

Supporting Information for:

Selective heterogeneous capture and release of actinides using carborane-functionalized electrodes

*Maxwell Mattejat^a and Gabriel Ménard^{*a,b}*

^aDepartment of Chemistry and Biochemistry, University of California, Santa Barbara, California
93106, USA

^bDepartment of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta
T2N 1N4, Canada

Table of Contents

S1 Materials and Physical Measurements.....	2
S2 Synthesis of Compounds	3
S3 Electrochemistry	5
S4 Heterogeneous Capture and Release.....	8
S5 References.....	11

S1 Materials and Physical Measurements

General Considerations

All manipulations were performed under an atmosphere of dry, oxygen-free N₂ by means of standard Schlenk or glovebox techniques (MBraun, equipped with a -38 °C freezer, or VAC gloveboxes). Hexanes, pentane, dichloromethane (DCM), and benzene were dried on an MBraun solvent purification system. THF was dried over sodium benzophenone and distilled. 1,2-dichloroethane (DCE) was dried over CaH₂ for several days prior to distillation and subsequent storage on activated 4 Å molecular sieves. Dry 1,4-dioxane and chloroform-*d* were brought into the box and stored over 4 Å molecular sieves. Deionized water (Milli-Q, 18.2 MΩ.cm) was degassed by bubbling with argon overnight before transferring into a wet N₂ box. Carbon fiber sheets were purchased from the Fuelcell Store (ELAT Hydrophilic, lot # 46759-15-EH). The carbon sheets were washed by dipping into acetone, hexanes, isopropyl alcohol, and DI and dried in an oven at 175 °C overnight before use. Single walled carbon nanotubes (90%) were purchased from SkypSprings nanomaterials and used as received. [Th(NO₃)₄•H₂O] was purchased from Stream Chemicals. [UO₂(NO₃)₂•(H₂O)₆] was purchased from International Bio-Analytical Industries Inc. [Sm(NO₃)₃•(H₂O)₆] was purchased from Strem chemicals. CsNO₃ was purchased from Aldrich. 1-Bromopyrene was purchased from Ambeed. *Ortho*-carborane was purchased from Boron Specialties and sublimed before use. Ph₂PCl was purchased from Aldrich and vacuum distilled prior to use. Nd(NO₃)₃(THF)₃,¹ 9-Iodo-*o*-Carborane,² [XPhos-Pd] Catalyst,³ and ¹⁴⁰Pb were prepared using literature procedures.⁴

Physical Measurements

NMR spectra were obtained on a Agilent Technologies 400 MHz spectrometer, and referenced to residual solvent resonances of chloroform (CDCl₃) or externally (¹¹B: 85% (Et₂O)BF₃, ³¹P: 85% H₃PO₄).

Elemental analyses (C, N, H) were recorded at the University of California, Santa Barbara using an Exeter Analytical CE440 elemental analyser.

Electrochemistry experiments were carried out using a Metrohm Autolab PGSTAT128N potentiostat/galvanostat and carried out inside a wet N₂ glovebox.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was performed on an Agilent 5800 and used to determine the concentrations of Th, Nd, Sm, Cs, and U in aqueous solutions. Nitric acid (J.T.Baker, ICP-OES grade for trace metal analysis, ACS testing specifications, LOT 1122090) and deionized water (Milli-Q, 18.2 MΩ.cm) were used for sample preparation and dilutions. A nine-point calibration curve was made by serial dilution (100-0.1 ppm) of a custom multi-element certified reference material from High Purity Standards in 2% nitric acid. The emissions lines used were Th (269.242 nm, 274.716 nm, 283.730 nm), Nd (401.224 nm, 406.108 nm, 410.945 nm, 430.357 nm), Sm (356.827 nm, 359.259 nm, 360.949 nm, 446.734 nm), Cs (495.311 nm, 672.328 nm) and U (263.553 nm, 367.007 nm, 385.957 nm). The calibrations curves for Th, Nd, Sm and U all had $R^2 > 0.9999$. An 8-point calibration curve was used for Cs with a $R^2 > 0.998$, due to an interference in the 0.1 ppm standard.

S2 Synthesis of Compounds

Synthesis of 1,2-(Ph₂PO)₂-9-Pyrenyl-*O*-Carborane (¹⁰Cb-Pyr). The synthesis of ¹⁰Cb-Pyr was accomplished by a three-step modified literature procedure.^{4,5}

Step 1. Magnesium shavings (0.75 g), Iodine (5 mg), and 1-bromopyrene (29.6 eq., 29.6 mmol) were charged into a 100 mL Schlenk round bottom with 30 mL THF (orange solution). Under N₂, the solution was heated for 1.5 hours at 55 °C resulting in a deep orange solution. THF was then pumped off resulting in a brown solid. 9-Iodo-*O*-Carborane (1 eq., 9.26 mmol), XPhos-Pd-G3 (0.01 eq., 0.09 mmol), and XPhos (0.01 eq., 0.09 mmol) were added to a 500 mL Schlenk round bottom and dissolved in ~25 mL 1,4-dioxane. The Grignard pyrene was then dissolved in ~100 mL 1,4-dioxane and slowly added to the carborane solution and subsequently heated to 75 °C for 4 hours. The reaction was then diluted with 100 mL DCM and quenched with 100 mL H₂O. The aqueous layer was extracted with DCM (3 × 100 mL) and the combined organic layers subsequently washed with brine and dried over MgSO₄. The crude product was

dried down and purified using a silica gel column obtaining a 28% yield (890 mg) of **1**. **¹H NMR** (400 MHz, CDCl₃) δ 8.96 (d, *J* = 9.4 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 8.16 – 8.09 (m, 2H), 8.09–8.03 (m, 2H), 8.01 (d, *J* = 2.6 Hz, 2H), 7.99–7.92 (m, 1H), 3.72 (d, *J* = 26.2 Hz, 2H). **¹¹B NMR** (128 MHz, CDCl₃) δ 7.81, -1.44, -8.12, -12.46 – -16.93 (m).

Step 2. A solution of *n*-BuLi in hexanes (2.5 M, 2.1 eq, 3.05 mmol) was dropwise added to a solution of **1** (1 eq., 1.45 mmol) in ~400 mL of dry diethyl ether at -78 °C resulting in a cloudy white solution. After 20 minutes, the solution was warmed to room temperature and stirred for an additional 45 minutes. The solution was cooled back down to -78 °C and Ph₂PCl (2 eq., 0.522 mL) was dropwise added to the solution. After stirring for 30 minutes, the solution was brought to room temperature and stirred for an additional hour. The solution was then dried down and dissolved in DCM before filtering over a celite. The purified product was precipitated out with the addition of pentane, yielding an orange solid with a 78.6% yield (536 mg) of 1,2-(Ph₂P)₂-9-Pyrenyl -*O*-Carborane (**2**). **¹H NMR** (400 MHz, CDCl₃) δ 8.75 (d, *J* = 9.4 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.13–8.06 (m, 2H), 8.01–7.90 (m, 14H), 7.52–7.43 (m, 12H). **³¹P NMR** (162 MHz, CDCl₃) δ 7.87 (d, *J* = 121.0 Hz), 5.41 (d, *J* = 121.0 Hz).

Step 3. A solution of **2** (1 eq., 1.14 mmols) was dissolved in 25 ml of DCM and cooled to 0 °C. A solution of *meta*-chloroperoxybenzoic acid (2 eq., 2.28 mmols) was dissolved in minimal DCM and was added dropwise to the solution. After stirring for 20 minutes, the solution was slowly warmed to room temperature and stirred for an additional 15 minutes. The reaction was stopped by the addition of an aqueous solution of NaHCO₃. The aqueous layer was extracted with DCM (3 × 25 mL) and washed with brine and dried over MgSO₄. The crude product was dried down and purified using a silica gel column obtaining a 69.5% yield (589 mg) of 1,2-(Ph₂PO)₂-9-Pyrenyl-*O*-Carborane (**^{PO}Cb-Pyr**). **¹H NMR** (400 MHz, CDCl₃) δ 8.53 (d, *J* = 9.4 Hz, 1H), 8.19–8.04 (m, 11H), 8.02–7.92 (m, 4H), 7.87 (d, *J* = 9.4 Hz, 1H), 7.66–7.51 (m, 12H). **¹¹B NMR** (128 MHz, CDCl₃) δ 11.72, 7.09 – -0.97 (m), -8.30 (d, *J* = 494.5 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 24.43, 24.20. *Anal. Calcd.* C₄₂H₃₈B₁₀P₂O₂: C, 67.73; H, 5.14. *Found:* C, 67.28; H, 5.15.

S3 Electrochemistry

Cyclic voltammetry on glassy carbon rods: The ends of glassy carbon (GC) rods were sanded down and polished to a mirror finish to have a working surface area of 0.1935 cm^2 . Films were made by drop casting solutions on the surface of freshly polished GC and let to dry open to air. For the pure carborane films, $10\text{ }\mu\text{L}$ of 1 mM solutions of $^{\text{PO}}\text{Cb}$ and $^{\text{PO}}\text{Cb-Pyr}$ were dropped onto the freshly polished electrodes and dried open to air ($\text{GC}|^{\text{PO}}\text{Cb}$, $\text{GC}|^{\text{PO}}\text{Cb-Pyr}$). For the CNT films, 73 mg of CNT were placed in a 20 mL vial and suspended in 20 mL of DCE. This solution was then ultra-sonicated for 30 minutes in a bath sonicator. A $10\text{ }\mu\text{L}$ drop of CNT suspended in DCE (3.65 mg/mL) was placed onto the surface of a fresh GC electrode and left to dry open to air ($\text{GC}|\text{CNT}$). Once all the DCE evaporated, $10\text{ }\mu\text{L}$ of 1 mM $^{\text{PO}}\text{Cb}$ or $^{\text{PO}}\text{Cb-Pyr}$ in DCE was dropped onto the surface and left to dry open to air ($\text{GC}|\text{CNT}|^{\text{PO}}\text{Cb}$, $\text{GC}|\text{CNT}|^{\text{PO}}\text{Cb-Pyr}$). All electrodes were then subsequently cycled into a wet N_2 glovebox. Cyclic voltammetry (CV) was then taken in 0.1 M KCl Milli-Q solutions with a Pt counter electrode and referenced to a standard calomel electrode (SCE). Variable scan rates were taken of each film after 20 CVs at 0.1 V/s were taken.

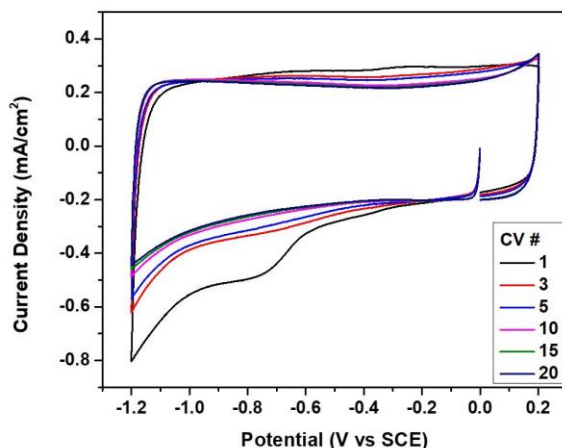


Figure S1: CVs of a film made by drop casting $10\text{ }\mu\text{L}$ of CNT suspended in DCE (3.65 mg/mL) on glassy carbon rod ($\text{GC}|\text{CNT}$) in 0.1 M KCl aqueous solutions at a scan rate of 0.1 V/s .

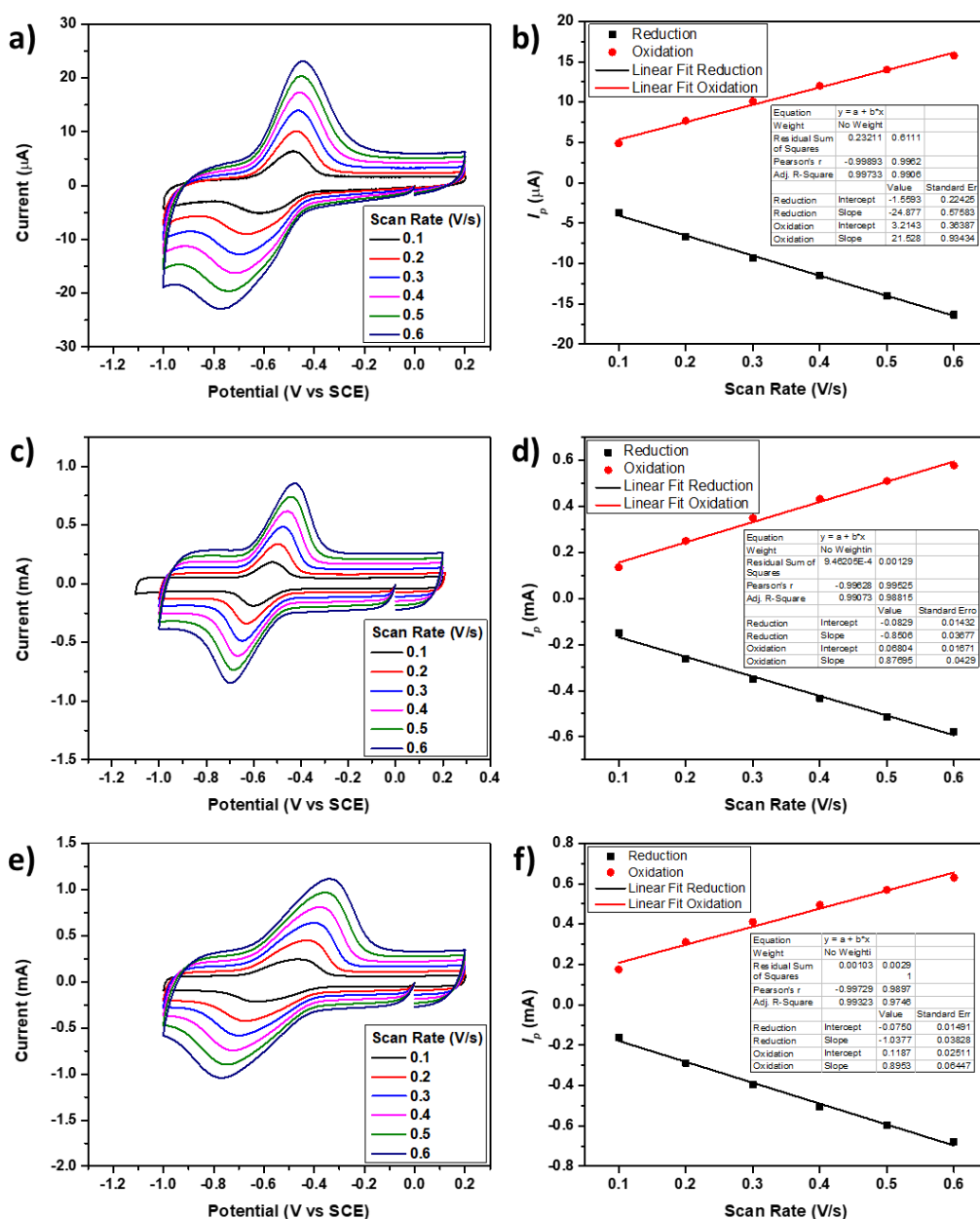


Figure S2: CVs of films on GC rods in 0.1 M KCl aqueous solutions at various scan rates and the peak current (I_p) vs scan rate plotted with a linear fit. a) GC|^{PO}Cb CVs. b) GC|^{PO}Cb I_p vs scan rate c) GC|CNT|^{PO}Cb CVs d) GC|CNT|^{PO}Cb I_p vs scan rate. e) GC|CNT|^{PO}Cb-Pyr CVs. f) GC|CNT|^{PO}Cb-Pyr I_p vs scan rate.

Cyclic voltammetry on carbon fiber: Carbon Fiber (CF) was cut into 2×2 cm square electrodes with a 1×2 cm tab (Fig S3a) attached to a steel holder. The cut electrodes were washed with acetone, hexanes, isopropyl alcohol, DI and dried in an oven at 350 °C overnight before being functionalized. For the pure

carborane functionalized CF electrodes, 120 μL of 1 mM solutions of $^{\text{PO}}\text{Cb}$ and $^{\text{PO}}\text{Cb-Pyr}$ was dispersed onto one side of the working area of the CF electrode and dried open to air. Once all of the DCE had evaporated the other side was also coated with 120 μL of 1 mM solutions of $^{\text{PO}}\text{Cb}$ and $^{\text{PO}}\text{Cb-Pyr}$ and left to dry open to air ($\text{CF}|^{\text{PO}}\text{Cb}$, $\text{CF}|^{\text{PO}}\text{Cb-Pyr}$). For the CNT functionalized CF electrodes, 73 mg of CNT were placed in 20 mL vial and suspended in 20 mL of DCE. This solution was then ultra-sonicated for 30 minutes in a bath sonicator. 200 μL of CNT suspended in DCE (3.65 mg/mL) was evenly dispersed over working area of CF electrode and left to dry open to air before the other side was coated ($\text{CF}|\text{CNT}$). Once all the DCE evaporated, 120 μL of 1 mM $^{\text{PO}}\text{Cb}$ or $^{\text{PO}}\text{Cb-Pyr}$ in DCE was dispersed onto the surface and left to dry open to air before the other side was coated ($\text{GC}|\text{CNT}|^{\text{PO}}\text{Cb}$, $\text{GC}|\text{CNT}|^{\text{PO}}\text{Cb-Pyr}$) (Fig S3b). The electrodes were attached to a steel holder (Fig S3c) before being cycled into a wet N_2 glovebox. Cyclic voltammetry (CV) was performed in 0.1 M KCl Milli-Q solutions with a Pt counter electrode and referenced to a standard calomel electrode (SCE).

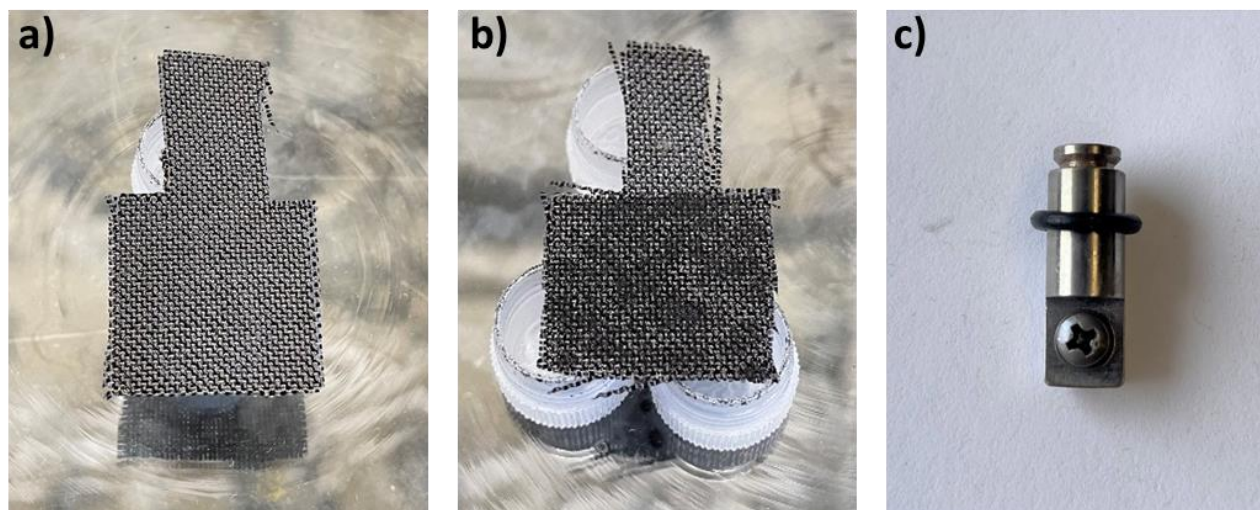


Figure S3 a) non-functionalized CF electrode. b) CF electrode functionalized with CNT and $^{\text{PO}}\text{Cb}$ ($\text{CF}|\text{CNT}|^{\text{PO}}\text{Cb}$). c) Steel electrode holder.

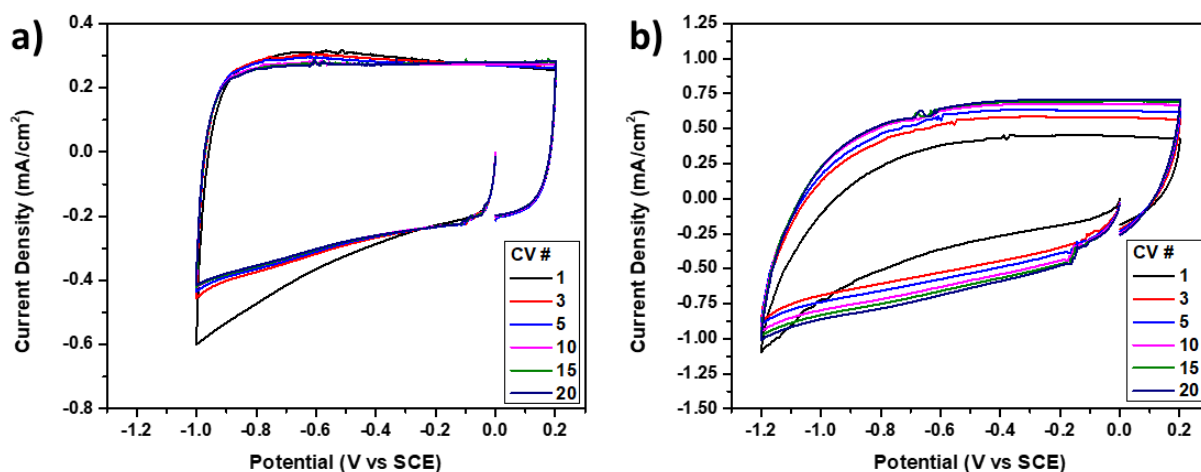


Figure S4: a) CVs of non-functionalized CF electrode. b) CVs of CNT-functionalized CF electrode (CF|CNT).

S4 Heterogeneous Capture and Release

Mixed Metal Stock Solution: Individual stock solutions of CsNO_3 , $\text{Nd}(\text{NO}_3)_3(\text{THF})_3$, $\text{Sm}(\text{NO}_3)_3(\text{H}_2\text{O})_6$, $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_x$, and $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ were made up to be roughly 2 mM in a 0.1M KCl Milli-Q solution. ICP-OES was used to determine the accurate concentrations of the individual stocks. Roughly 100 mL aliquots of each stock solution was added to 1 L volumetric flask and diluted to the 1 L mark with 0.1 M KCl Milli-Q solutions to achieve a final concentration of 0.2 mM for each metal. The mixed metal stock solution concentration was determined by ICP-OES (Table 1).

Table 1: Concentrations of filtered mixed metal stock solution determined by ICP-OES

Metal	mM
Cs	0.2156
Nd	0.1848
Sm	0.1891
Th	0.1870
U	0.1926

Electrode Preparation: CF was cut into 8.5×4 cm (34 cm^2) electrodes with a 1.5×1.5 cm tab. The cut electrodes were washed with acetone, hexanes, isopropyl alcohol, DI and dried in an oven at 350°C

overnight before being functionalized. CNT (73 mg) were placed in 20 mL vial and suspended in 20 mL of DCE. The solution was then ultra-sonicated for 30 minutes in a bath sonicator. 1.7 mL of this CNT solution DCE (3.65 mg/mL) was evenly dispersed onto each side of a 34 cm² carbon fiber cloth and left to dry in open air before coating the second side. Once dried, 1 mL of 2 mM solutions of carborane (^{PO}Cb, ^{PO}Cb-Pyr) was dispersed on each side and left to dry between sides (Fig. S5). Once dried these electrodes were cycled into a wet N₂ glovebox.



Figure S5: Example of 34 cm² CF electrode functionalized with CNT and ^{PO}Cb (CF|CNT|^{PO}Cb)

Charging Electrodes: An H-cell (Fig S6) separated by a glass frit was filled with ~60 mL 0.1 M KCl on each side and a washed 20 × 20 cm sheet of CF attached to a steel holder was placed in the counter electrode compartment of the H-cell. An SCE electrode was placed in separate compartment attached to the working electrode compartment with a luggin capillary to measure the potential at the working electrode. The functionalized electrodes (CF|CNT, CF|CNT|^{PO}Cb, and CF|CNT|^{PO}Cb-Pyr) were attached to steel holders and submerged in the working electrode compartment. A -5 mA current was applied between the counter electrode and the working functionalized electrode for 124 seconds to reach an 80% state of charge or hit a potential cut-off of -1.2 V vs SCE (Fig S7). A potential cut off higher than the solvent window of water observed in the CVs was set at -1.2 V vs SCE to avoid hydrogen evolution reaction occurring on the electrode while charging. Once charging was complete, the electrode was removed from the H-cell and allowed to drip dry before being placed into a 20 mL vial.



Figure S6: Glass Frit separated H-Cell

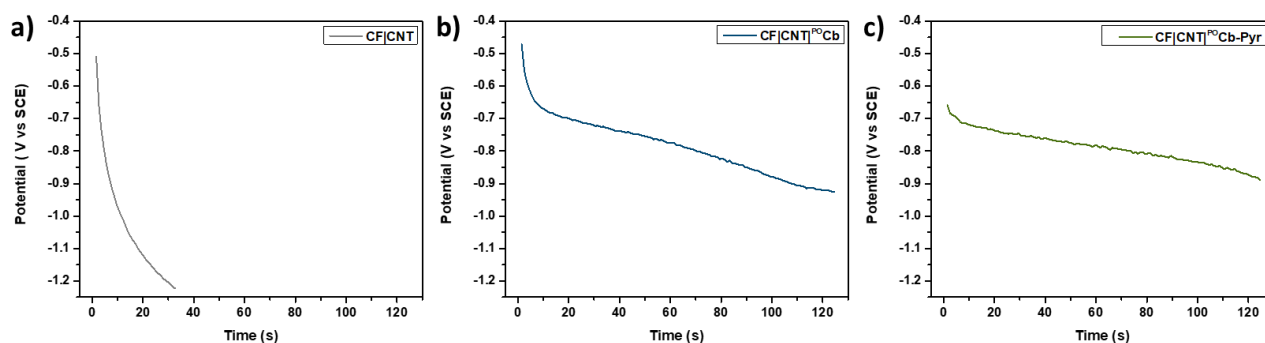


Figure S7: Charging curves for 34 cm² electrodes. a) CF|CNT b) CF|CNT|^{ⁱ⁰}Cb c) CF|CNT|^{ⁱ⁰}Cb-Pyr.

Capture Experiment: The 20 mL vial containing the charged electrode was tared before ~10 ml of the mixed solution was poured into the vial. The weight of the mixed metal solution dispensed was recorded. The solution was swirled to ensure the electrode came into full contact with the solution and was left to sit in the solution for 10 minutes. The solution was then drawn off and put into a separate vial. The vial containing the electrode was weighed again to measure and record the residual mixed metal solution trapped in the electrode. The captured solutions were brought outside the glove box and filtered with a 0.22 μ m

PVDF syringe filter to remove particulates before being diluted with nitric acid to achieve a 2% nitric acid solution for ICP-OES analysis.

Release Experiment: Outside the box, the electrodes in 20 mL vials were tared before ~10 mL of 2% nitric acid was put into the vials. The amount of nitric acid transferred was recorded. The solution was shaken with the electrode and allowed to sit in the nitric acid overnight. The solution was drawn off and filtered with a 0.22 μ m PVDF syringe filter into a pre-leached flacon tube for ICP-OES analysis.

Non-charged Control Experiments: Non-Charged functionalized electrodes (CF|CNT, CF|CNT|^{PO}Cb, and CF|CNT|^{PO}Cb-Pyr) went through the same process for capture and release process with the only difference being no current being passed through the electrode.

S5 References

1. W. J. Evans, D. G. Giarikos, P. S. Workman and J. W. Ziller, *Inorg. Chem.*, 2004, **43**, 5754-5760.
2. J. S. Andrews, J. Zayas and M. Jones, *Inorganic Chemistry*, 1985, **24**, 3715-3716.
3. N. C. Bruno, M. T. Tudge and S. L. Buchwald, *Chemical Science*, 2013, **4**, 916-920.
4. M. Keener, C. Hunt, T. G. Carroll, V. Kampel, R. Dobrovetsky, T. W. Hayton and G. Ménard, *Nature*, 2020, **577**, 652-655.
5. K. P. Anderson, H. A. Mills, C. Mao, K. O. Kirlikovali, J. C. Axtell, A. L. Rheingold and A. M. Spokoyny, *Tetrahedron*, 2019, **75**, 187-191.