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Final Technical Report for:
"Selective Electrochemical Capture and Release of Uranyl in Solution"

Selective Electrochemical Capture and Release of UO_2^{2+} from Mixed-Metal Solutions: Our original report investigating UO_2^{2+} capture and release using Cb prior to DOE funding used L = Ph_2PO binding groups in its *closo* (**^{PO}Cb**) or reduced *nido* (**^{PO}Cb^{2-}**) forms (Fig. 1a).[1] In follow-up work published in *Chem. Sci.*,[2] we reported the selective electrochemical biphasic capture of UO_2^{2+} from mixed-metal alkali (Cs^+), lanthanide (Nd^{3+}, Sm^{3+}), and actinide (Th^{4+}, UO_2^{2+}) aqueous solutions to an organic, 1,2-dichloroethane (DCE), phase using **^{PO}Cb^{2-}**. The reduced **^{PO}Cb^{2-}** is generated by electrochemical reduction of **^{PO}Cb** prior to mixing with the aqueous mixed-metal solution. Subsequent UO_2^{2+} release from the captured product, **$[UO_2(^{PO}Cb)_2]^{2-}$**, was performed by galvanostatic bulk electrolysis

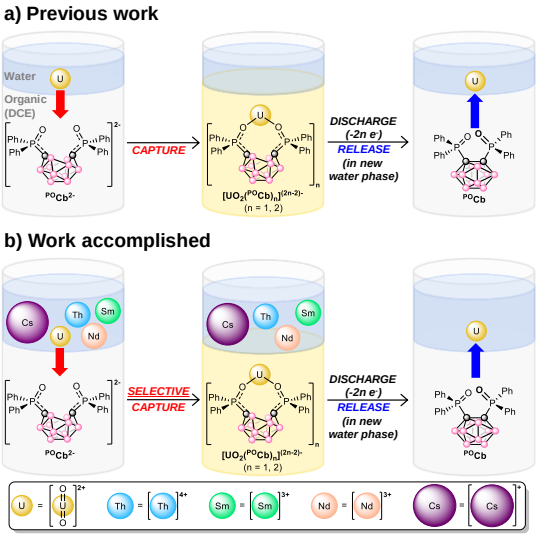

Fig. 1. a) Our previous work demonstrating the biphasic capture and release of UO_2^{2+} using the **^{PO}Cb^{2-}/^{PO}Cb** system. b) Our work accomplished highlighting the *selective* capture and release of UO_2^{2+} from aqueous solutions containing alkali, lanthanide, and actinide metals.

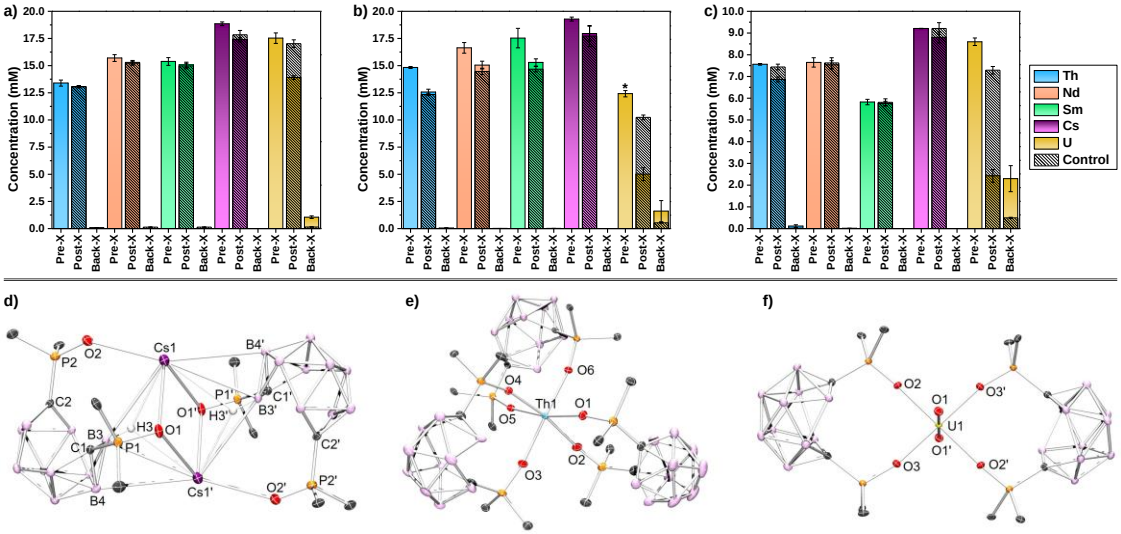

Fig. 2. ICP-OES data for the selective electrochemical capture and release of UO_2^{2+} from mixed-metal (Cs^+, Nd^{3+}, Sm^{3+}, Th^{4+}, UO_2^{2+}) aqueous solutions using the **^{PO}Cb/^{PO}Cb^{2-}** system in DCE. (a-c) Average concentrations (from triplicate runs) of each metal species initially (pre-X) and following post-X and back-X using the following conditions and assuming 1.0 equiv of **^{PO}Cb^{2-}**: (a) a non-buffered (pH = 2.6) aqueous mixed-metal solution with ca. 1.25 equiv of each metal; (b) a NaOAc-buffered (pH = 5.2) aqueous mixed-metal solution with ca. 1.25 equiv of each metal (*slightly lower for UO_2^{2+} due to saturation concentration); (c) a NaOAc-buffered (pH = 5.2) aqueous mixed-metal solution with ca. 0.6 equiv of each metal. (d-f) Example solid-state molecular structures obtained by XRD studies of: (d) **$[[CoCp^*_2][Cs(^{PO}Cb)]]_2$**; (e) **$[CoCp^*_2]_2[Th(^{PO}Cb)_3]$**, and; (f) **$[CoCp^*_2]_2[UO_2(^{PO}Cb)_2]$** (for comparison).[1] $[CoCp^*_2]^+$ counter cations, phenyl C–H linkages, co-crystallized solvent molecules, and all H atoms, except those in (d), are omitted for clarity.

of the DCE phase and back-extraction of UO_2^{2+} to a fresh aqueous phase. The selective capture and release of UO_2^{2+} was confirmed by combined ICP-OES (Fig. 2a-c) and NMR spectral analyses of the aqueous and organic phases, respectively, against the newly synthesized *nido*-carborane complexes, **[[CoCp*$_2$][Cs(POCb)]]$_2$**, **[CoCp*$_2$]$_3$[Nd(POCb)$_3$]**, **[CoCp*$_2$]$_3$[Sm(POCb)$_3$]**, and **[CoCp*$_2$]$_2$[Th(POCb)$_3$]** (Fig. 2d-f).

Tuning Lewis basicity and redox: In subsequent work which is in the final stages of edits, we are investigating how the electronic properties of the **POCb** cage can be tuned to control the selectivity towards UO_2^{2+} versus other metals in solution. Various cage-modified and aryl-group modified species have been generated (Fig. 3a) and their electrochemical properties interrogated (Fig. 3b-c). We are presently investigating how these changing redox properties affect the donicity of the PO centers and how these can be tuned for selective electrochemical separations. Using known spectroscopic techniques,[3] we have estimated the ranging pK_b values of these various species in order to gauge their relative Lewis basicities. The effect of these modifications will be used to gauge relative selectivity in biphasic extractions using separation factors as the key measure. Future work here will focus on using the knowledge gained here for other selective metal-metal separations, in particular with respect to An/Ln or Ln/Ln separations.

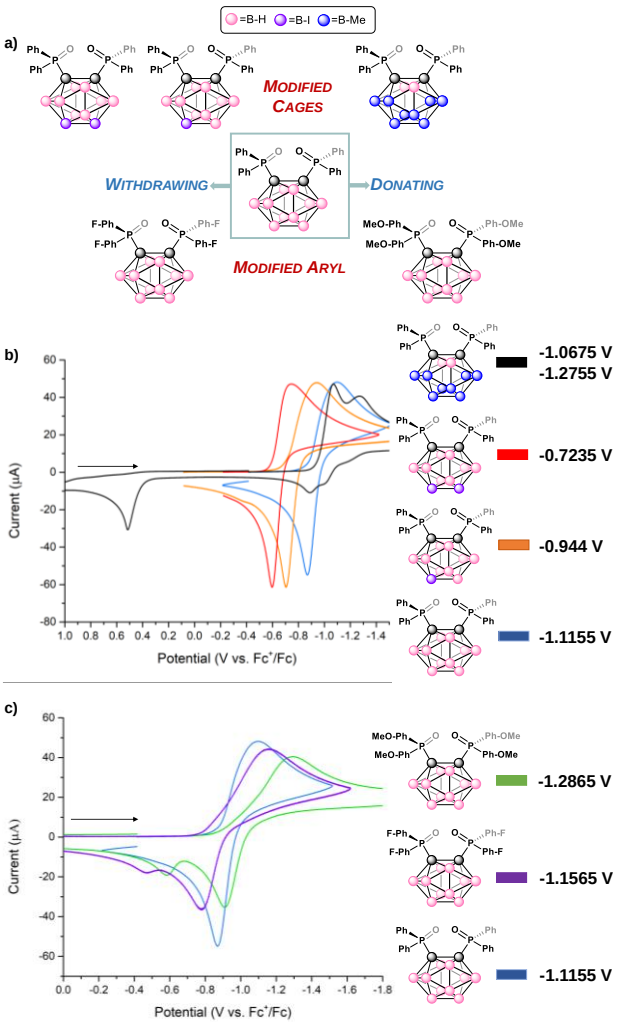

Fig. 3. a) Synthesized modified **POCb** species. b) CVs of cage-modified species with their reported peak cathodic peaks shown. c) CVs of aryl-modified species with their reported peak cathodic peaks shown.

Heterogeneous Selective Capture: In work very recently submitted and under review entitled "Selective heterogeneous capture and release of actinides using carborane-functionalized electrodes," we report the heterogenization of **POCb** for selective metal capture. Films of **POCb** and pyrene-substituted, **POCb-Pyr**, were prepared on glassy carbon and carbon fiber (CF) electrodes demonstrated heterogeneous electrochemical behaviour that was enhanced by the inclusion of single-walled carbon nanotubes (CNTs) (Fig. 4). Galvanostatically charged CF|CNT|POCb and CF|CNT|POCb-Pyr electrodes selectively captured and released actinides

(Th^{4+}, UO_2^{2+}) from a mixed solutions containing alkali (Cs^+), lanthanide (Nd^{3+}, Sm^{3+}) and actinide (Th^{4+}, UO_2^{2+}) metal ions.

Statement of unexpended funds:

No unexpended funds are anticipated at the end of the grant period.

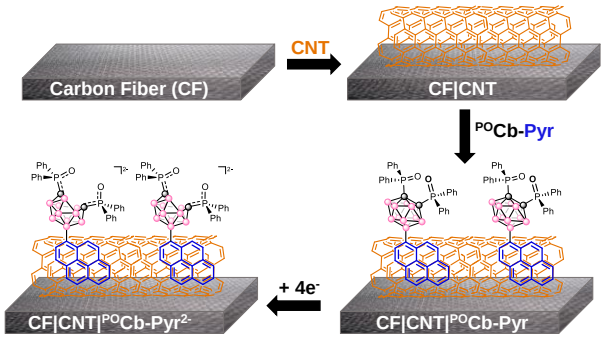

Fig. 4. Assembly and charging scheme of CF|CNT|^{PO}Cb-Pyr.

References:

1. Keener, M.; Hunt, C.; Carroll, T. G.; Kampel, V.; Dobrovetsky, R.; Hayton, T. W.; Ménard, G. Redox-switchable carboranes for uranium capture and release. *Nature* **2020,** *577*, 652-655.
2. Keener, M.; Mattejat, M.; Zheng, S.-L.; Wu, G.; Hayton, T. W.; Ménard, G. Selective electrochemical capture and release of uranyl from aqueous alkali, lanthanide, and actinide mixtures using redox-switchable carboranes. *Chem. Sci.* **2022,** *13*, 3369-3374.
3. Milic, M.; Targos, K.; Tellez Chavez, M.; Thompson, M. A. M.; Jennings, J. J.; Franz, A. K. NMR Quantification of Hydrogen-Bond-Accepting Ability for Organic Molecules. *J. Org. Chem.* **2021,** *86*, 6031-6043.