Supplementary Information for:

Covalent POM-Ir hybrid assemblies: tuning redox properties for light-driven multiple charge accumulation

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1. General Methods

High Resolution Mass Spectrometry. mass spectra were recorded using an LTQ Orbitrap hybrid mass spectrometer (Thermofisher Scientific, Bremen, Germany) equipped with an external ESI source operated in the negative ion mode. Sample solutions in acetonitrile (10 pmol. μ L⁻¹) were infused into the ESI source by using a syringe pump at a flow rate of 180 μ L.h⁻¹. Spray conditions included a spray voltage of 3.5 kV, a capillary temperature maintained at 270 °C, a capillary voltage of -40 V, and a tube lens offset of -100 V. Mass spectra were acquired in the Orbitrap analyzer with a theoretical mass resolving power (R_p) of 100 000 at m/z 400, after ion accumulation to a target value of 10⁵ and a m/z range detection from m/z 300 to 2000. All data were acquired using external calibration with a mixture of caffeine, MRFA peptide and Ultramark 1600 dissolved in Milli-Q water/HPLC grade acetonitrile (50/50, v/v).

Electrochemistry. Electrochemical data were recorded with an Autolab PGSTAT 100 work station (Metrohm) or a CH660 potentiostat (CH Instruments). Measurements were carried out at 1mM in an argon-purged N-dimethylformamide (DMF) solution containing 0.1 M n-Bu₄NPF₆ as supporting electrolyte, using a three-electrode cell combining a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE).

Spectroelectrochemical measurements were carried out using a custom electrolysis cell in which a Hellma 661.202-UV all-quartz immersion UV-visible probe (1 cm optical path length) is dipped into the electrolytic solution. A mercury pool (\sim 5 cm²) was used as the working electrode and a SCE was used as the reference electrode. A vitrous carbon counter electrode was placed in a separate compartment connected by a glass-frit and filled with the supporting electrolyte. The supporting electrolyte was a 0.1 mol.L–1 solution of TBAPF₆ in DMF.

Steady-state spectroscopy. UV-vis absorption spectra were recorded either on a UV-visible spectra were recorded on a Jasco V-670 or an Agilent Technologies Cary 60 UV-Vis spectrometer. Emission spectra were recorded using a FLS980 fluorescence spectrometer from Edinburgh Instruments Ltd. or an Perkin-Elmer LS-50B. All solvents used for spectroscopy were of spectroscopic grade.

Emission lifetime measurements. The emission lifetimes were recorded on a custom build flash photolysis setup in emission mode. To pump the excited state a 10 Hz Nd: YAG laser (Continuum Surelite) with a 5 ns pulse width was used. The fundamental (1064 nm) passes a second-harmonic generation step (532 nm) followed by a third-harmonic generation to gain the frequency-tripled wavelength (355 nm). The beam is transmitted to an optical parametric oscillator (Continuum Surelite) generating tunable wavelengths from 400 nm to 650 nm with energies ranging from 0.15 mJ to 0.80 mJ. If not stated otherwise an excitation wavelength of 410 nm and 0.2 mJ pulse energy

was used. The emitted light is spectrally dispersed (Acton Princeton Instrument 2300), detected by a photomultiplier tube (Hamamatsu R928).

Photolysis experiments. Photolysis experiments were performed in a 1 cm quartz cuvette adapted for measurements under inert conditions. DMF solutions containing triethylamine (TEA, 1 M) as sacrificial electron donor and either Im-K^W_{Sn}[Ir] (0.15 mM) or Im-K^{Mo}_{Sn}[Ir] (0.15 mM) were degazed through a typical freeze-pump-thaw procedure (4 x 20 min) in the cuvette under dark conditions (aluminum foil protection). When needed, 500 equiv. of degazed trifluoroacetic acid (TFA) were added before irradiation of the sample with a Newport 300W ozone-free Xenon lamp (operated at 280W) equipped with a water-filled Spectra-Physics 6123NS liquid filter to eliminate infrared radiation ($\lambda > 800$ nm) and a 400 nm long-pass filter (Spectra-Physics 59472). The photochemical reaction was monitored by UV-vis absorption spectroscopy.

2. Synthesis.

All reagents were obtained from commercially available sources and used as received. Solvents were dried from appropriate drying agents and freshly distilled under argon before use. The complex [Ir(ppy)₂((ethynylphenyl)-imidazo-1,10-phenanthroline)](PF₆) (**Ir-EPIP**)¹ and the polyoxotungstate and polyoxomolybdate-based hybrids bearing the iodoaryl moieties, respectively noted **TBA-K**^W**s**_n[**I**]² and **TBA-K**^{Mo}**s**_n[**I**],³ were prepared according to previously-reported procedures. The ¹H (300.3 MHz), {1H} ³¹P (121.5 MHz) NMR spectra were obtained at 300K in 5 mm o.d. tubes on a Bruker AvanceII 300 spectrometer equipped with a QNP probehead. Elemental analyses were performed at the Institut de Chimie des Substances Naturelles, Gif sur Yvette, France.

Synthesis of Im-K^W_{Sn}[Ir]. A mixture of TBA-K_{Sn}^W[I] (100 mg, 25.2 µmol), [Ir] (42.5 mg, 44.1 µmol, 1.75 eq.), CuI (0.40 mg, 2.0 µmol) and [PdCl₂(PPh₃)₂] (1.6 mg, 2.3 µmol) was prepared in a Schlenk tube under Ar atmosphere. 4 mL of pure and fresh DMF were added, under Ar atmosphere. After careful degassing with argon for 15 minutes, 100 mg (0.99 mmol, 39 equiv.) of freshly distilled TEA were added, and the solution changed its colour, from orange to red. The mixture was stirred at 80°C for 1h, under microwawe irradiation. After cooling at room temperature, the obtained solution was precipitated with diethyl ether, and the precipitate filtered. The obtained solid wash washed with ethanol, to remove the excess of Ir complex. The solid was filtered and dissolved in the minimal amount of DMSO. 1-butyl-3-methylimidazolium chloride (ionic liquid) was added, to exchange the counter-ion, and ethanol was added to allow the precipitation of the product. The recovered solid was dissolved again in the minimal quantity of DMSO and a double volume of acetonitrile was added to allow the impurities to precipitate. The supernatant was collected, precipitated with diethyl ether to isolate Im-K^Wsn[Ir] as a bright yellow solid. Yield: 72 mg, 65%. ¹H NMR (DMSO-d₆): δ 9.21 (d, J = 7.7 Hz, 2H), 9.08 (s, 3H), 8.37 (d, J = 8.2 Hz, 2H), 8.26 (d, J = 8.2 Hz, 2H), 8.15 (d, J = 4.4 Hz, 2H), 8.12 – 8.01 (m, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.88 (m, 2H), 7.75 (s, 3H), 7.71 (m, 4H), 7.69 (s, 3H), 7.53 (d, J = 5.6 Hz, 2H), 7.13 – 6.90 (m, 6H), 6.30 (d, J = 7.4 Hz, 2H), 4.17 (t, J = 7.3 Hz, 6H), 3.85 (s, 9H), 1.77 (q, J = 7.4 Hz, 6H), 1.26 (sex, J = 7.4 Hz, 6H), 0.90 (t, J = 7.3 Hz, 9H). ³¹P NMR $(DMSO-d_6): \delta -10.90 (s + d, J_{SnP} = 24.4 \text{ Hz})$. IR (KBr, cm⁻¹): v = 3143 (w), 3110 (w), 3072 (w), 2957 (w), 2926 (w), 2870 (w), 1607 (w), 1582(w), 1564 (w), 1478 (m), 1456 (w), 1439 (w), 1420 (w) 1165 (m), 1067 (s), 965 (s), 888 (s), 805 (vs), 516 (s), 381 (s). MS (ESI): most abundant ion m/z PW11SnO39C49H31N6Ir [POM]³⁻ EA: 1230.43; calcd 1230.45. Calcd for C₇₃H₇₆IrN₁₂O₃₉PSnW₁₁.DMSO.HCl_{0.5} (%): C, 21.42; H, 1.98; N, 4.00; Found: C 21.77; H 1.96; N 3.67.

Synthesis of Im-K^{Mo}Sn[*Ir*]. A mixture of **TBA-K**_{Sn}^{Mo}[**I**] (100 mg, 33.3 µmol), [**Ir**] (56.3 mg, 58.3 µmol), 1.75 eq.), CuI (0.5 mg, 2.8 µmol) and [PdCl₂(PPh₃)₂] (2.2 mg, 3.0 µmol) was prepared in a

Schlenk tube under Ar atmosphere. 4 mL of pure and fresh DMF were added, under Ar atmosphere. After careful degassing with argon for 15 minutes, 100 mg (0.99 mmol, 30 equiv.) of freshly distilled TEA were added, and the solution changed its colour, from orange to red. The mixture was stirred at 80°C for 1h, under microwawe irradiation. After cooling at room temperature, the obtained solution was precipitated with diethyl ether, and the precipitate filtered. The solid was filtered and dissolved in the minimal amount of DMSO. 1-butyl-3-methylimidazolium chloride (ionic liquid) was added, to exchange the counter-ion, and ethanol was added to allow the precipitation of the product. The recovered solid was dissolved again in the minimal quantity of DMSO and a double volume of acetonitrile was added to allow the impurities to precipitate. The supernatant was collected, precipitated with diethyl ether to isolate Im-K^{Mo}sn[Ir] as a yellow solid. Yield: 58 mg, 55%. ¹H NMR $(DMSO-d_6)$: δ 9.21 (d, J = 7.6 Hz, 2H), 9.10 (s br., 3H), 8.37 (d, J = 7.2 Hz, 2H), 8.26 (d, J = 8.2 Hz, 2H), 8.26 (d, J = 8.2 Hz, 2H) 2H), 8.15 (d, J = 4.5 Hz, 2H), 8.12 – 8.01 (m, 2H), 7.96 (d, J = 7.9 Hz, 2H), 7.88 (m, 2H), 7.77 (s br., 3H), 7.70 (s. br., 3H), 7.64 (s, 4H), 7.52 (d, J = 5.6 Hz, 2H), 7.13 – 6.90 (m, 6H), 6.30 (d, J = 7.4 Hz, 2H), 4.18 (s, 6H), 3.87 (s, 9H), 1.75 (s, 6H), 1.25 (s, 6H), 0.90 (t, J = 6.7 Hz, 9H). ³¹P NMR (DMSO d_6): δ -2.93 (s + d, J_{SnP} = 35.0 Hz). IR (KBr, cm⁻¹): v = 3140 (w), 3106 (w), 3072 (w), 2958 (w), 2930 (w), 2871 (w), 1606 (w), 1582 (w), 1564 (w), 1478 (m), 1456 (w), 1439 (w), 1413 (w) 1166 (m), 1060 (s), 1036 (s), 947 (vs), 868 (s), 802 (vs), 788 (vs), 621 (w), 385 (s). MS (ESI⁻): most abundant PMo₁₁SnO₃₉C₄₉H₃₁N₆Ir [POM]³⁻ 908.29; ion m/z calcd 908.29. EA: Calcd for C₇₃H₇₆IrN₁₂O₃₉PSnW₁₁.DMSO.HCl_{0.8} (%): C, 27.72; H, 2.57; N, 5.17; Found: C 27.52; H 2.62; N 4.94.



Figure S1. ¹H NMR (300 MHz) and ³¹P NMR (121.5 MHz inset) spectra of **Im-K^Wsn[Ir]** (top) and **Im-K^{Mo}sn[Ir]** (bottom) recorded in DMSO-*d*₆.



Figure S2. Comparison of experimental (upper trace) and calculated (lower trace) isotopic peaks for the most abundant ion i.e. $[\mathbf{K}^{\mathbf{W}}\mathbf{sn}[\mathbf{Ir}]]^{3-}$ (top) or $[\mathbf{K}^{\mathbf{Mo}}\mathbf{sn}[\mathbf{Ir}]]^{3-}$ (bottom).

3. UV-vis absorption spectroscopy



Figure S3. Absorption spectra recorded for **Ir-EPIP** (a) and the hybrids **Im-K**_{Sn}^W[**Ir**] (b) and **Im-K**_{Sn}^{Mo}[**Ir**] (c) in DMF solutions (black) and following the addition of trifluoroacetic acid (red) or triethylamine (blue).

The absorption spectra of **Im-Ks**ⁿ^W[**Ir**] and **Im-Ks**ⁿ^{Mo}[**Ir**] are dominated by the chromophore unit in the visible range, since the POM itself only absorbs in the UV range. The absorption features of **Ir-EPIP** in the 350-550 nm region are attributed to singlet–singlet and formally spin forbidden singlet– triplet metal to ligand transitions. For both hybrids, these bands are affected by (i) the addition of acid (TFA), (ii) the addition of base (triethylamine), which underlines that the protonation state of the imidazole unit considerably influences the electronic properties of the complex. Actually, the absorption spectra of the as-synthesized hybrids lie in between the absorption features recorded in the presence of an excess of acid or base, while several isosbestic points are observed. This indicates that the imidazole of the chromophore unit is partially protonated in both hybrids at the end of the synthesis; from the absorbance at 400 nm, we estimate that the protonation of the polyoxotungstate hybrid **Im-Ks**ⁿ^W[**Ir**] is *ca.* 50 % while it is 80 % for the polyoxomolybdate analogue **Im-Ks**ⁿ^{Mo}[**Ir**].

4. Cyclic voltammetry



Figure S4. Cyclic voltammograms of 1 mM solutions of **Ir-EPIP** in DMF containing 0.1 M TBAPF₆ as synthesized (black) and upon the addition of 1 equiv. TFA (red). Scan rate: 100 mV.s⁻¹.



Figure S5. Cyclic voltammograms of 1 mM solutions of $Im-K^{W}sn[Ir]$ (a) $Im-K^{Mo}sn[Ir]$ (b) in DMF containing 0.1 M TBAPF₆ as synthesized (black), upon the addition of TBAOH (0.5 equiv. for $Im-K^{W}sn[Ir]$ and 0.8 equiv. for $Im-K^{Mo}sn[Ir]$; blue). Scan rate: $Im-K^{Mo}sn[Ir]$, 100 mV.s⁻¹; $Im-K^{W}sn[Ir]$: 20 mV.s⁻¹. The appearance of the irreversible wave at *ca*. 0.9 V vs SCE labelled * is attributed to the presence of methanol that is added with TBAOH.

	PS ⁺ /PS (irr)	$PS/PS^{-}(\Delta E)^{-}$	POM/POM+ne	POM+ne/POM+	POM+2ne/POM
			(ΔE), n	2ne (ΔE), n	$+3$ ne (ΔE), n
Ir-EPIP	+1.32	-1.55 (75)			
+ 1 equiv. TFA	+1.31	-1.28 (70)			
Im-K _{Sn} ^W [Ir]	+1.27	-1.26 /-1.55 (nc)	-1.05 (80), 1	-1.40 (nc) , 1	
+ 0.5 equiv. TBAOH	+1.25	-1.55 (90)	-1.08 (80), 1	-1.42 (nc), 1	
+10 equiv. TFA	nc	nc	-0.74 (nc), 2	-0.92 (150), 2	
+50 equiv. TFA	nc	nc	-0.65 (50), 2	-0.81 (60), 2	
+250 equiv. TFA	+1.24	nc	-0.62 (50), 2	-0.78 (60), 2	
Im-Ksn ^{Mo} [Ir]	+1.29	-1.28 / -1.56 (nc)	-0.51 (130), 1	nc	nc
+ 0.8 equiv. TBAOH	+1.29	-1.55	-0.52 (170), 1	-0.86 (nc), 1	-1.3 (80), 1
+10 equiv. TFA	nc	nc	+0.04 (140), 1	-0.09 (110), 1	-0.32 (80), 1
+50 equiv. TFA	nc	nc	+0.10 (100), 1	+0.00 (70), 1	-0.24 (80), 1
+250 equiv. TFA	+1.32	nc	+0.15 (90), 1	+0.06 (80), 1	-0.18 (80), 1

Table S1. Half-wave potential (V *vs.* SCE) and peak-to-peak separation (mV) of the redox processes for the reported hybrids and reference compound (nc = non-calculable).



Figure S6. Evolution of the cyclic voltammogram of a 1 mM solution of $K^{Mo}s_n[I]$ in DMF containing 0.1 M TBAPF₆ and 1 M TEA (black) upon the addition of 20, 50 and 100 equivalents TFA (red curves). Scan rate: 20 mV.s⁻¹.

We evaluated the effect of the presence of triethylamine (used as sacrificial electron donor in the photolysis experiments) on the reduction potential of the reference hybrid parent, its electrochemical behaviour being very similar whether TEA was present or not in the solution.

5. Emission spectroscopy



Figure S7. Steady-state emission (plain, $\lambda_{exc} = 410 \text{ nm}$) and excitation (dotted, $\lambda_{em} = 590 \text{ nm}$) spectra of deaerated solutions of **Ir-EPIP** before (black) and after the addition of 10 equiv. of TFA (red).

Of note, the excitation spectrum of **Ir-EPIP** recorded in the presence of 10 equiv. of TFA mostly matches the initial one; this suggests that the nature of the excited state responsible for the luminescence is similar for the protonated and unprotonated species, this state being more easily populated in the presence of TFA.

Table S2. Luminescence lifetime τ , rate constant k_{CS} ($k_{CS} = (1/\tau) - (1/\tau_0)$ with τ_0 the lifetime of **Ir-EPIP**), estimated driving force (ΔG_{CS}) and charge injection efficiency for **Im-K^{Mo}sn[Ir]** in deaerated DMF solution at room temperature upon the addition of TFA.

	τ / ns	k_{CS} / s^{-1}	$\Delta G_{CS}^{a}/ eV$	Charge injection efficiency / %
Ir-EPIP	560	/	/	/
+ 10 equiv. TFA	560	/	/	/
Im-K ^W Sn[Ir]	560	/	+0.2	/
+ 50 equiv. TFA		/	-0.2	/
Im-K _{Sn} ^{Mo} [Ir]	60	1.50×10^{7}	-0.3	89
+ 10 equiv. TFA	48	1.91×10 ⁷	-0.9	91
+ 25 equiv. TFA	44	2.10×10 ⁷	/	92
+100 equiv. TFA	35	2.66×10 ⁷	/	94
+250 equiv. TFA	26	3.71×10 ⁷	/	95

a. $\Delta G_{CS} \sim E_{ox}^* - E_{red} = (E_{ox} - E^{00}) - E_{red}$; with $E^{00} \sim 2.1$ eV for the **Ir-EPIP** center, $E_{ox} = +1.25$ and $E_{red} = -1.08$ V vs SCE for **Im-K^Wsn[Ir]** in the absence of TFA, $E_{ox} = +1.29$ and $E_{red} = -0.52$ V vs SCE for **Im-K^{Mo}sn[Ir]** in the absence of TFA, $E_{ox} = +1.25$ and $E_{red} = -0.65$ V vs SCE for **Im-K^Wsn[Ir]** in the presence of 50 equiv. TFA, $E_{ox} = +1.29$ and $E_{red} = +0.04$ V vs SCE for **Im-K^{Mo}sn[Ir]** in the presence of 10 equiv. TFA.

6. Spectroelectrochemistry



Figure S8. Spectroelectrochemical reduction of $K^{Mo}sn[I]$ (black) in DMF containing 0.1 M TBAPF₆ upon reduction at -0.9V vs SCE (the artefact around 900 nm is due to the change in the grating).



Figure S9. Spectroelectrochemical reduction of $K^{Mo}s_n[I]$ in the presence of a large excess of TFA in DMF containing 0.1 M TBAPF₆ upon reduction at -0.1V (blue), -0.35 V (red) and -0.50 V (black) vs SCE.

The signature of the 3-electron reduced species (black) was rather tedious to obtain. Indeed, a decrease of the absorbance above 700 nm was quickly observed when the electrolysis was performed at potential below that of the 3e⁻-reduced species, while reduced forms of POMs tends to absorb more in the visible-NIR region along their reduction. This phenomenon that we also observe for other POMs is possibly due to the slow diffusion of the oxidized species formed at the counter electrode with our electrolysis setup.

7. Photolysis.



Figure S10. *Top*: Evolution of the visible absorption spectrum of a solution of $Im-K^{W}sn[Ir]$ (0.20 mM) in DMF containing TEA (1 M) under continuous visible light irradiation in the presence of 500 equiv. TFA (*inset*: differential absorption spectra). *Bottom*: Comparison of the visible absorption spectra of solutions of $Im-K^{W}sn[Ir]$ (0.20 mM; red line) and $Im-K^{Mo}sn[Ir]$ (0.20 mM; black line) in DMF containing TEA (1 M) after 30 min of continuous visible light irradiation in the presence of 500 eq. TFA (100 mM).

8. References.

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