Multiple electrochemically accessible colour states in surface-confined metal-organic monolayers: Stepwise embedding individual metal centres

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Electronic Supplementary Information

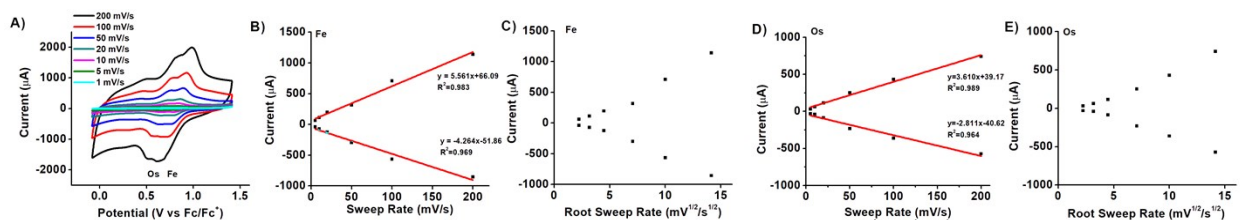**The results of selected electrochemical measurements.**

Figure S1. CV of Os-Fe stepwise ECM **A)** varying scan rates, **B)** peak current versus scan rate at Fe $E_{1/2}$, **C)** peak current versus root of scan rate at Fe $E_{1/2}$, **D)** peak current versus scan rate at Os $E_{1/2}$, **E)** peak current versus root of scan rate at Os $E_{1/2}$.
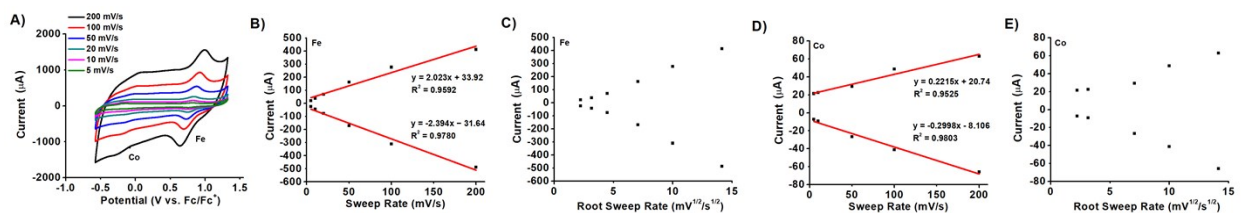

Figure S2. CV of Co-Fe stepwise ECM **A)** varying scan rates, **B)** peak current versus scan rate at Fe $E_{1/2}$, **C)** peak current versus root of the scan rate at Fe $E_{1/2}$, **D)** peak current versus scan rate at Co $E_{1/2}$, and **E)** peak current versus root of the scan rate at Co $E_{1/2}$.
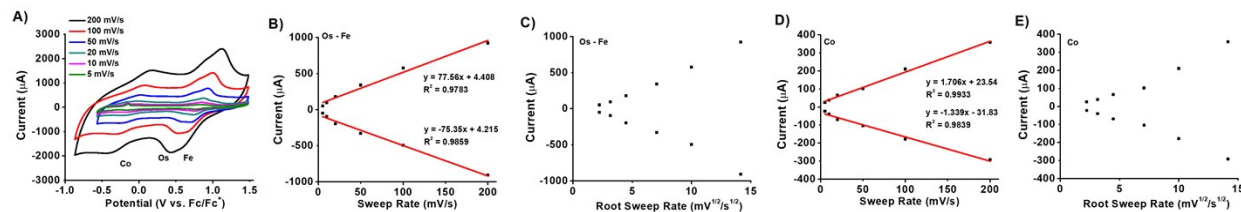
Figure S3. CV of Co-Os-Fe stepwise ECM **A)** varying sweep rates, **B)** peak current versus sweep rate at Os-Fe $E_{1/2}$, **c)** peak current versus root of the sweep rate at Fe+Os $E_{1/2}$, **c)** peak current versus sweep rate at Co $E_{1/2}$, and **d)** peak current versus root of the sweep rate at Co $E_{1/2}$.
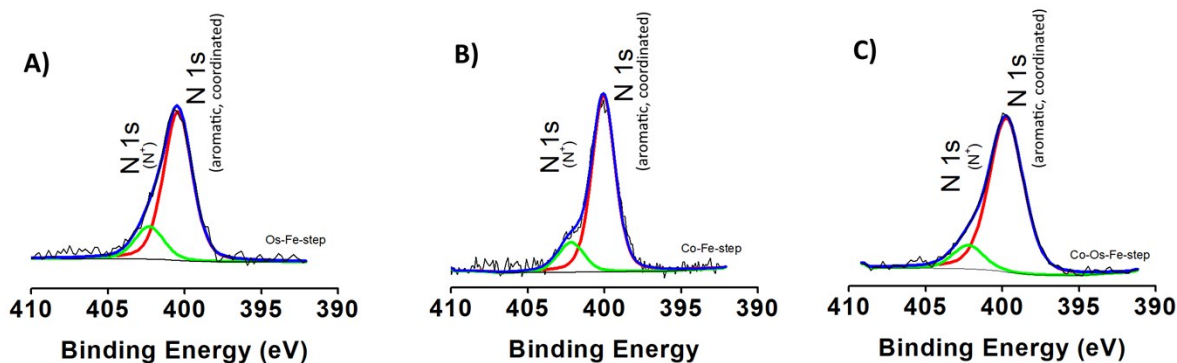
The results of selected XPS measurements

Figure S4. X-ray photoelectron spectroscopy (XPS) spectra showing the N 1s regions for A) Os-Fe, B) Co-Fe, and C) Co-Os-Fe ECMs

Laviron Kinetics of ECM

CVs at fast scan rates were plotted versus the log of the peak potential (Figure S4-S6) and their slopes determined to give the electron transfer coefficient α:

$$\alpha = \frac{s_a}{(s_a - s_c)}$$

The electron transport constants (k_{ET}) of materials were calculated form the following formula:

$$k_{ET} = \frac{\alpha n F v_c}{RT} = \frac{(1 - \alpha)F v_a}{RT}$$

where v_a and v_c are the scan rates where the slope intersects the x-axis and the anodic or cathodic branches, respectively. A symmetry exhibited in the Laviron (aka trumpet) plots (Figure S5-S7) is a consequence of transfer coefficient values being close to 0.5.
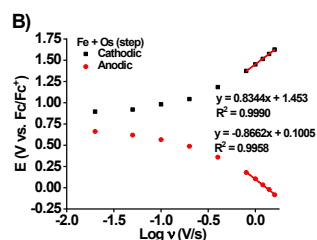

Figure S5: Laviron plot for Os-Fe stepwise ECMs. At high scan rates, it was impossible to distinguish between the Os and Fe peaks. The constant determined evaluates joint electron rate for Os and Fe species.
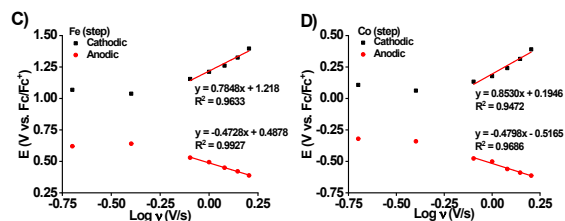
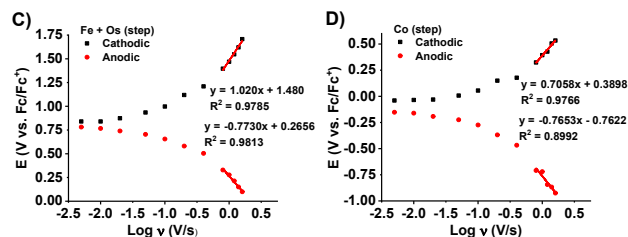**Figure S6:** Laviron plot for Co-Fe stepwise ECMs: **c)** Fe and **d)** Co.

Figure S7: Laviron plot for Fe + Os + Co stepwise ECM at **c)** Fe and Os, and **d)** Co.

Table S1. Electron transfer-rate constants of ECM obtained from cyclic voltammetry.

Metal System	k_{ET} (s^{-1})		
Sequential Deposition	Fe	Os	Co
Os-Fe	3.3 ± 0.3		
Co-Fe	4.6 ± 0.5		5.3 ± 0.8
Fe + Os + Co	5.1 ± 1.1		3.0 ± 0.8

Table S2. Diffusion coefficient and internal resistance magnitude for the ECMs. $E_{1/2(M)}$ represents the electrochemical potential of the metal in which the constant was determined at.

ECM	D (cm^2 s^{-1})			R_Σ ($\Omega*$cm^2)			R_S ($\Omega*$sq)
	$E_{1/2(Fe)}$	$E_{1/2(Os)}$	$E_{1/2(Co)}$	$E_{1/2(Fe)}$	$E_{1/2(Os)}$	$E_{1/2(Co)}$	
Os-Fe	$1.1*10^{-9}$	$1.4*10^{-9}$	-	$1.5*10^2$	$1.3*10^2$	-	164
Co-Fe	$2.7*10^{-9}$	-	$1.1*10^{-9}$	$1.0*10^2$	-	99	149
Co-Os-Fe	$4.4*10^{-9}$		$2.0*10^{-9}$	79		$1.3*10^2$	156

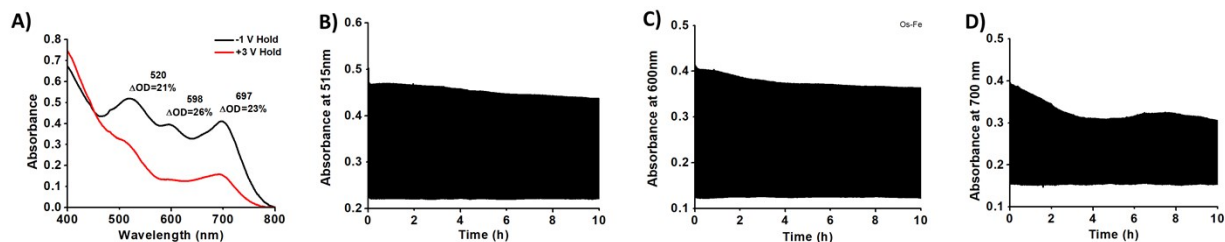**The results of selected spectroelectrochemical measurements.**

Figure S8. Spectroelectrochemical results for the Os-Fe stepwise ECM using -1V and +3V holds: **A)** UV-Vis spectra, and durability cycling with 60s holds: **B)** at 515 nm, **C)** at 600 nm, **D)** at 700 nm.
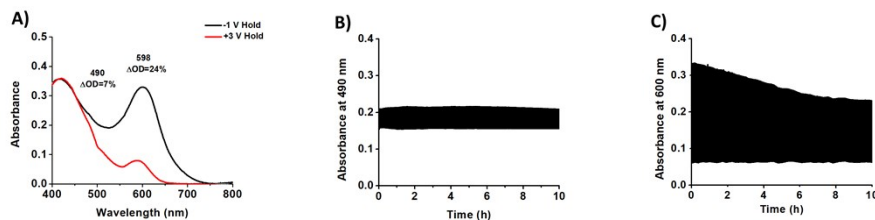
Figure S9. Spectroelectrochemical results for the Co-Fe stepwise ECM using -1V and +3V holds **A)** UV-Vis, and durability cycling with 60s holds: **B)** at 490 nm, **C)** at 600 nm.
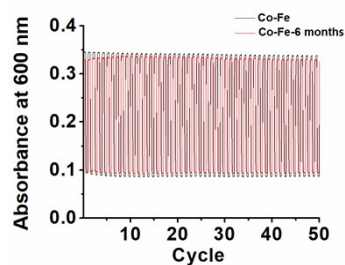

Figure S10. Reproducibility test: Chronoabsorptometry of Co-Fe ECDs prepared six month apart by screen printing of different batches of screen-printed paste, followed by depositin of 4-(chloromethyl)phenyltrichlorosilane taken from different bottles, subsequently depositing of metal complexes from different batches and using separately prepared batches of gel electrolyte.