ESI to accompany

# An explanation of chloride impact on materials for light-emitting electrochemical cells

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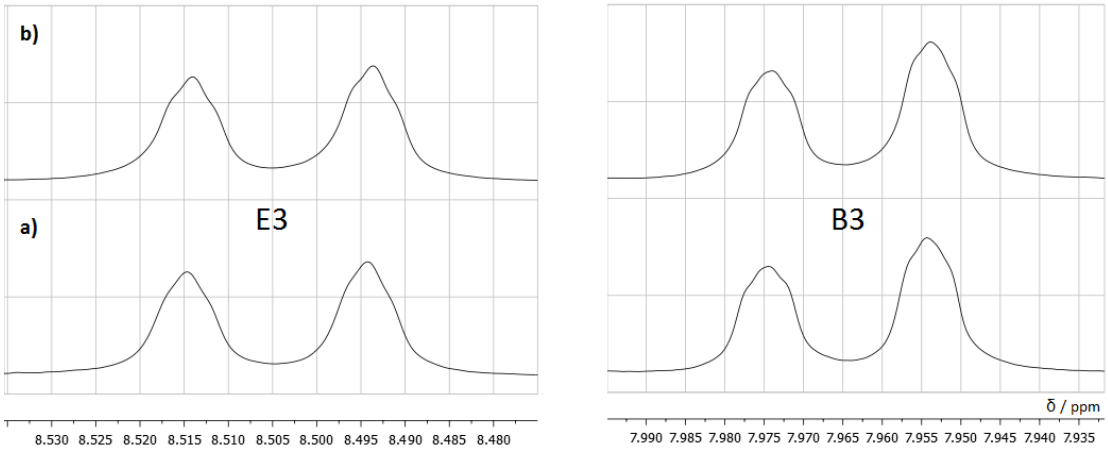



Fig. S1. Signals for protons $H^{E3}$ and $H^{B3}$ (see Scheme 1) in the 500 MHz $^1H$ NMR spectra ($CD_2Cl_2$) of (a) batch 2 and (b) batch 1 of the materials used for the two devices shown in Fig 1.

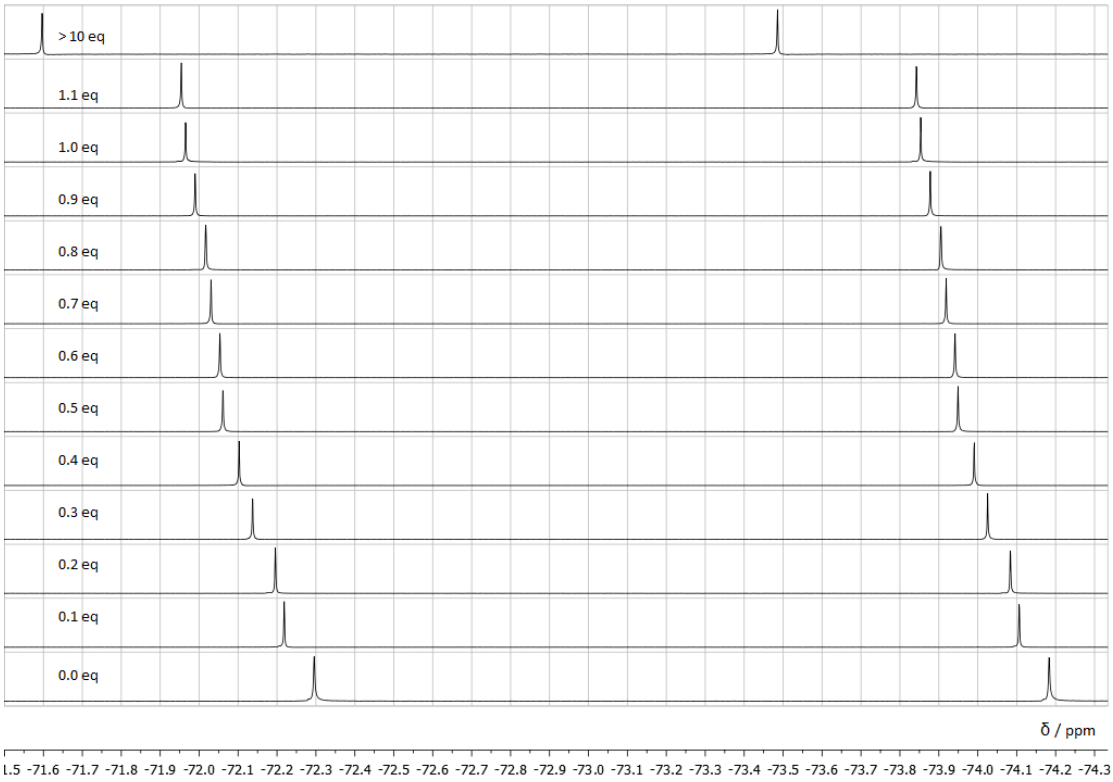


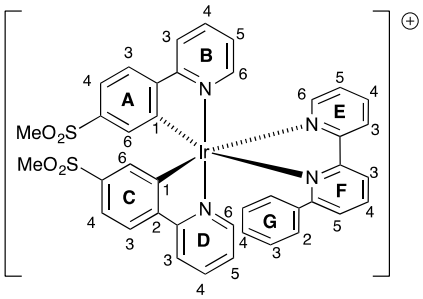

Fig. S2. 376 MHz $^{19}F$ NMR spectra showing the effect of adding 1.1 equivalents of $[^{n}Bu_4N]Cl$ in 0.1 aliquots to a $CD_2Cl_2$ solution of $[Ir(ppy)_2(bpy)][PF_6]$. Each spectrum exhibits one doublet ($J_{PF}$ = 710 Hz).

**Preparation of chloride-free $[Ir(ppy)_2(bpy)][PF_6]$ with reproducible device performance.**

A yellow suspension of $[Ir_2(ppy)_4Cl_2]$ (700 mg, 0.653 mmol) and bpy (205 mg, 1.31 mmol) in MeOH (20 mL) was heated in a microwave reactor (Biotage Initiator 8) for 2 h at 120°C (P = 14 bar). The yellow solution was cooled to room temperature and an excess of solid $NH_4PF_6$ and $AgPF_6$ were added. The mixture was stirred at room temperature for 1 h and the yellow solid that formed was separated by filtration. The volume of the filtrate was reduced and the precipitate that formed was collected by filtration. The two batches of yellow precipitate were combined, washed with MeOH (2 x 10 mL) and $Et_2O$ (3 x 20 mL), and dried under vacuum. The solid was then purified by column chromatography (Fluka Silica 60, $CH_2Cl_2$ changing to $CH_2Cl_2$/MeOH 100 : 3), redissolved in $CH_2Cl_2$ and filtered. The pure product was precipitated by addition of $Et_2O$. After filtration and drying under vacuum, $[Ir(ppy)_2(bpy)][PF_6]$ was isolated as a yellow solid (825 mg, 1.03 mmol, 78.9%). Found: C 47.82, H 3.12, N 7.32; requires C 47.94, H 3.02, N 6.99%.

**$[Ir(msppy)_2(6\text{-Phbpy})][Cl]$**

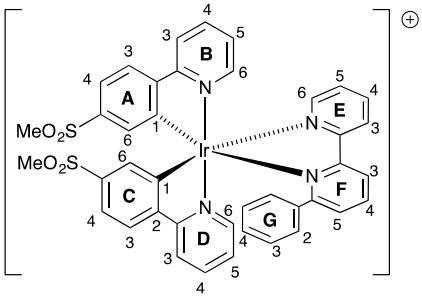
$[Ir(msppy)_2Cl]_2$[1] (Hmsppy = 2-(4-methylsulfonylphenyl)pyridine) (239 mg, 0.173 mmol) and 6-phenyl-2,2'-bipyridine (6-Phbpy) (80.0 mg, 0.344 mmol) were suspended in MeOH (20 mL) and the mixture was heated at 120 °C for 1 h in a microwave reactor (Biotage Initiator 8 reactor). The mixture was filtered through cotton-wool and the filtrate concentrated under reduced pressure. The crude product was purified by column chromatography ($SiO_2$; $CH_2Cl_2$ changing to $CH_2Cl_2$/5 % MeOH changing to $CH_2Cl_2$/10 % MeOH). The solvent from the major fraction was evaporated under reduced pressure and the residue precipitated by addition of toluene to a $CH_2Cl_2$ solution. The precipitate was filtered to yield $[Ir(msppy)_2(6\text{-Phbpy})][Cl]$ as a dark yellow solid (72.3 mg, 0.0782 mmol, 22.7 %).



$^1$H NMR (500 MHz, $CD_3CN$, 295 K) δ / ppm 8.70 (*pseudo*-dt, *J* = 8.3, 1.1 Hz, 1H, $H^{F3}$), 8.66 (d, *J* = 8.2 Hz, 1H, $H^{E3}$), 8.27 (*pseudo*-t, *J* = 7.9 Hz, 1H, $H^{F4}$), 8.19 – 8.03 (m, 4H, $H^{B3+D3+D6+E4}$), 7.98 – 7.91 (m, 2H, $H^{B4+D4}$), 7.83 (ddd, *J* = 5.5, 1.6, 0.7 Hz, 1H, $H^{E6}$), 7.81 (d, *J* = 8.2 Hz, 1H, $H^{A3}$), 7.56 (ddd, *J* = 5.8, 1.5, 0.8 Hz, 1H, $H^{B6}$), 7.51 (dd, *J* = 7.7, 1.2 Hz, 1H, $H^{F5}$), 7.49 (d, *J* = 8.2 Hz, 1H, $H^{C3}$), 7.47 – 7.42 (m, 2H, $H^{A4+E5}$), 7.32 – 7.23 (m, 2H, $H^{B5+D5}$), 7.06 (dd, *J* = 8.2, 1.9 Hz, 1H, $H^{C4}$), 6.92 (*pseudo*-tt, *J* = 7.5, 1.3 Hz, 1H, $H^{G4}$), 6.76 (br s, 4H, $H^{G2+G3}$), 6.32 (d, *J* = 1.9 Hz, 1H, $H^{A6}$), 6.00 (d, *J* = 1.9 Hz, 1H, $H^{C6}$), 2.80 (s, 6H, $H^{Me}$). $^{13}$C{$^1$H} NMR (126 MHz, $CD_3CN$, 295 K): *δ* / ppm 167.3 ($C^{D2}$), 166.2 ($C^{F6}$), 165.6 ($C^{B2}$), 157.8 ($C^{E2}$), 157.7 ($C^{F2}$), 152.2 ($C^{C1}$), 151.5 ($C^{E6}$), 151.4 ($C^{D4}$), 151.2 ($C^{B6}$), 149.4 ($C^{A2}$), 149.3 ($C^{C2}$), 148.0 ($C^{A1}$), 142.2 ($C^{A5}$), 140.9 ($C^{F4}$), 140.7 ($C^{E4}$), 140.31 ($C^{C5}$), 140.30 ($C^{B4}$), 140.2 ($C^{D6}$), 139.1 ($C^{G1}$), 131.1 ($C^{F5}$), 130.0 ($C^{G4}$), 129.2 ($C^{C6}$), 129.1 ($C^{E5}$), 128.9 ($C^{G3}$), 128.5 ($C^{G2}$), 128.2 ($C^{A6}$), 126.5 ($C^{B5}$), 126.4 ($C^{E3}$), 125.9 ($C^{A3}$), 125.7 ($C^{C3}$), 125.4 ($C^{D5}$), 125.0 ($C^{F3}$), 122.74 ($C^{A4}$), 122.71 ($C^{D3}$), 122.5 ($C^{B3}$), 120.6 ($C^{C4}$), 44.22 ($C^{Me}$), 44.16 ($C^{Me}$). ESI-MS: *m/z* 889.5 [*M* – Cl]$^+$ (calc. 889.2). Found: C 49.85, H 3.98, N 6.00; $C_{40}H_{32}ClIrN_4O_4S_2 \cdot 2H_2O$ requires C 50.02, H 3.78, N 5.83%.

## Conversion of [Ir(msppy)$_2$(6-Phbpy)][Cl] to [Ir(msppy)$_2$(6-Phbpy)][PF$_6$]

[Ir(msppy)$_2$(6-Phbpy)][Cl] was dissolved in little MeOH, an excess of solid $NH_4PF_6$ was added and the resulting suspension was stirred for 1.5 h at room temperature. The yellow precipitate was separated by filtration, washed with $H_2O$ and MeOH and redissolved in $CH_2Cl_2$. The solution was dried over $Na_2SO_4$ and the solvent was removed under reduced pressure. The residue was recrystallised from MeOH to yield the hexafluoridophosphate complex as a bright yellow solid. Addition of $Bu_4NPF_6$ to a $CD_3CN$ solution of the complex resulted in no shift of the signals arising from protons $H^{E3}$ and $H^{F3}$ confirming the lack of chloride impurity.




$^1$H NMR (500 MHz, $CD_3CN$, 295 K): *δ* = 8.59 (dd, *J* = 8.1, 1.2 Hz, 1H, $H^{F3}$), 8.56 (*pseudo*-dt, *J* = 8.4, 1.0 Hz, 1H, $H^{E3}$), 8.26 (*pseudo*-t, *J* = 7.9 Hz, 1H, $H^{F4}$), 8.18 – 8.04 (m, 4H, $H^{B3+D3+D6+E4}$), 7.98 – 7.92 (m, 2H, $H^{B4+D4}$), 7.83 (ddd, *J* = 5.6, 1.5, 0.7 Hz, 1H, $H^{E6}$), 7.79 (d, *J* = 8.2 Hz, 1H, $H^{A3}$), 7.56 (*pseudo*-dt, *J* = 5.5, 1.0 Hz, 1H, $H^{B6}$), 7.51 (dd, *J* = 7.7, 1.2 Hz, 1H, $H^{F5}$), 7.49 (d, *J* = 8.2 Hz, 1H, $H^{C3}$), 7.47 – 7.42 (m, 2H, $H^{A4+E5}$), 7.32 – 7.23 (m, 2H, $H^{B5+D5}$),

7.06 (dd, $J$ = 8.2, 1.9 Hz, 1H, $H^{C4}$), 6.93 (*pseudo*-tt, $J$ = 7.5, 1.3 Hz, 1H, $H^{G4}$), 6.76 (br s, 4H, $H^{G2+G3}$), 6.32 (d, $J$ = 1.9 Hz, 1H, $H^{A6}$), 6.00 (d, $J$ = 1.8 Hz, 1H, $H^{C6}$), 2.80 (s, 3H, $H^{C5SO2CH3}$), 2.79 (s, 3H, $H^{A5SO2CH3}$). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_3CN$, 295 K): $\delta$ = 167.3 ($C^{D2}$), 166.3 ($C^{F6}$), 165.6 ($C^{B2}$), 157.74 ($C^{E2}$), 157.68 ($C^{F2}$), 152.2 ($C^{C1}$), 151.6 ($C^{E6}$), 151.4 ($C^{D4}$), 151.1 ($C^{B6}$), 149.4 ($C^{A2}$), 149.3 ($C^{C2}$), 147.9 ($C^{A1}$), 142.3 ($C^{A5}$), 140.8 ($C^{F4}$), 140.6 ($C^{E4}$), 140.33 ($C^{C5}$), 140.30 ($C^{B4}$), 140.2 ($C^{D6}$), 139.1 ($C^{G1}$), 131.1 ($C^{F5}$), 130.0 ($C^{G4}$), 129.2 ($C^{C6}$), 129.1 ($C^{E5}$), 128.9 ($C^{G3}$), 128.5 ($C^{G2}$), 128.2 ($C^{A6}$), 126.5 ($C^{B5}$), 126.2 ($C^{E3}$), 125.9 ($C^{A3}$), 125.7 ($C^{C3}$), 125.4 ($C^{D5}$), 124.8 ($C^{F3}$), 122.8 ($C^{A4}$), 122.7 ($C^{D3}$), 122.4 ($C^{B3}$), 120.6 ($C^{C4}$), 44.22 ($C^{Me}$), 44.15 ($C^{Me}$). ESI-MS $m/z$ 889.2 $[M - PF_6]^+$ (calc. 889.2). Found C 45.61, H 3.36, N 5.37; $C_{40}H_{32}F_6IrN_4O_4PS_2 \cdot H_2O$ requires C 45.67, H 3.26, N 5.33%.

## Crystallographic data

**2{[Ir(ppy)$_2$(bpy)][Cl]}·2CH$_2$Cl$_2$·[H$_3$O]·[Cl]**: $C_{66}H_{55}Cl_7Ir_2N_8O$, $M$ = 1608.78, yellow plate, monoclinic, space group $C2/c$, $a$ = 37.3549(8), $b$ = 9.4126(2), $c$ = 18.9672(5) Å, $\beta$ = 113.3400(10)°, $U$ = 6123.3(2) Å$^3$, $Z$ = 4, $D_c$ = 1.742 Mg m$^{-3}$, $\mu$(Cu-K$\alpha$) = 11.506 mm$^{-1}$, $T$ = 123 K. Total 17336 reflections, 5280 unique, $R_{int}$ = 0.0351. Refinement of 4703 reflections (388 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0263 ($R1$ all data = 0.0303), $wR2$ = 0.0646 ($wR2$ all data = 0.0676), gof = 1.026. CCDC 959828.

**[Ir(msppy)$_2$(6-Phbpy)][Cl]**: $C_{40}H_{32}ClIrN_4O_4S_2$, $M$ = 924.51, yellow block, monoclinic, space group $P2_1/n$, $a$ = 10.9510(5), $b$ = 19.9122(10), $c$ = 16.3883(8) Å, $\beta$ = 97.298(2)°, $U$ = 3544.7(3) Å$^3$, $Z$ = 4, $D_c$ = 1.732 Mg m$^{-3}$, $\mu$(Cu-K$\alpha$) = 9.491 mm$^{-1}$, $T$ = 123 K. Total 45537 reflections, 6367 unique, $R_{int}$ = 0.0546. Refinement of 5634 reflections (471 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0290 ($R1$ all data = 0.0356), $wR2$ = 0.0679 ($wR2$ all data = 0.0706), gof = 1.107. CCDC 971737.

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[1] E. C. Constable, C. D. Ertl, C. E. Housecroft and J. A. Zampese, 2013, to be submitted.