows. First, glass substrates with sputtered ITO contact (Naranjo Substrates) were cleaned by sequentially washing and sonication with soap, deionized water, isopropanol and UV-O_3 lamp for 20 min. Then, a 90-nm layer of PEDOT:PSS (CLEVIOS™ P VP AI 4083, aqueous dispersion, 1.3–1.7% solid content, Heraeus) was spin-coated on the ITO substrates to improve the reproducibility of the devices and to prevent the formation of pinholes. After the previous layer deposition, a 100 nm transparent film of the iTMC and the ionic liquid 1-ethyl-3-methylimidazolium hexafluoridophosphate (>98.5%, Sigma-Aldrich) in a 1 : 1 molar ratio were spin-coated from CH_2Cl_2 (20 mg/mL). The devices were transferred in an inert atmosphere glovebox (< 0.1ppm O_2 and H_2O, M. Braun). The Al electrode (70 nm) was thermally vapour-deposited using a shadow mask under a vacuum ($<1 \times 10^{-6}$ mbar) with an Edwards Auto500 evaporator integrated in the glovebox. The final device configuration was ITO/PEDOT:PSS/iTMC:IL/Al. The device lifetime was measured by applying a pulsed current (average current density 10 A/m^2, 50% duty cycle, 1 kHz, block wave) or 4V constant voltage and monitoring the voltage, current and luminance versus time by a True Colour Sensor MAZeT (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System. The electroluminescent spectra were measured using an Avantes AvaSpec-2048 Fiber Optic Spectrometer.

Table S1 Comparison of structural parameters of [Cu(POP)(bpy)]$^+$, (Cu(POP)(6-Mebpy)]$^+$ and [Cu(POP)(6,6'-Me$_2$bpy)]$^+$.

Complex cation	d(Cu-N$_A$) / Å	d(Cu–ring plane A) / Å	∡ (I) / deg	d(Cu-N$_B$) / Å	d(Cu-ring plane B) / Å	∡(II) / deg	∡(III) / deg	∡(IV) / deg
[Cu(POP)(bpy)]$^+$ (ref. 4)	2.048(2)	0.02	0.4	2.074(2)	0.21	5.7	4.6	88.5
[Cu(POP)(6-Mebpy)]$^+$	2.047(1)	0.15	4.1	2.116(1) [a]	0.31[a]	8.4	9.1	87.4
[Cu(POP)(6,6'-Me$_2$bpy)]$^+$	2.117(6)	0.69	18.9	2.085(7)	0.05	1.3	19.0	83.7

[a] bpy ring with N$_B$ contains the methyl group in position 6.





I = Angle between Cu-N vector and least square plane through pyridine ring A

II = Angle between Cu-N vector and least square plane through pyridine ring B

III = Torsion angle between rings A and B

IV = Dihedral angle between the planes containing N-Cu-N and P-Cu-P

Table S2 PL data for thin PMMA film and solid-state [Cu(POP)(6-Mebpy)][PF$_6$].

	QY / %	τ_{ave} / µs[a]	τ_1 / µs (A_1)	τ_2 / µs (A_2)
Film	10.7	6.0	2.985 (4796)	7.891 (2931)
Powder	9.5	2.6	1.837 (3019)	4.303 (605)

[a] Biexponential fit using the equation $\tau_{ave} = \Sigma A_i\tau_i / \Sigma A_i$ where A_i is the pre-exponential factor for the lifetime.

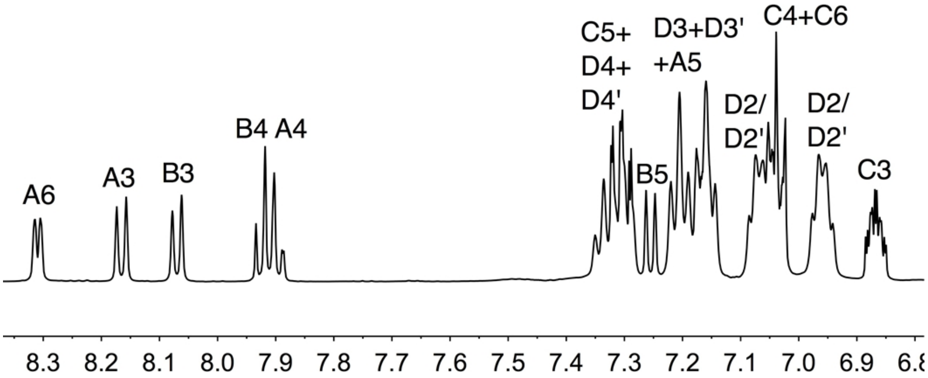


Fig. S1 Aromatic region of the ^{1}H NMR spectrum of a CD_2Cl_2 solution of [Cu(POP)(6-Mebpy)][PF_6]. See Scheme 1 for atom labels.

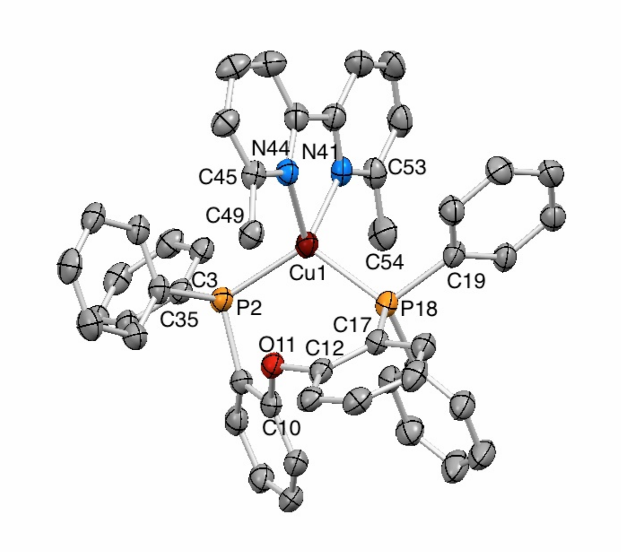


Fig. S2 Structure of the [Cu(POP)(6,6'-Me_2bpy)]$^+$ cation in [Cu(POP)(6,6'-Me_2bpy)][PF_6] with ellipsoids plotted at the 40% probability level; H atoms omitted for clarity. Selected bond parameters: Cu1–P2 = 2.267(2), Cu1–P18 = 2.288(2), Cu1–N41 = 2.085(6), Cu1–N44 = 2.116(6), O11–C10 = 1.393(9), O11–C12 = 1.393(8) Å; P2–Cu1–P18 = 113.36(8), P2–Cu1–N41 = 125.98(17), P18–Cu1–N41 = 109.16(16), P2–Cu1–N44 = 111.51(16), P18–Cu1–N44 = 112.00(17), N41–Cu1–N44 = 80.2(2), C10–O11–C12 = 118.6(5)°.

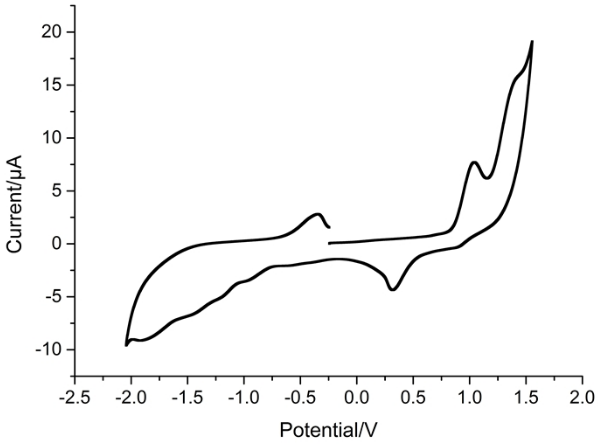


Fig. S3. Cyclic voltammogram of a CH_2Cl_2 solution of [Cu(POP)(6-Mebpy)][PF_6] (vs. Fc^+/Fc, [$^nBu_4N$][PF_6] supporting electrolyte, scan rate = 0.1 V s^{-1}).

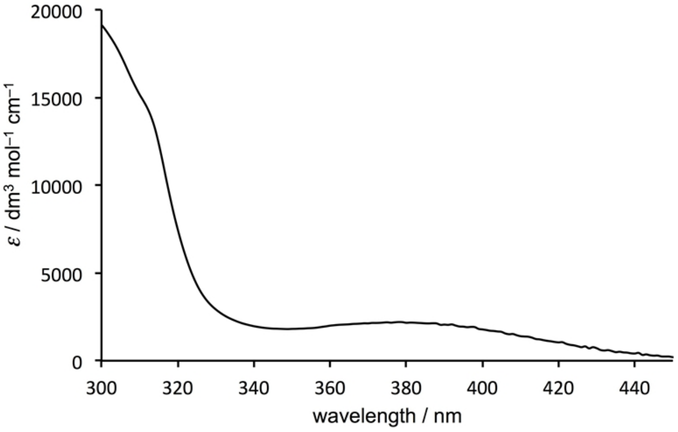


Fig. S4. Absorption spectrum of a CH_2Cl_2 solution of [Cu(POP)(6-Mebpy)][PF_6] (2.5×10^{-5} mol dm^{-3}).

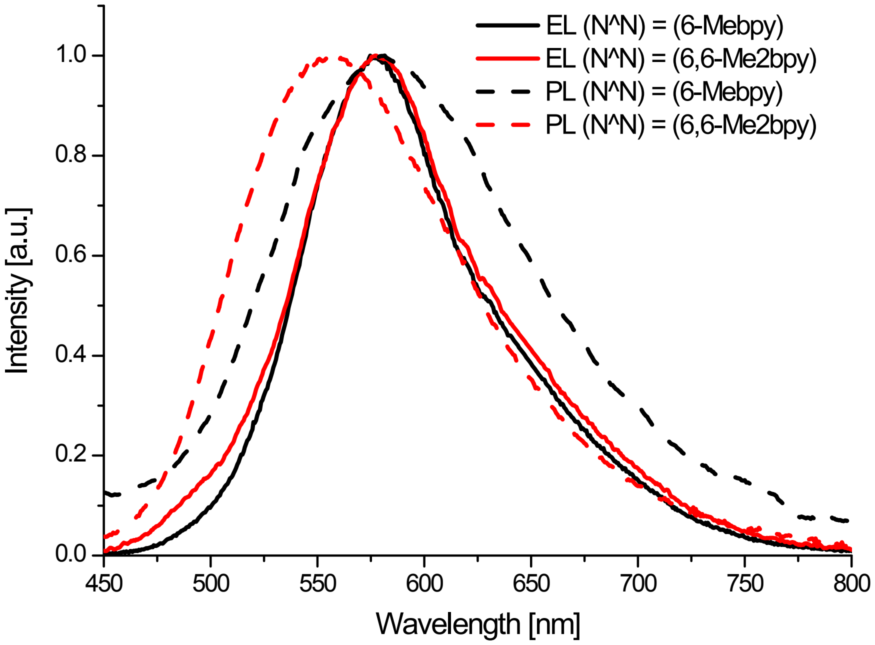


Fig. S5. Normalized EL spectra (solid line) for ITO PEDOT:PSS/iTMC:[Emim][PF_6] 1:1/Al and PL spectra (dashed line) for the complexes [Cu(POP)(6-Mebpy)][PF_6] (black) and [Cu(POP)(6,6'-Me_2bpy)][PF_6] (red). PL spectra were measured on a quartz plate coated with the iTMC:[Emim][PF_6] 1:1 molar ratio.

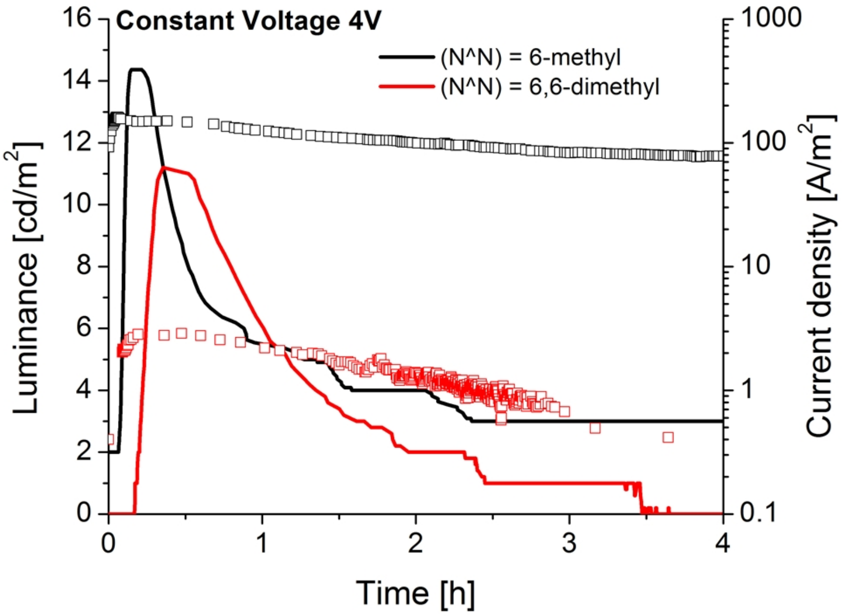


Fig. S6. Luminance (solid line) and current density (open squares) versus time for ITO PEDOT:PSS/iTMC:[Emim][PF_6] 1:1/Al LECs measured at 4V.

References

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