DOE BES Grant No: DE-FG02-03ER15420

Title: The Synthesis, Structures and Chemical Properties of Macrocyclic Ligands Covalently Bonded to Layered Arrays

Principal Investigator:
Abraham Clearfield, Distinguished Professor, FRSC, FACA
Department of Chemistry, Texas A&M University
College Station, TX

November 2014

Time Extent: 08/15/2003 to 11/14/2014

Texas A&M University
Chemistry Department
College Station, Texas 77843-3255
Tel: (979) 845-2936
Email: Clearfield@chem.tamu.edu

Preface

This grant during the period 10/20/11 to 10/20/14 was supported by two divisions of DOE Basic Energy Sciences, Heavy Element Chemistry, Program Manager Dr. Philip A. Wilk and Materials Chemistry, Program Director Dr. Michael Sennett. Progress in both areas of research will be presented in this final report.

EXECUTIVE SUMMARY

A. Heavy Element Chemistry

Our work has been focused on separation of actinides from lanthanides and actinide separations from each other. This is an important step in the nuclear fuel cycle as the recovered actinides may be reused as fuel and the neutron absorbing lanthanides removed as waste.

The basis for these separations is a new class of materials which have been given the name UMOFs for unconventional metal organic frameworks. They are porous frameworks of zirconium and tin phenylphosphonate phosphates that differ from conventional MOFs in that they are poorly crystalline. Their utility stems from the fact that they are ion exchangers that are mildly selective for ions of plus one and two charge but highly selective for ions of charge 3+ and 4+. These preferences allow separations of lanthanides from actinides by oxidizing the actinides to the oxidation state five as actinyl compounds, AcO_2^{+1}. Under these conditions the lanthanides remain with the plus three charge and are taken up while the actinides are rejected. Because the ease of oxidation of actinides depends upon their mass, lighter ions Np, Pu can be separated from Am and Cm. One highlight of our study has demonstrated the separation of Am as AmO_2^+ from Cm^{3+}.

We have shown that the highest selectivity for lanthanides occurs at pH 3 and recovery of the lanthanides is manifested below pH 1. One of our difficulties has been the inability to use the actinides at Texas A&M and therefore must resort to carry out these studies at National laboratories. This is a slow process but we have demonstrated a separation of Americium from Curium and Nd from Am. Recently we obtained an NEUP grant with which to complete the goals of our DOE Separations program.

B. Materials Science Program

In this part of the proposal we have concentrated on the surface functionalization of α-zirconium phosphate of composition $Zr(O_3POH)_2 \cdot H_2O$. It is a layered compound that can be prepared as particles as small as 30 nm to single crystals in the range of cm. This compound is an ion exchanger with a capacity of 6.64 meq per gram. It finds use as a catalyst, proton conductor, sensors, biosensors, in kidney dialysis and drug delivery. By functionalizing the surface additional uses are contemplated as will be described. The layers consist of the metal, with 4+ charge, that is positioned slightly above and below the mean layer plane and bridged by three of the four phosphate oxygens. The remaining POH groups point into the interlayer space creating double rows of POH groups but single arrays on the surface layers. The surface groups are reactive and we were able to bond silanes, isocyanates, epoxides, acrylates ` and phosphates to the surface POH groups. The layers are easily exfoliated or filled with ions by ion exchange or molecules by intercalation reactions. Highlights of our work include, in addition to direct functionalization of the surfaces, replacement of the protons on the surface with ions of different charge. This allows us to bond phosphates, biophosphates, phosphonic acids and alcohols to the surface. By variation of the ion charge of the ions that replace the surface protons, different surface structures are obtained. We have already shown that polymer fillers, catalysts and Janus particles may be prepared. The combination of surface functionalization with the ability to insert molecules and ions between the layers allow for a rich development of numerous useful other applications as well as nano-surface chemistry.

Part I. Separation of Heavy Elements

Synthesis and Properties of UMOFs: The UMOFs are prepared from mixtures of zirconyl chloride, $ZrOCl_2{\cdot}8H_2O$ or tin chloride $SnCl_4{\cdot}5H_2O$, to which are added a mixture of 1,4-phenylenediphosphonic acid and phosphoric acid in a 1:2 mole ratio. The mixture is then heated hydrothermally at 120 °C for 4 days.[2] For the sodium ion phases Na_3PO_4 is substituted for the phosphoric acid and K_3PO_4 for the potassium phases. The yields are typically between 90-100%. An interesting property of these UMOFs is that a second ligand may be incorporated to produce compounds of the type $M(O_3PC_6H_4PO_3)_{1-x/2}(O_3POH)_x{\cdot}nH_2O$, M = Zr^{4+}, Sn^{4+}. Analytical data are provided in Table 1.

Table 1: Elemental analysis information along with the derived formulas. Estimate of error <5%.

						%C	%H		
Sample	Formula	FW	M	:P	:Na	Calc.	Exp.	Calc.	Exp.
H-Zr-hybrid	$Zr(O_6P_2C_6H_4)_{0.49}(O_3POH)_{0.86}(OH)_{0.32}{\bullet}2.04H_2O$	330.65	1.00	1.84	-	10.68	10.60	2.21	2.31
Na-Zr-hybrid	$Zr(O_6P_2C_6H_4)_{0.43}(O_3POH)_{0.18}(O_3PONa)_{0.66}(OH)_{0.60}{\bullet}1.68H_2O$	327.53	1.00	1.69	0.66	9.46	9.45	1.83	2.05
H-Sn-hybrid	$Sn(O_6P_2C_6H_4)_{0.44}(O_3POH)_{0.80}(OH)_{0.53}Cl_{0.11}{\bullet}1.61H_2O$	340.40	1.00	1.68	-	9.31	9.41	1.87	2.31
Na-Sn-hybrid	$Sn(O_6P_2C_6H_4)_{0.44}(O_3POH)_{0.74}(O_3PONa)_{0.05}(OH)_{0.66}{\bullet}2.42H_2O$	353.45	1.00	1.67	0.05	8.97	9.34	2.29	2.44

The separation factors for Nd^{3+} with lower charged ions are shown in Table 2.

Table 2. Separation factors of Nd^{3+} from Cs^+, Sr^{2+}, and Ni^{2+} at pH 2.

Sample	Nd^{3+} / Cs^+	Nd^{3+} / Sr^{2+}	Nd^{3+} / Ni^{2+}
H–Zr–hybrid	15	>1,000	19
Na–Zr–hybrid	78	>100,000	520
H–Sn–hybrid	480	1900	910
Na-Sn-hybrid	800	2400	1,000

The separation factors are very large indicating the extreme preference of our materials for the ions of higher charge. Surface areas and microporosity of the UMOFs are listed in Table 3. These results were obtained by N_2 sorption and treated by the BET t-plot theory.

Table 3. Surface area data of the ion exchange materials determined by BET and t-plot methods. Estimate of error <100%.

Sample	Total Surface Area ($m^2\ g^{-1}$)	Microporous (%)
H-Zr-hybrid	440	72%
Na-Zr-hybrid	250	56%
K-Zr-hybrid	270	15%
H-Sn-hybrid	400	98%
Na-Sn-hybrid	370	98%
K-Sn-hybrid	350	96%

It should be noted that the tin compounds all contained high levels of microporosity whereas the zirconium compounds had lesser amounts of micropores and much higher levels of mespores. The poorly crystalline nature of the UMOFs is shown in Figure1. The powder X-ray diffraction patterns contain a few broad peaks but the first one is at 9.6 Å, which modeling shows is the value expected by the crosslinking. K_d values for Nd^{3+} and Sm^{3+} are given in Table 4 and log K_d for Nd^{3+} as a function of pH is illustrated in Figure 2. The highest values of uptake are at pH 3 and almost no ions are taken below pH 0.5.

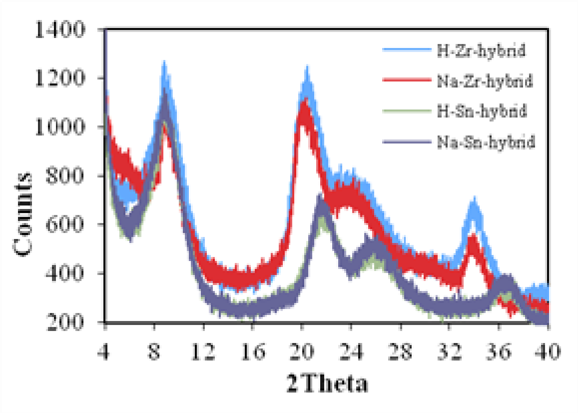


Figure 1. X-ray powder diffraction patterns (XRPD) of metal(IV) phosphate-phosphonate hybrid materials, having the ideal formula $M(O_6P_2C_6H_4)_{0.5}(O_3POA){\bullet}nH_2O$ where A= H^+ or Na^+. The Zr-hybrids have d-spacings of *ca.* 9.6, 4.3, and 2.6 Å, while the Sn-hybrids have d-spacings of *ca.* 9.6, 4.0, and 2.4 Å.

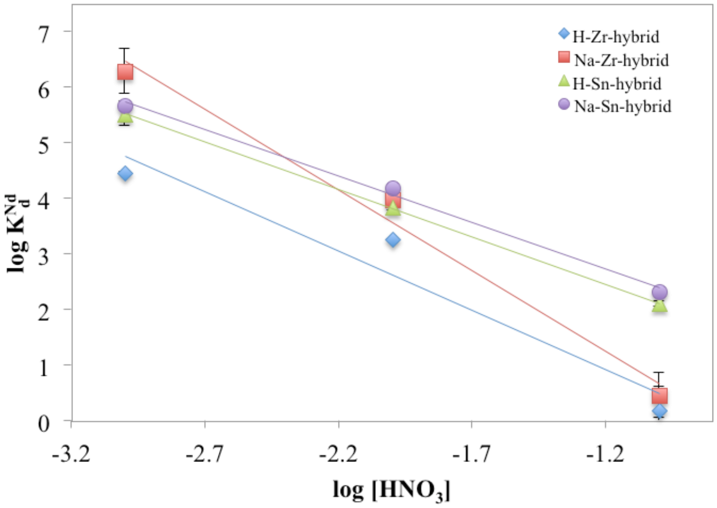


Figure 2. Extraction of Nd^{3+} as a function of [HNO_3], the initial [Nd^{3+}] was ~ 10^{-4} M. No uptake was observed for [HNO_3] < 0.1.

Table 4. K_d values observed at pH 3 in HNO_3 and reported in mL/g for selected ions.

Sample	Nd^+	Sm^{3+}
H-Zr-hybrid	29,000 ± 2,000	80,5000 ± 10,000
Na-Zr-hybrid	220,000 ± 110,000	178,000 ± 10,000
K-Zr-hybrid	3,700 ± 320	4,3000 ± 1,500
H-Sn-hybrid	224,000 ± 160,000	317,000 ± 16,000
Na-Sn-hybrid	480,000 ± 50,000	297,000 ± 13,000
K-Sn-hybrid	32,000 ± 2,000	

C. Actinides Research

Actinide research studies were carried out both at Los Alamos Carlsbad, under the direction of Dr. Daniel T. Reed and Savanah River National Laboratory under the direction of Dr. David T. Hobbs. At the Carlsbad laboratory the K_d values were determined for solutions of actinides at pH values in the vicinity of 2. The results are shown in Table 5. It is seen that the K_d for AmO_2^+ is very low for all of the UMOFs, as is that for NpO_2^+ which is in the medium range. However, the K_d values of actinides in the 3+ state are very high. Furthermore, the separation factors (SF) of trivalent to monovalent ions are also high indicating that chromatographic methods would certainly effect their separation.

Table 5. The K_d values and separation factors (SF) for several actinides. K_d values are reported in (mL/g).

Sample	K_d AmO_2^+ pH 1.99	K_d NpO_2^+ pH 2.11	K_d Am^{3+} pH 2.00	K_d PuO_2^{2+} pH 2.13	Am^{3+}/ AmO_2^+ SF	Am^{3+}/ NpO_2^+ SF	Am^{3+}/ PuO_2^{2+} SF
H–Zr–hybrid	2 ± 1	80 ± 2	4,870 ± 50	1,440 ± 50	2000 ± 1000	61 ± 2	3.4 ± 0.1
Na–Zr–hybrid	13 ± 1	3,000 ± 300	640,000 ± 30,000	240,000 ± 20,000[a]	49,000 ± 4000	210 ± 20	2.7 ± 0.3
H–Sn–hybrid	14 ± 1	230 ± 5	12,000 ± 100	3,200 ± 200	860 ± 60	52 ± 1	3.8 ± 0.2
Na–Sn–hybrid	15 ± 1	480 ± 10	38,800 ± 800	6,100 ± 200	2600 ± 200	81 ± 2	6.4 ± 0.2

a: K_d obtained at pH 1.94

Separation of Cm from Am: Separation of Cm from Am is one of the major tasks as part of the actinide lanthanide separations program. Our strategy was to oxidize americium to oxidation state five as AmO_2^+. Cm would remain as a three plus ion and be taken up with the lanthanides. However, Am^{3+} is also difficult to oxidize and is relatively unstable in the 5+ state. After several trials we fixed on using $Na_2S_2O_8$ as the oxidizing agent. The process was carried out at 80 °C and monitored using UV spectroscopy. After 30 min at 80 °C the characteristic bands of Am(III) at 503 and 806 nm disappeared and those characteristic of Am(VI) as AmO_2^{2+}were obtained. While the solution was still warm, $Ca(OCl)_2$ was added and the solution cooled to room temperature, whereupon AmO_2^+ was obtained as shown by the bands in the UV spectrum (Figure 3) at 513 and 717 nm. To prevent reduction of Am(V) to Am(III) $Ca(OCl)_2$ was added. The presence of excess hypochlorite allowed us to hold the Am(V) state for five days with only a 3% reduction to Am(III). This work was executed at the Carlsbad laboratory.

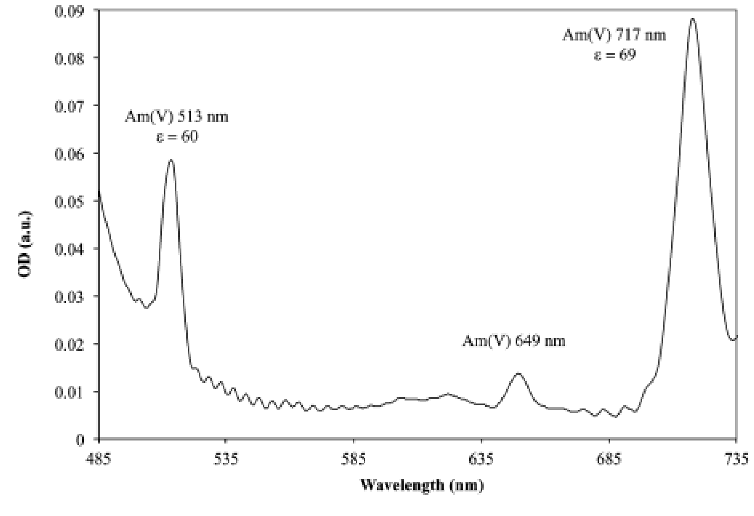


Figure 3. Spectrum of pure AmO2$^+$ in 0.01 M HNO_3 after the solution was allowed to age resulting in precipitation of $CaSO_4$ and coprecipitation of any Am^{3+} not oxidized.

The actual separation was carried out at the Savannah River site as they were able to supply the Cm. The results are collected in Table 6 and are lower than expected. In Table 5 the K_d value for AmO_2^+ was very low. In Table 6 it is seen that these Am K_{ds} are much larger. This may be due to the presence of some Am^{3+} in the solution. Also, the Cm was already mixed with the Am so we had no way of measuring the K_d of pure Cm^{3+} and no way to determine the oxidation state of the Am. We also need to determine the Cm^{3+} uptakes as a function of pH.

Table 6. K_d values and separation factors for AmO_2^+ and Cm^{3+}.

Sample	K_d AmO_2^+	K_d Cm^{3+}	SF Cm^{3+} / AmO_2^+
H–Zr–hybrid	62 ± 3.1	96 ± 4.8	1.6
Na-Zr-hybrid	85 ± 4.3	1300 ± 65	15
H–Sn–hybrid	120 ± 6.1	1600 ± 80	13
Na-Sn-hybrid	220 ± 11	4400 ± 220	20

Conclusion

The work described here has provided two possible procedures to effect a workable separation of the lanthanides from the actinides. If the K_d values of the actinides in the 3+ state are high at pH values less than 1, the separation can be carried out at this pH because the K_d values for Ln^{3+} would be very low. Conversely, the actinides can be oxidized to the five plus state with ion charge one and the lanthanides taken up by the UMOFs. Before a decision can be made of which process is more feasible we need to determine the K_d values for the actinides as a function of pH.

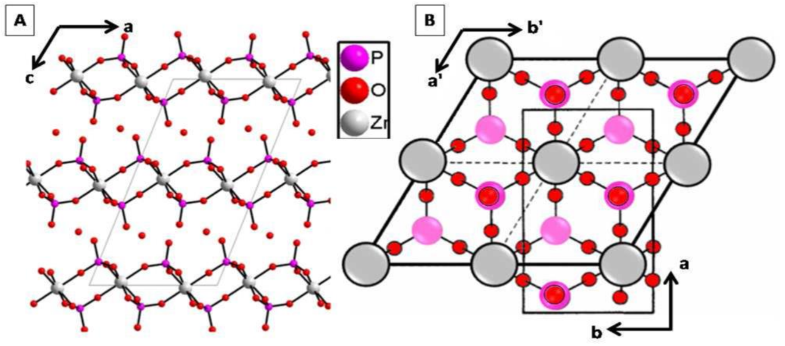
D. What have we accomplished?

The original goal was to be able to separate the lanthanides from the actinides using the ion exchange properties of our phosphate phosphonates.

1. Indeed these ion exchangers did show a high level of uptake of 3+ lanthanides and a low level of selectivity for actinyl ions of charge one plus. Thus two strategies for the desired separation were devised.
2. The separation of Am from Cm was effected with a separation factor of 20. Further, studies to improve this value are contemplated. It entails prevention of AmO_2^+ reverting to Am^{3+} and determination of the best pH for uptake of Cm^{3+}.
3. This research will now be carried on with the aid of an NEUP grant that will allow more time at national laboratories to carry out the actinide studies.
4. Additional separations contemplated.
   Separation of lanthanides from recycled electronic and electric light materials.
   Preliminary work has been started with a small internal grant.
   Separation of Al^{3+}, Co^{3+}, and Fe^{3+} from lower valent materials.
5. Development of a family of UMOFs by changing the crosslinking species and the reactive ligand to carboxylates, thiols, Amines, etc.

Part II. Materials Chemistry

Our goal was to combine intercalation processes and surface modification of α-zirconium phosphate, (α-ZrP) of formula $Zr(O_3POH)_2 \cdot H_2O$, to obtain materials with interesting and unusual properties. Figure 4 is a schematic of the layer connectivity and the surface of the layers of α-ZrP.



aThe hydrogen atoms were omitted for clarity.

Figure 4. Schematic representation of α-ZrP viewed down the b-axis showing the layered structure (A) and down the c-axis (B) showing the surface layer. The outlined rectangle is the true unit cell.

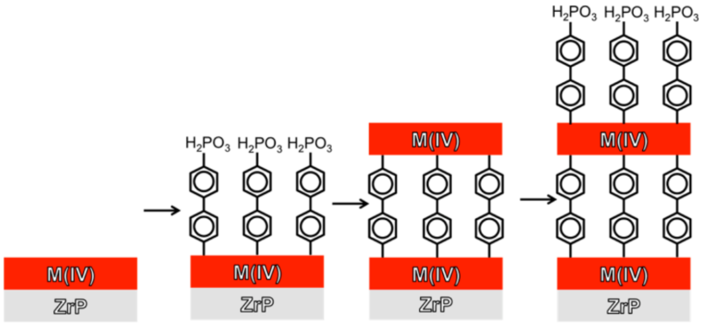
Three of the phosphate oxygen atoms cross-link Zr^{4+} above and below the central plane. This leaves a P-OH group that points into the interlayer space. The top and bottom surfaces terminate in P-OH groups as shown in Figure 4B. We have been able to bond silanes, isocyanates, epoxides, diimides and acrylates to the surface.

A second technique that we have developed is to replace the surface protons with Zr^{4+}, Sn^{4+}, Hf^{4+}. It is then possible to add phosphates, phosphonates and alcohols to bond to the four valent cations. In the case of the alcohols, they are first oxidized to phosphate groups. This is an important reaction as it also allows the surface to be covered by polyethylene glycols (PEGs) and many bio-organics.

One of the great advantages that α-ZrP provides in connection to surface studies is that the particles may be as small as 50 nm and as large as micron or centimeter size. We have utilized particles that are 100-150 nm in length and about ten to 12 layers thick. Thus, the functionalized surface is a significant portion of the whole and the amount and nature of the coverage may be determined by a variety of techniques, IR, AFM, NMR, IC, TGA, etc. It is then possible to use micron sized particles and adduce from similar tests knowledge of the surface structure that could not be gained without the earlier study on nanoparticles.

Designable Architectures on Nanoparticle Surfaces:

Technique 1: The surface of the ZrP nanoparticles was used as a platform to create layer by layer structures. This was done by placing a layer of 4+ ions on the surface and then binding a diphosphonic acid to the surface as shown in Figure 5. The process is then repeated again to build the LBL structure to the desired length. We have prepared four layers on each surface more than doubling the thickness of the particles as measured by AFM. There is no loss of the 4+ ions as additional layers are added.



aNote the assemblies are formed on both sides of the ZrP; however, only one is shown for clarity.

Figure 5. Formation of Layer-by-Layer Assemblies on the ZrP Surface by Alternating Treatment of M(IV) and Bisphosphonic Acids.

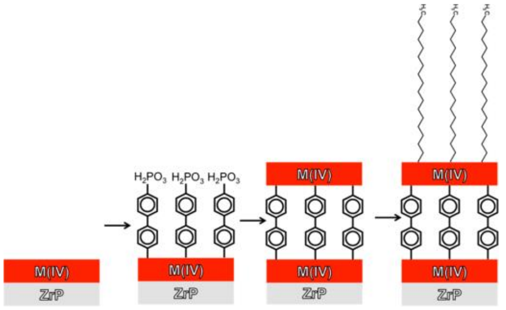


Figure 6. An example of adding a new ligand to a LBL structure.

Technique 2: At any one point in building LBL structures a different ligand may be added as shown in Figure 6. In fact, any phosphonic acid or phosphate can be added to the first, so one can mix ligands to design surfaces to fit applications.

Technique 3: If instead of using pure phosphoric acid in the preparation of α-ZrP methyl phosphonic acid is added, a mixed derivative, $Zr(O_3POH)_x(O_3P\text{-}CH_3)_{2-x}$, results. Then the surface will also have both ligands present. In this way, the surface functionalization arrangement can be changed as the methyl groups prevent reaction at those sites. This technique may induce porosity in LBL structures or space catalysts on the surface.

Technique 4: A molecule may be placed between the layers and then interact with a reactive functionalized surface. Examples include electron transfer reactions where an electron donor is placed between the layers and an acceptor on the surface. Drug delivery is another example where the drug in between the layers is shielded by protective molecules on the surface.

Technique 5: We have found that not only four valent ions may replace the surface protons but ions of lower charge may be used. We have obtained new surfaces using Cs^+ and Ca^{2+} as the replacement ion. This fact provides another means of designing surface structures.

APPLICATIONS

Our studies have led to several applications as described briefly below.

1. Polymer Composites: We had earlier prepared ZrP-polymer (composites) using single exfoliated sheets of ZrP. To increase the stiffness we now functionalize the surface of nanoparticles to make them compatible with the polymer so that the entire particle is inserted into the polymer. This was done by placing styrene oxide (StO) on the surface

of ZrP nanoparticles and adding them to a solution of styrene which was then polymerized. As much as 15% of the ZrP:StO was added to the styrene to prepare transparent films.[3*]

2. Electron Transfer Reactions: In order to understand how the surface coverage affects the electron transfer reactions, $Ru(bpy)_3^{2+}$ was placed between the layers of the nano-ZrP particles and the surfaces functionalized by three different modifiers, octadecyltrichlorosilane(OTS), Octadecylisocyanate, (ODI) and 1,2-epoxyoctadecane(EOD). P-Benzoquinone(P-BQ) served as the electron acceptor. A 0.01% (W/v) suspension of the nanoparticles was prepared in 1,2-dichlorobenzene to which was added a known volume of the P-BQ solution. The kinetics of the electron transfer reactions were studied following the Stern-Volmer model. The Stern-Volmer plot shows a quenching process where dynamic and static quenching are both present in the electron transfer reaction for all the surface modified derivatives. The system is complex and needs further study. The system will be simplified by attaching the acceptor to the functionalized particles. Given the number of variables that can be probed much new information should be forthcoming.

3. Catalysis: α-Zirconium phosphate has a long history of catalytic behavior. However the ability to functionalize the surface creates new opportunities for catalyst synthesis. This is based on the hydrophilic, hydrophobic character of the surface functionalized ZrP. Consider a beaker with water and toluene totally separated. When α-ZrP nanoparticles are added to the beaker, the particles all go to the water. Add a C_{18} function to the surface and all the particles migrate to the toluene. Our plan is to prepare organometallic catalysts bonded to the nanoparticle surface and made to disperse in the reaction media. This will be as close to homogeneous catalysis as possible but with easy recovery of the catalyst. A start in this direction has already been made. Wilkenson's catalyst has been bonded to the surface of ZrP with a silane and a hydrogenation reaction carried out with 15 repetitions by recovery and reuse of the catalyst. The rate of reaction was not visibly affected by the consecutive trials.

4. Colloid Stabilizers: Colloidal Mixtures of hydrophobic and hydrophilic components are often unstable. Our ZrP nanoparticles with surface functionalization have been shown to stabilize several such mixtures by the Pickering effect.

5. Lubricants: Tribiological characterization revealed that micron sized α-ZrP particles were effective as lubricant additives in both aqueous and non-aqueous media. Friction was reduces as much as 91% and 65%, respectively in the two media.

What Have We Learned?

Mainly what we have learned is to think outside the box. We have shown that we can decorate the surface in many different ways, also we can alter the size of the particles, change the surface functionalization in numerous ways and control electron transfer reactions. How best to utilize this knowledge will be our challenge.

E. Publication, Acknowledgements and Distribution of Funds

1. Gagnon, Kevin J.; Perry, Houston P.; Clearfield, Abraham. Conventional and Unconventional Metal-Organic Frameworks Based on Phosphonate Ligands: MOFs and UMOFs. *Chemical Reviews* (2012), 112, 1034-1054.

ACKNOWLEDGMENT

The authors thankfully acknowledge the National Science Foundation (Grants DMR-0652166, HRD-0832993, and DGE-0750732), the Department of Energy (Grant DE-FG02-03ER15420), Savannah River National Laboratory (Grant AC-70059-0), and the Robert A. Welch Foundation (Grant A0673) for financial support.

DISTRIBUTION: NSF 25%; DOE 25%; SRNL 25%; Welch 25%

This is a review article and so it brings together several aspects of wide ranging studies. The DOE-BES grant was used to prepare the UMOFs described in this report and the ion change data obtained at this early stage of investigations. The NSF Grant DMR-0652166 was used to prepare new families of zirconium alkyl MOFs which we termed ZACs, ZATs and ZAGs depending on their structure. The SR grant AC70059-0 funds were used to prepare pharmacosiderites for removal of Cs^+, Sr^{2+} from nuclear waste. The Welch grant A0673 was used to synthesize porous. Aluminum biphenyl phosphonate phosphates.

2. Burns, J. D.; Clearfield, A.; Borkowski, M.; Reed, D. T. Pillared metal (IV) phosphate-phosphonate extraction of actinides. *Radiochim. Acta* (2012), 100, 381-387.

ACKNOWLEDGMENT

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, through Grant DE-FG02-03ER15420 and Savannah River National Laboratories through Grant AC-70059-0, for which grateful acknowledgment is made. A very special thanks to the entire LANL team at the Carlsbad Environmental Monitoring and Research Center, who are supported by the Waste Isolation Pilot Plant program under the direction of the DOE/EM Carlsbad field office (CBFO), for allowing me to conduct the actinide studies in their facilities, as well as lending their expertise to help better shape the experiments.

DISTRIBUTION: DOE BES 50%; SRNL 50%

DOE, BES Grant DE-FG02-03ER15420 was used to characterize the UMOFs and separate lanthanides in the 3+ state from ions with charges of 2+ and 1+. The SR funds Grant AC-70059-0 was allocated to work done at the Carlsbad Research Center for training to handle actinides and to determine their reactions with ion exchangers.

3. Clearfield, A.; Medvedev, D. G.; Kerlegon, S.; Bosser, T.; Burns, J. D.; Jackson, M. Rates of Exchange of Cs^+ and Sr^2 for Poorly Crystalline Sodium Titanium Silicate (CST) in Nuclear Waste Systems. *Solv. Extra. Ion Exch.*, (2012), 30, 229-243.

ACKNOWLEDGMENT

It is a pleasure to acknowledge that this research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. Heavy Element Chemistry Program under Grant No. DE-FG02-03ER15420. The undergraduate authors, S. Kerlegon, T. Bosser, and M. Jackson, were supported by the National Science Foundation supplement to Grant No. DMR-0652166.

DISTRIBUTION: DOE 90%; NSF 10%

The research on kinetics of Cs^+ and Sr^{2+} uptake by sodium titanium silicate (CST) was supported by DOE, BES Grant DE-F602-03ER15420. The NSF funds were used to support three undergraduates in a summer research program.

4. Burns, J. D.; Shehee, T. C.; Clearfield, A.; Hobbs, D. T. Separation of Americium from Curium by Oxidation and Ion Exchange. *Analytical Chemistry*, (2012), 84, 6930-6932.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, Fuel Cycle Research and Development Program via Grant AC-70059-0 through the Savannah River National Laboratory and the Office of Basic Energy Sciences through Grant DE-FG02 03ER15420, for which grateful acknowledgement is made.

DISTRIBUTION: DOE BES 50%; SRNL 50%

Distribution similar to number 2.

5. Burns, J. D.; Borkowski, M.; Clearfield, A.; Reed, D. T. Separation of oxidized americium from lanthanides by use of pillared metal(IV) phosphate-phosphonate hybrid materials. *Radiochim. Acta*, (2012), 100, 901–906.

ACKNOWLEDGMENT

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, through Grant DE-FG02-03ER15420 and Savannah River National Laboratories through Grant AC-70059-0, for which grateful acknowledgement is made. A special thanks to the entire LANL team at the Carlsbad Environmental Monitoring and Research Center, who are supported by the Waste Isolation Pilot Plant program under the direction of the DOE/EM Carlsbad field office (CBFO), for allowing the actinide work to be conducted in their facilities, as well as lending their expertise to help better shape the experiments. We thank Michael Richmann who conducted the ICP-MS analyses of the Am/Nd systems.

DISTRIBUTION: DOE BES 50%; SRNL 50%

Distribution same as paper numbers 2 and 4.

6. Clearfield, A. Twenty-five Years of Nuclear Waste Remediation Studies, in *Environmental Application of Nanomaterials - Synthesis, Sorbents and Sensors* 2nd edition, Fryxell, G. E.; Cao, G.; Eds.: Imperial College Press, London, UK. Chapter 7, 159-206 (2012).

ACKNOWLEDGMENT

The author gratefully acknowledges financial support from the Department of Energy Basic energy Science for Grant DE-FG02-03ER 15420, Savannah River Nuclear Solutions – AC 70059-0 and earlier grants from both organizations.

DISTRIBUTION: DOE 50%; SRNL 50%

This paper is a summary of the work done in separations related to nuclear waste remediation in papers 1, 2, 4 and 5.

Materials Science

7. Clearfield, A., Perry, H.P. and Gagnon, K. J. Porous Pillared clays and Layered Phosphates. In: Comprehensive Inorganic Chemistry II, Jan Reedijk and Kenneth Poeppelmeier, editors. Vol 5. Oxford: Elsevier; 2013. pp. 170-211. Electronic ISBN: 9780080965291, Print ISBN: 9780080977744

ACKNOWLEDGMENTS

The authors would like to thank the following funding organizations for their continued support for some of the work presented herein as well as the authors themselves: Department of Energy Basic Energy Science under grant DEFG02-O3ER15420, National Science Foundation under grants DMR-0652166 and DGE-0750732 (K.J.G.), the Robert A. Welch Foundation under grant A-0673, and Savanah River National Lab under grant AC70059-0.

DISTRIBUTION: DOE 35%; NSF 30%; SRNL 15%; Welch 20%

This article for Comprehensive Inorganic Chemistry II is a summary of work done with clays and references 294 papers. The DOE Grant DE-FG02-03ER15420 summarized a great deal of work dealing with UMOFs synthesis, characterization, structure and theory of their strange ion exchange behavior. The Savannah River Grant AC 70059-0 dealt with some of the nuclear studies, the NSF grants DGE-076732 was a fellowship to Kevin J. Gagnon (now at Lawrence Berkeley Synchrotron) NSF DMR 0652166 covered work on pillared clays and related subjects and the Welch Grant A-0673 dealt with zirconium phosphate studies.

8. Mosby, B.M.; Goloby, M.; Díaz, A.; Bakhmutov ,V.I.; Clearfield, A. Designable Architectures on Nanoparticle Surfaces: Zirconium Phosphate Nanoplatelets as a Platform for Tetravalent Metal and Phosphonic Acid Assemblies. *Langmuir*, (2014), 30 (9), 2513-2521. dx.doi.org/10.1021/la404839n

ACKNOWLEDGMENTS

This work was supported by the Texas A&M University Graduate Diversity Fellowship (B.M.M.), the Robert A. Welch Foundation Grant No. A-0673, the National Science Foundation Grant # DMR-0652166, and the US Department of Energy Grant DE-FG02-03ER15420, for which grateful acknowledgment is made. We also acknowledge the X-ray Diffraction Laboratory and Department of Geology and Geophysics at Texas A&M University for the use of the XRPD and electron microprobe facilities.

DISTRIBUTION: DOE 70%; Welch 10%; NSF 15%

The work was begun with funds from NSF DMR-0652166 which expired early in the study and was not reviewed. The Welch funds were used to support an undergraduate Mark Goloby during the summer of 2012 after the NSF funds expired. Then the project was funded for the Materials Science Division DOE, BES Grant DE-FG02-03-ER15420. It is seen that the bulk of the work was done under this grant.

9. Mosby, B.M.; Díaz, A.; Clearfield, A. Surface Modification of Layered Zirconium Phosphates: A Novel Pathway to Multifunctional Materials. *Dalton Trans.*, (2014), 43(27), 10328-39. DOI:10.1039/c4dt00613e

ACKNOWLEDGEMENTS

This work was supported by the Texas A&M University Graduate Diversity Fellowship (B.M.M.), the Robert A. Welch Foundation Grant no. A-0673, the National Science Foundation Grant # DMR-0652166, and the US Department of Energy Grant DE-FG02-03ER15420, for which grateful is made. We also acknowledge the X-ray. Diffraction Laboratory at Texas A&M University for the use of the X-ray powder diffract meter. We acknowledge Dr Angel Martí for his help with the steady-state fluorescent and transient lifetime measurements at the Department of Chemistry at Rice University, and for his help in the data interpretation. We also acknowledge Dr Vladimir Bakhmoutov at the Chemistry NMR Laboratory for assistance with the solid-state NMR experiments.

DISTRIBUTION: DOE 80%; Welch 10%; NSF 10%

The same situation as in paper number 8.

10. Silbernagel, Rita; Díaz, Agustín; Steffensmeier, Eric; Clearfield, Abraham; Bluemel, Janet. Wilkinson-type Hydrogenation Catalysts Immobilized on Zirconium Phosphate Nanoplatelets. *J. of Mol. Catal.A: Chemical* 394 (2014) 217-223.

ACKNOWLEDGEMENTS

We thank The Robert A. Welch Foundation (A-1706), NSF (CHE-0911207 and CHE-1300208), and the APPEAL Consortium for financial support. The authors also thankfully acknowledge the U.S.Department of Energy, Office of Nuclear Energy, Fuel Cycle Research and Development Program (AC-70059-0) through the Savannah River National Laboratory. Furthermore, we thank the Office of Basic Energy Sciences (DE-FG02-03ER15420), the National Science Foundation (DMR-0652166), and the Robert A. Welch Foundation (A-0673) for financial support. We thank

B. Mosby for performing SEM measurements, Dr. V. Bakhmutov and J. Pope for recording solid-state NMR spectra, and R. Guillemette for the use of the micro-probe.

DISTRIBUTION: DOE-BES 40%; Welch 5%; NSF 5%

This study was a collaboration between Dr. Bluemel and Dr. Clearfield. Thus, our share was about 50%. We prepared the zirconium phosphate particles and fixed the catalyst on the surface. My graduate student ran the experiment with the help of Dr. Bluemel's student. Thus, our percent of the study was 60% in which the NSF and Welch were each about 5% and DOE 50% of the total.

F. Publications not acknowledging DOE BES but representing applications related to the present study through collaborations.

1. Mejia, Andres F.; Diaz, Agustin; Pullela, Srinivasa; Chang, Ya-Wen; Simonetty, Michael; Carpenter, Carrie; Batteas, James D.; Mannan, M. Sam; Clearfield, Abraham; Cheng, Zhengdong. Pickering emulsions stabilized by amphiphilic nano-sheets. *Soft Matter*, (2012), 8, 10245-10253.
2. He, X.; Xiao, H.; Choi, H.; Díaz, A.; Mosby, B.M.; Clearfield, A.; Liang, H. α-Zirconium Phosphate Nanoplatelets as Lubricant Additives. *Colloids and Surfaces A*, (2014), 452, 32-38.
3. Silbernagel, Rita; Díaz, Agustín; Steffensmeier, Eric; Clearfield, Abraham; Bluemel, Janet. Wilkinson-type Hydrogenation Catalysts Immobilized on Zirconium Phosphate Nanoplatelets. *J. of Mol. Catal.A: Chemical* 394 (2014) 217-223.

G. Personnel Involved

1. Agustin Diaz, Post- doc. Surface functionalization electron transfer reactions, Janus Particles, Applications. Current Position: Senior Research Chemist at REM Surface Engineering, Brenham, Texas.
2. Jonathan D. Burns, Graduate Student. Separations of lanthanides and actinides, nuclear waste. Graduated December 2012, Ph.D. Current Position: Staff Position at Oak Ridge National Laboratory.
3. Kevin J. Gagnon, Graduate Student. UMOFs and ZACs, ZATs, ZAGs a alkyl MOFs under pressure, Synthesis and structure. Graduated August 2013, Ph.D. Current Position: Project Scientist at Lawrence Berkeley Synchrotron.
4. Tiffany L. Kinnibrugh, Graduate Student. Synthesized porous aluminum phosphonate phosphates, X-ray powder pattern data structure solutions. Graduated June 2013, Ph.D. Current position: Post-doc at Argonne National Laboratory.
5. Brian M. Mosby, Graduate Student. Materials Science Self assembled monolayers (SAMS), Designable Surface Architectures, Nanoparticles. Graduated May 2014. Current Position: Post-doc at University Illinois.
6. Rita Silbernagel, third year graduate student. Separation of lanthanides and actinides, Catalysis.

7. Undergraduates:
   Undergraduate Students:
   1. Grant McElhany
   2. Kylee Stouder
   3. Eliazar Candanoza
   4. Sarah Herstein
   5. Alyssa Rosas
   6. Mark Goloby
   7. Nancy Garcia
   8. Zachary Beal

H. Current Research Support

1. Nuclear Energy University Program (DOE)
Title: Mixed Metal Phosphonate-Phosphate Resins for Separation of Lanthanides from Actinides
Grant Award #: DE-NE0000746
Total Award Amount: $589,039.00
Award Period: 02/05/2014 – 02/04/2017

2. The Welch Foundation
Title: Metal Phosphonates as Crystal Engineered Solids and Platforms for Drug Delivery
Grant #: A-0673
Total Award Amount: $75,000 per year
Award Period: 6/1/13 – 5/31/16