SAND2022-14435C

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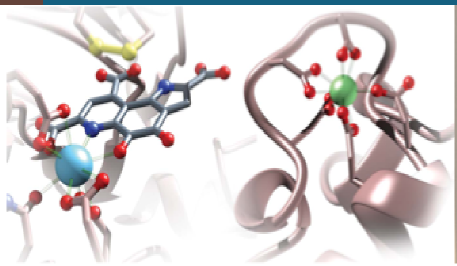
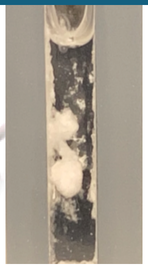
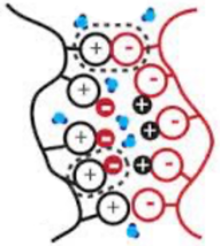
Polyelectrolyte Slime: A Tool for Critical Materials Harvesting

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TechConnect World Innovation Conference & Expo

Polymers and Nanotechnology 2022
October 16-19, 2022
Napa, CA

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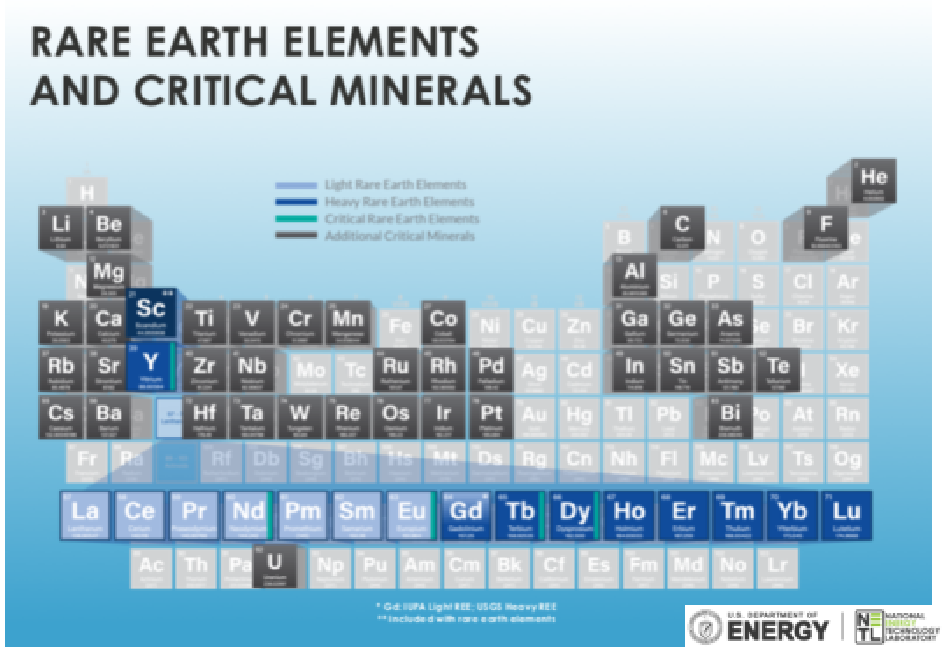
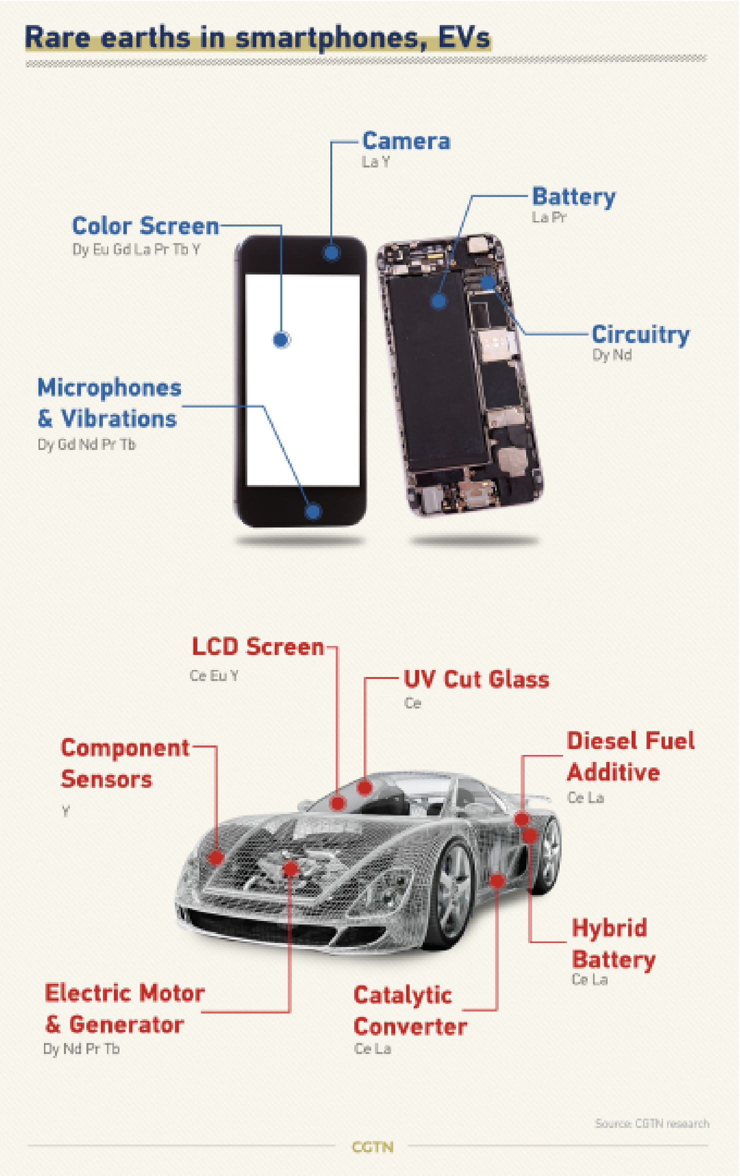
Rare Earths Metals (REMs) Are Technologically Important



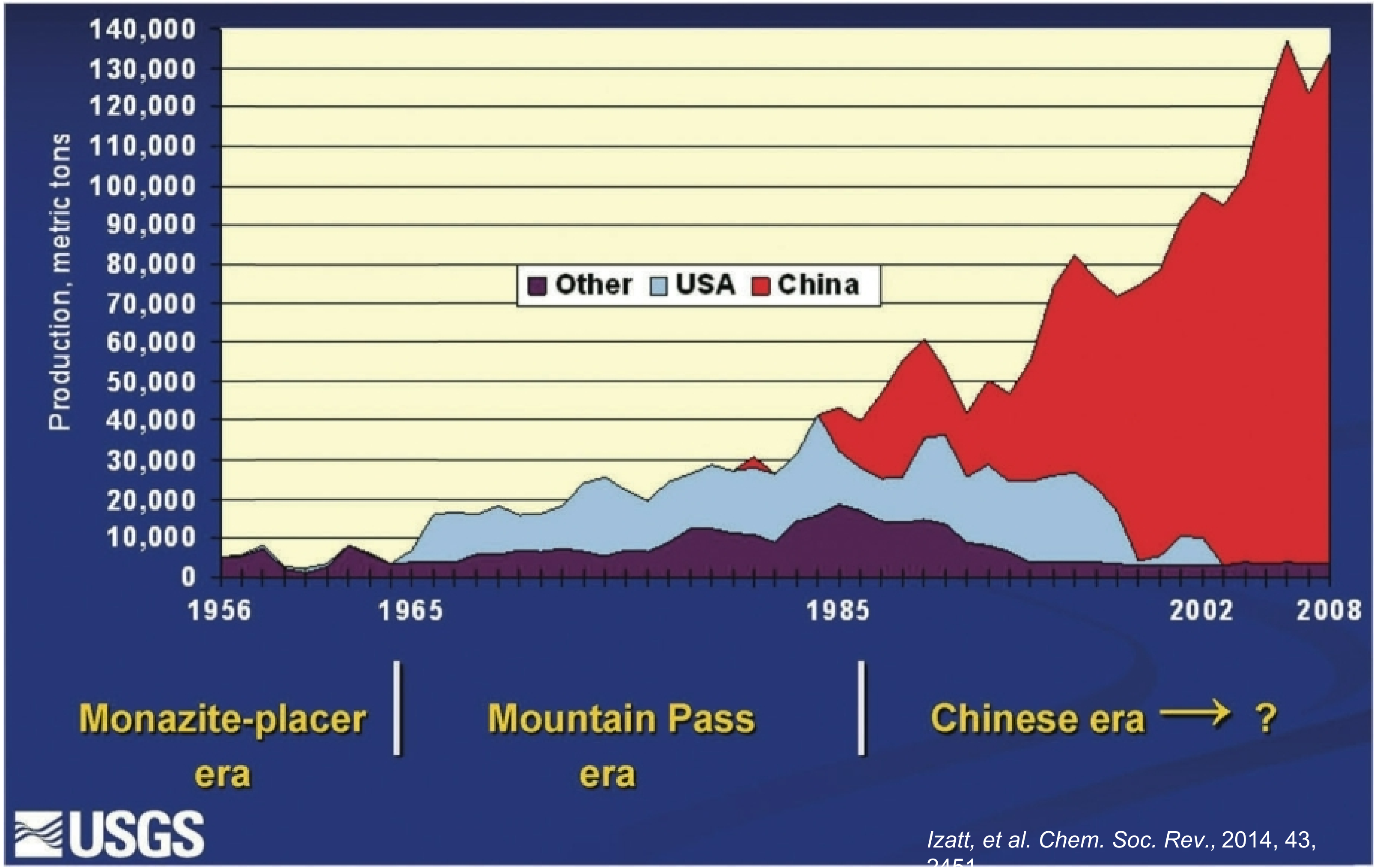
Rare earth metals (REMs; lanthanides plus yttrium and scandium) are critical materials:

- telecommunications,
- energy infrastructure and renewable energy
- lighting
- medical technologies,
- defense technologies
- other essential advanced systems.



Where Do We Get REMs?

The U.S. was once a leader in REM mining and production…



Izatt, et al. Chem. Soc. Rev., 2014, 43, 2451

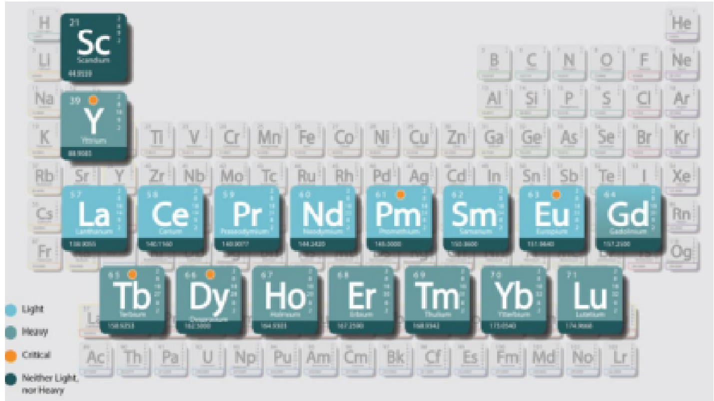
Where Do We Get REMs?

Today, the U.S. relies on 100% import for many critical minerals.

Mineral Commodity	2019 U.S. net import reliance	Top Producer	Mineral Commodity	2019 U.S. net import reliance	Top Producer
arsenic	100%	China	**barite**	87%	China
cesium	100%	Canada	**antimony**	84%	China
fluorspar	100%	China	**rhenium**	82%	Chile
gallium	100%	China	**cobalt**	78%	Congo
graphite (natural)	100%	China	**tin**	77%	China
indium	100%	China	**aluminum (bauxite)**	>75%	China
manganese	100%	China	**chromium**	>75%	South Africa
niobium	100%	Brazil	**platinum group**	64%	South Africa
rare earth group	100%	China	**magnesium**	52%	China
rubidium	100%	Canada	**germanium**	>50%	China
scandium	100%	China	**tungsten**	>50%	China
strontium	100%	Spain	**lithium**	>25%	Australia
tantalum	100%	Rwanda	**beryllium**	<21%	U.S.
bismuth	96%	China	**hafnium**	n.d.	Australia
tellurium	>95%	China	**uranium**	n.d.	Kazakhstan
vanadium	94%	China	**helium**	net exporter	U.S.
titanium	93%	China	**zirconium**	net exporter	Australia
potash	91%	Canada			

n.d. not enough information to calculate the import reliance

USGS Mineral Commodity Summaries 2020



Rare Earth Metals (REE)

Critical:
Nd, Tb, Dy, Eu, Y, Er, Pr

Uncritical: La, Sm, Gd

Excessive (supply > demand):
Ce, Ho, Tm, Yb, Lu

REM Harvesting Challenges

REMs are:

- Naturally dilute
- Found in complex mixtures
- Similar charge, size, and chemistry

Current methods:

- Thousands of mixer-settler tanks
- Energy & chemically-intensive
- Large ammonia consumption
- ***Toxic, carcinogenic and hazardous to aquatic life/environment.***

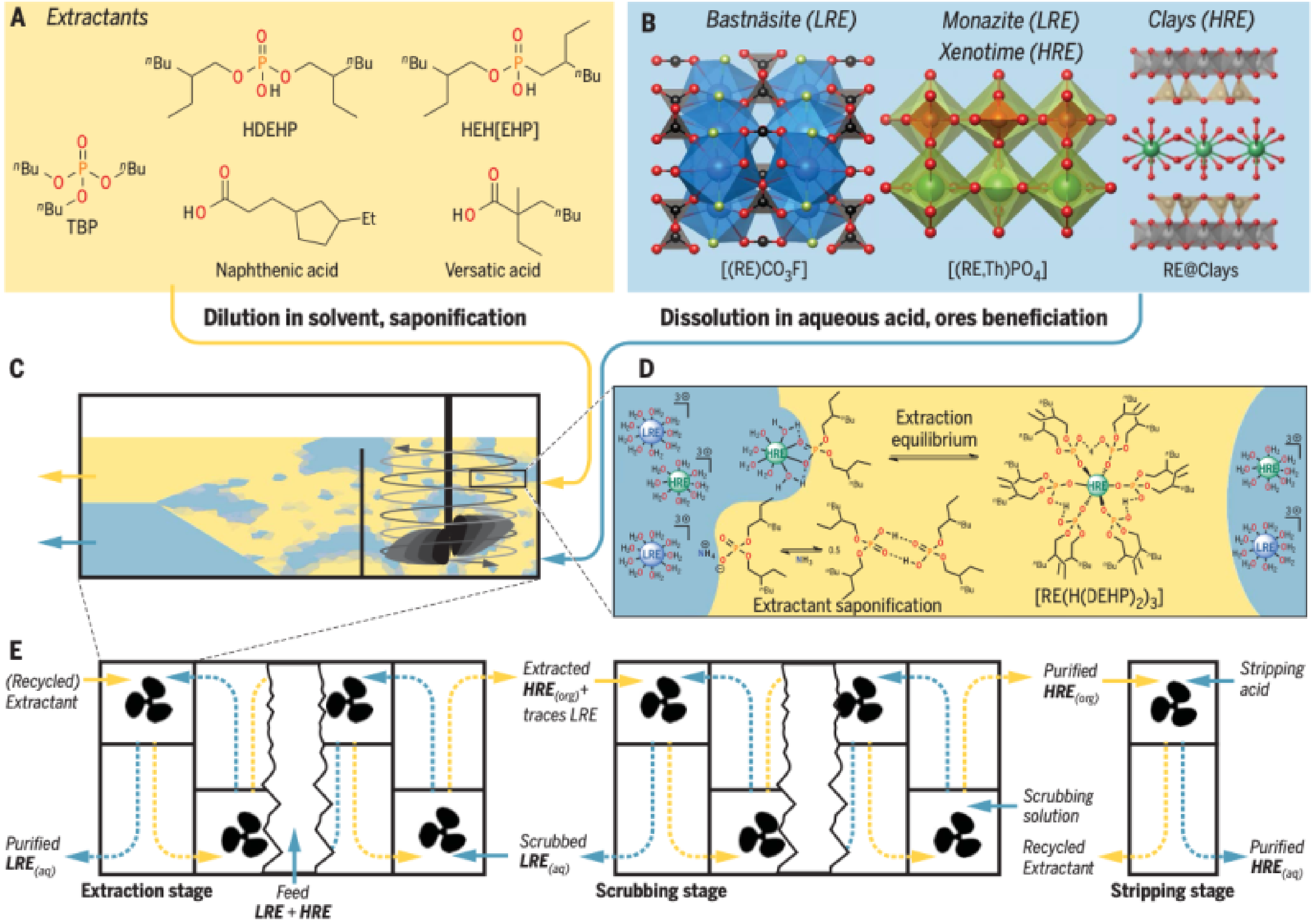


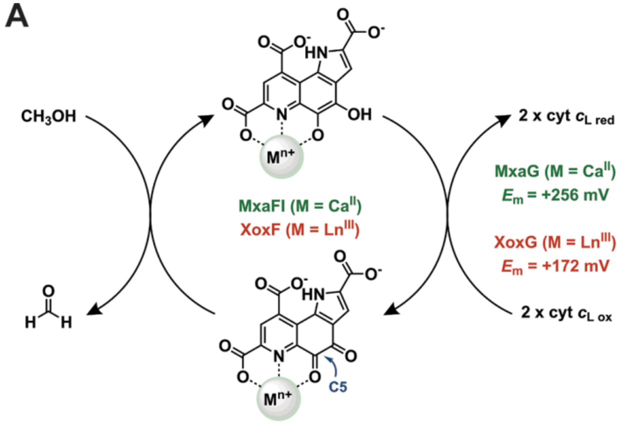
Fig. 2. Solvent extraction. (**A**) Commonly used extractants. (**B**) Typical RE-containing minerals. (**C**) Cut-off side view of a simple mixer-settler unit. (**D**) Schematic extraction equilibria. (**E**) Flow chart (top view) of batteries of mixer-settlers in a model industrial process with extraction, scrubbing, and stripping stages.

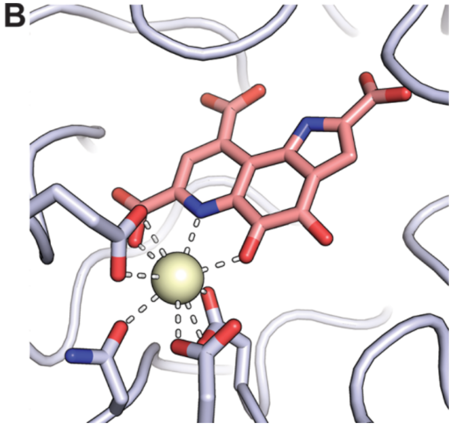
Cheisson, T. & Schelter, E. J. Rare earth elements: Mendeleev's bane, modern marvels. *Science* **363**, 489-493 (2019).

Selective Bio-Inspired Harvesting of Rare Earth Metals

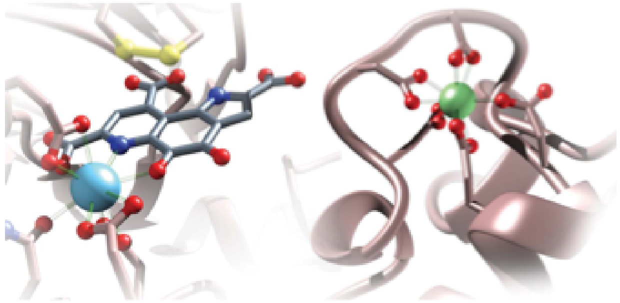
Biological Systems Have Created a Solution…

Methyltrophic bacteria, which rely on the catalytic conversion of methanol as a primary carbon and energy source, *depend on highly-selective binding* of lanthanide (LN)-group REMs to enable these critical catalytic processes.

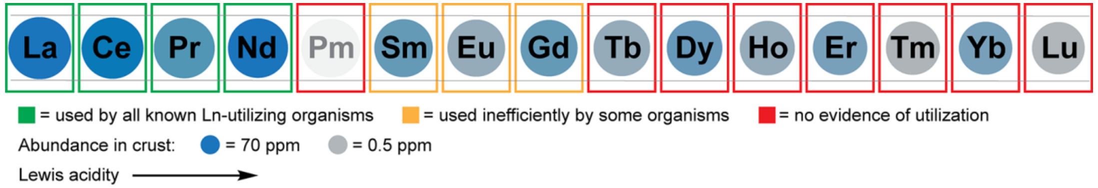




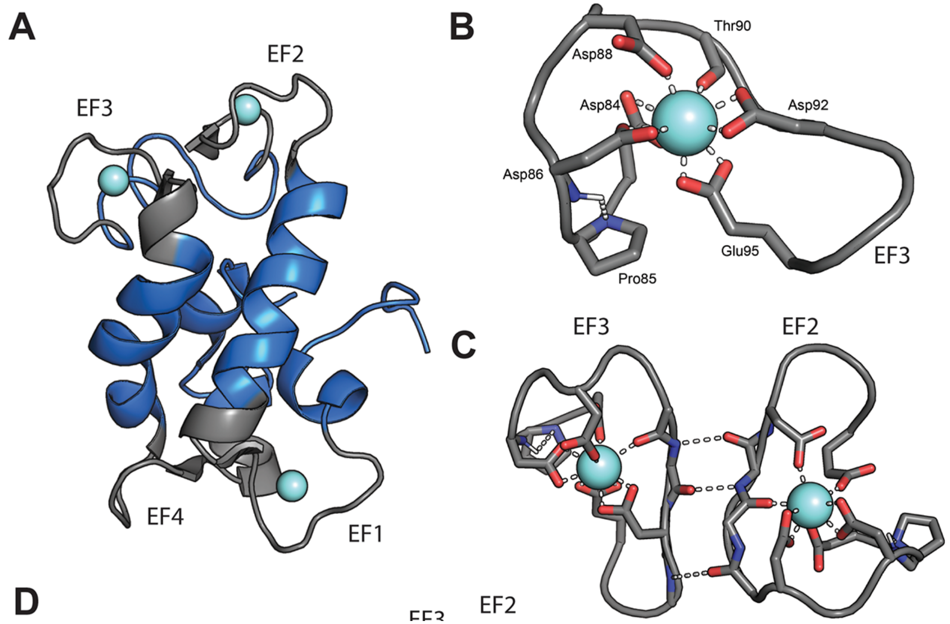
J.A. Cotruvo, *ACS Cent. Sci*. 2019, **5**, 1496

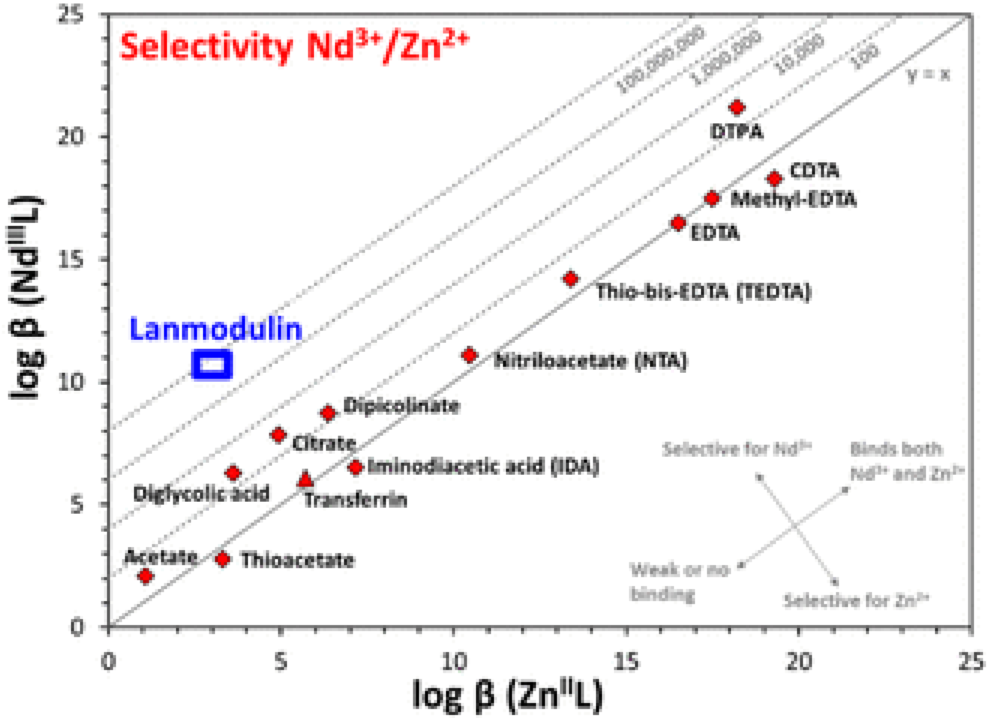


Cheisson, T. & Schelter, E. J. *Science* **363**, 489-493 (2019).



Lanmodulin (LanM) has remarkable REM Binding Selectivity





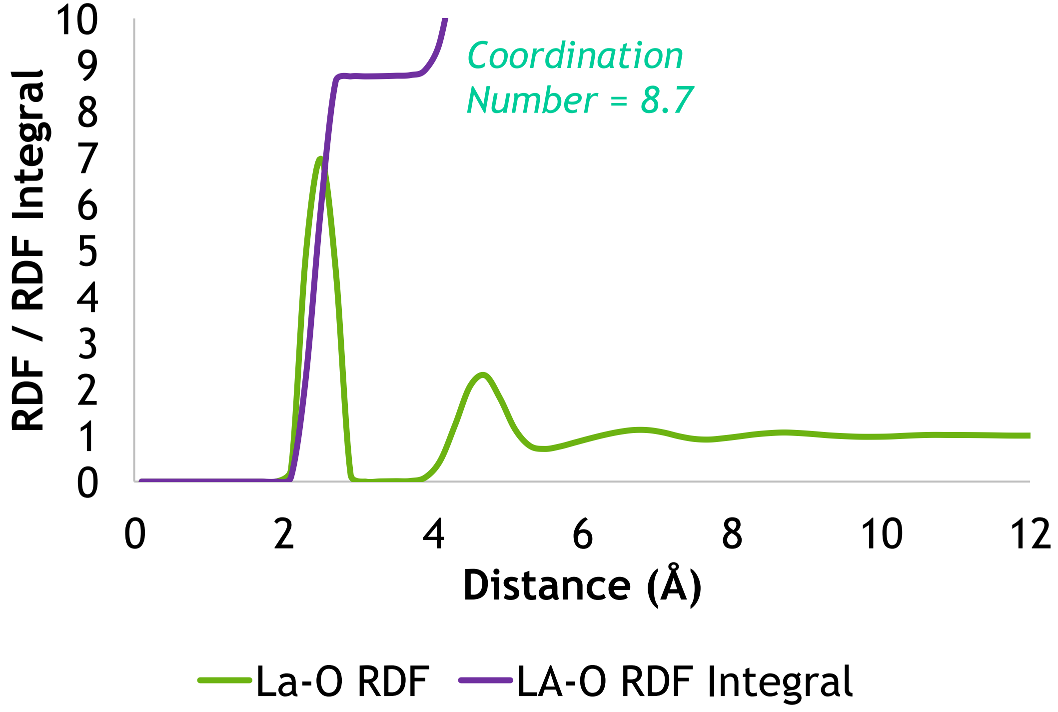
LanM has been shown to have a strong affinity, (K_d ~1-10 pM for a range of lanthanides, compared to ~1 mM for Ca^{2+}).

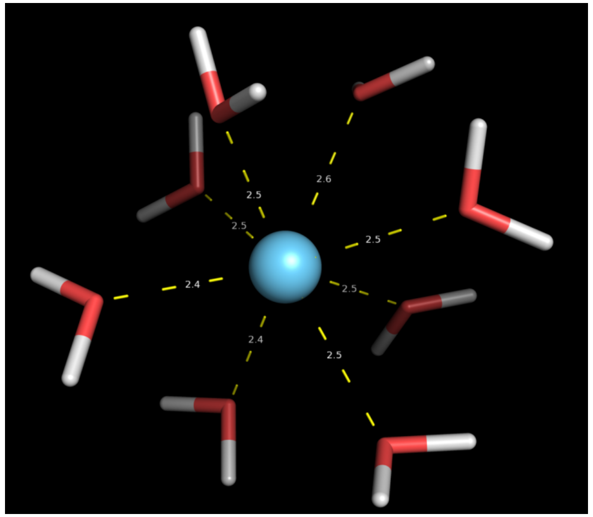
"REE/non-REE selectivity of LanM is orders of magnitude higher than most small molecules or macromolecules ever studied."
- Deblonde, et al.

***We hypothesize** that specific compositional and structural properties of biological ligands that govern selective interactions with solubilized REMs can be distilled to inform synthetic bio-inspired analogs for REM extraction and separation.*

Deblonde, G. J. P. *et al.* Selective and Efficient Biomacromolecular Extraction of Rare-Earth Elements using Lanmodulin. *Inorganic Chemistry* **59**, 11855-11867, (2020).

Lanthanides are Strongly Coordinated by Waters!

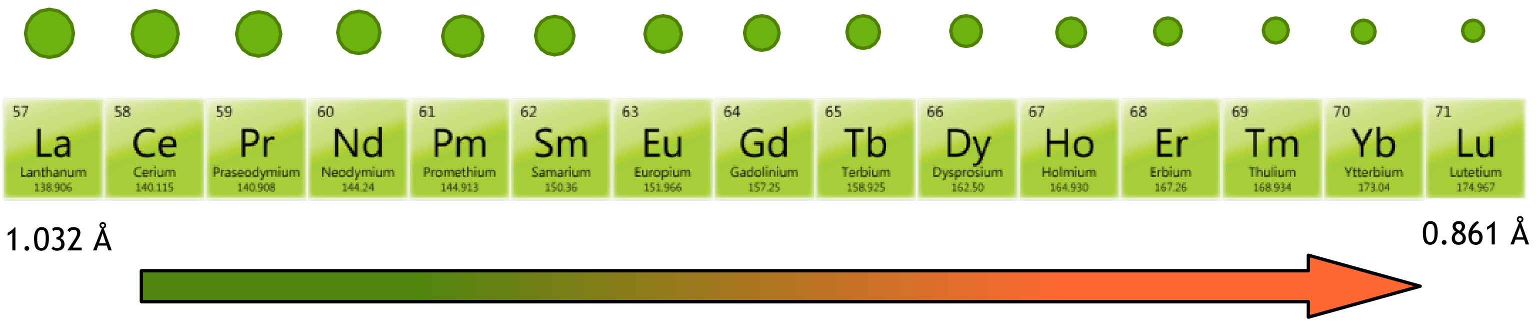




Example first shell of La^{3+} in water from an MD trajectory with distances displayed in angstroms (2.4-2.6Å).

Size decreases across the series

Coordination Number ~9



Coordination Number ~8

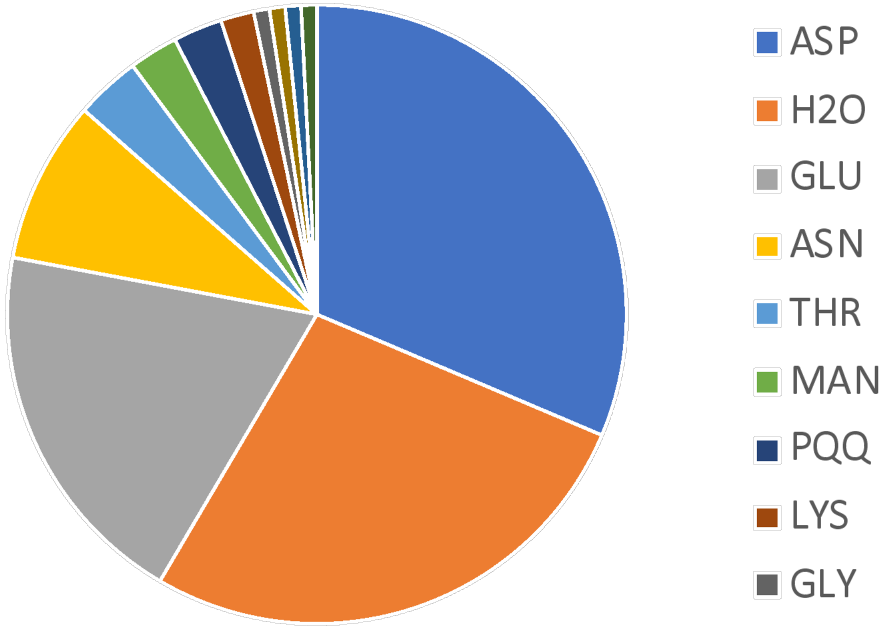
Lowest hydration energy

Highest hydration energy

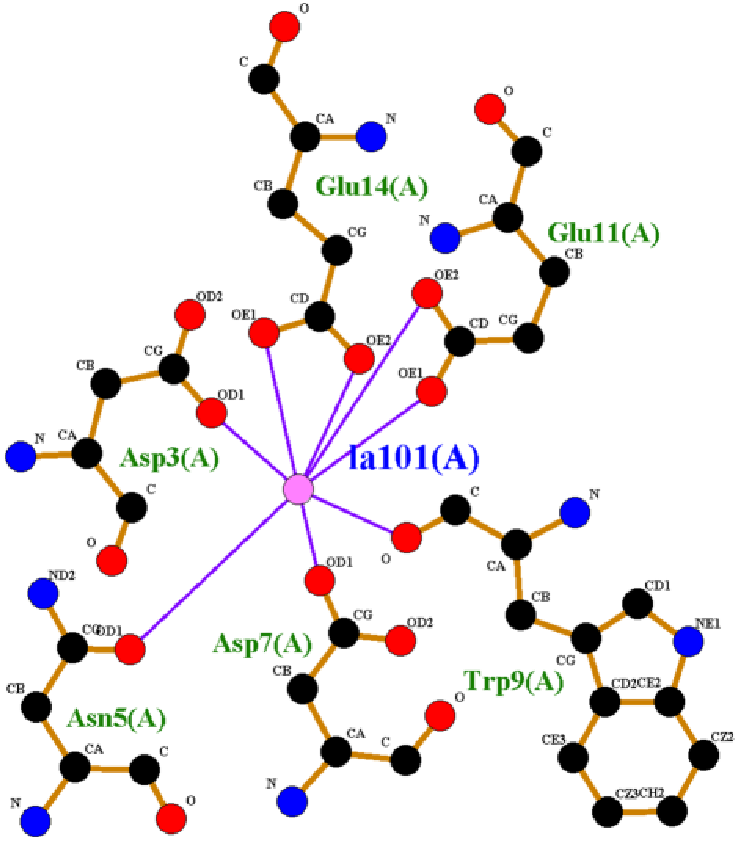
THE UNIVERSITY OF TEXAS AT AUSTIN

J. Gourary, P. Ren, and S. Rempe

Computational Modeling: Binding Pocket is Rich in Acid, Amide, and Amines, and Water



- 15 Lanthanum Containing PDB Structures
- 27 Valid Lanthanum Binding Sites
- 153 Binding Site Residues
- 5.9 Residues per Binding Site
- 7.8 Contacts per Binding Site



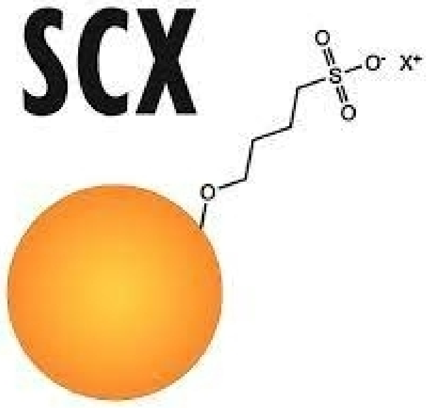
Binding Site from a Lanthanum Binding Tag protein (7CCO)

Natural REM binding structures are structurally complex, but share common ligand chemistries.

J. Gourary, P. Ren, and S. Rempe

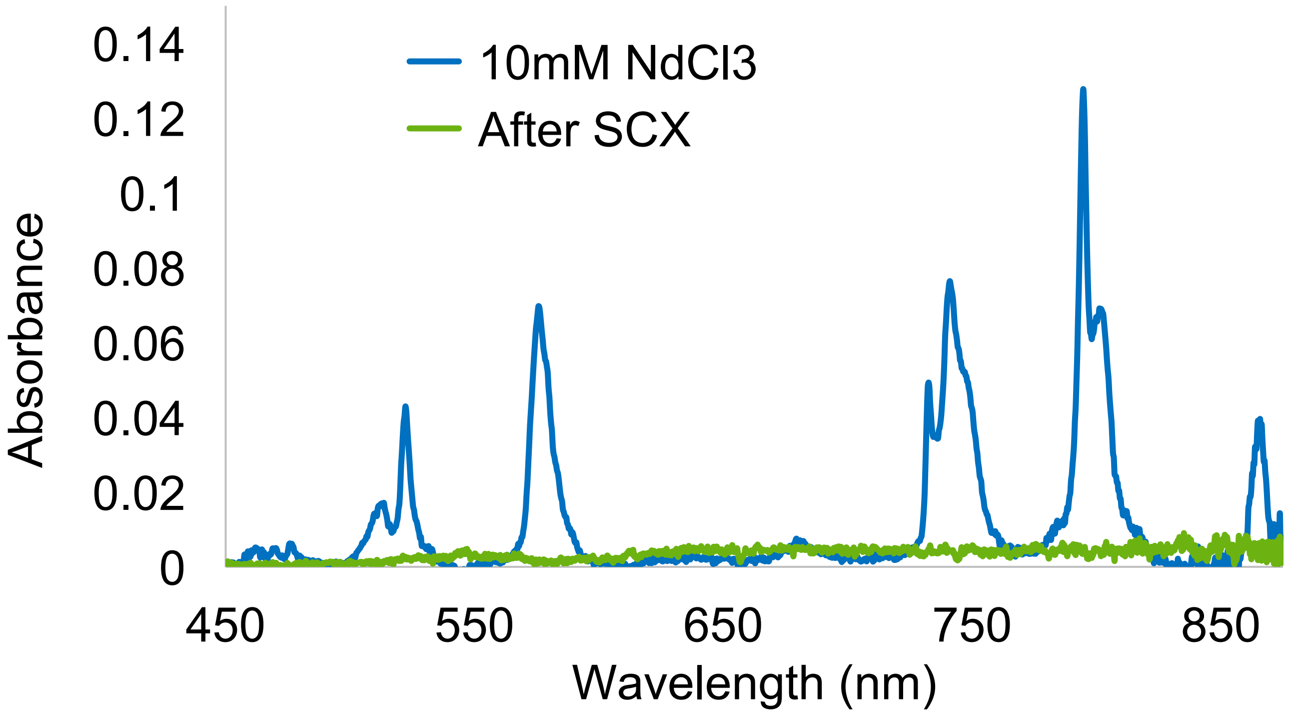
Proof of Principle Ion Capture: Acid Ion Exchange Resin

Flowing dissolved Nd^{3+} solution through commercial ion-exchange resin, showed feasibility of removing REM from solution.



Burdick & Jackson strong cation exchange resin (sulfonic acids)

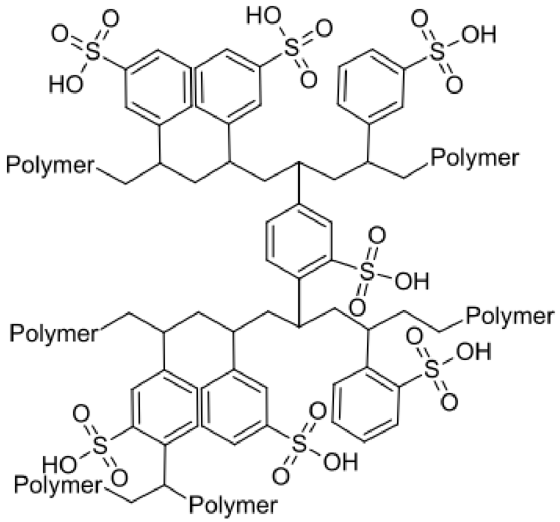
UV-Vis Spectroscopy



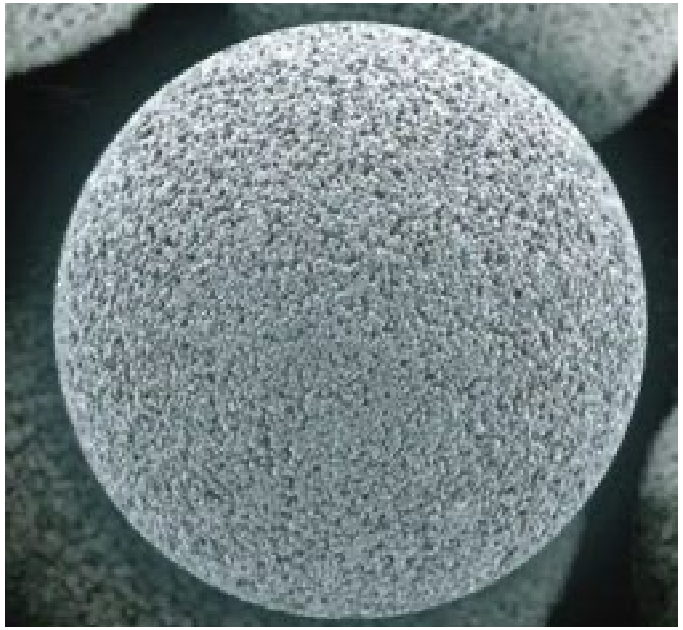
This process is not selective or reversible, however.

Composition Alone is Not Enough!

The the environment created by the solid support, as well as the structure of the ligand may be important!



Successful capture was enabled with a micro/nanoporous matrix…

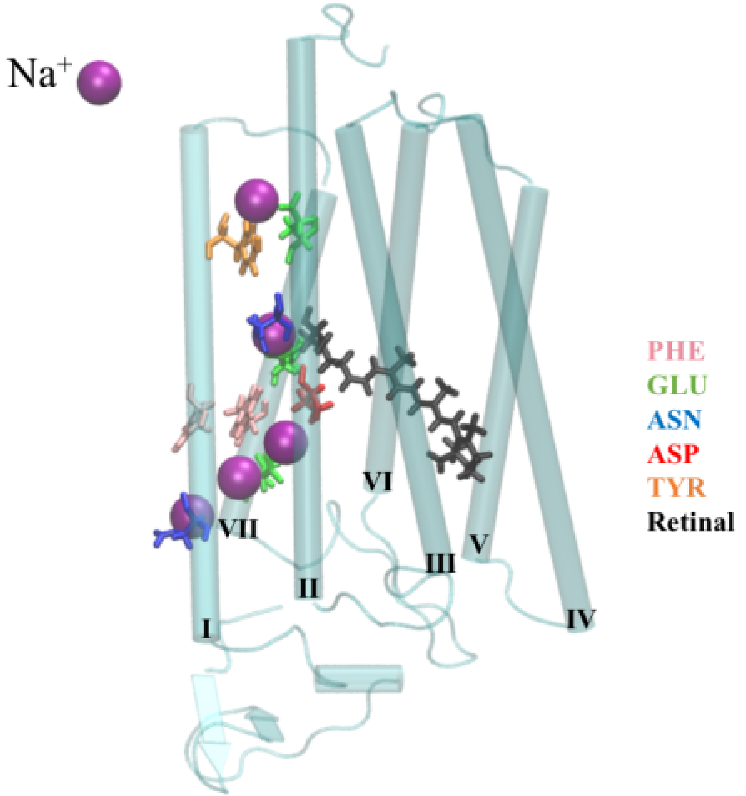


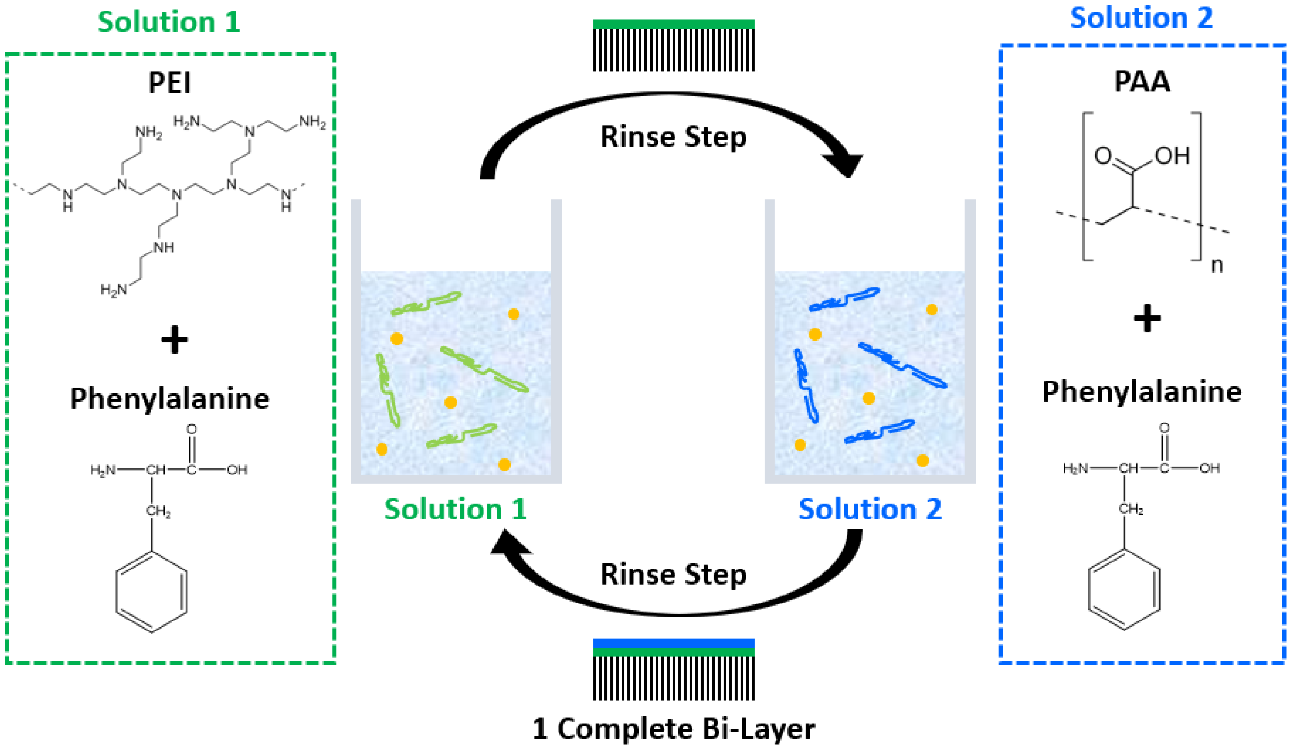
Commercial PSDVB-PA
(~ 5 μm diameter)

Exploring Supramolecular Alternative Capture

We have previously explored the use of bio-inspired polyelectrolytes to *moderate ion transport* in thin films.

Discovery of Phe-role in biological ion channel inspired introduction of Phe into synthetic thin films.

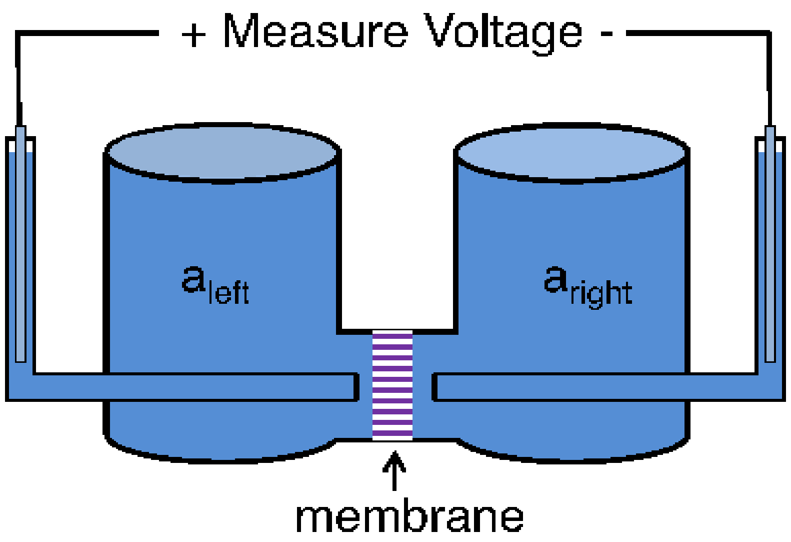




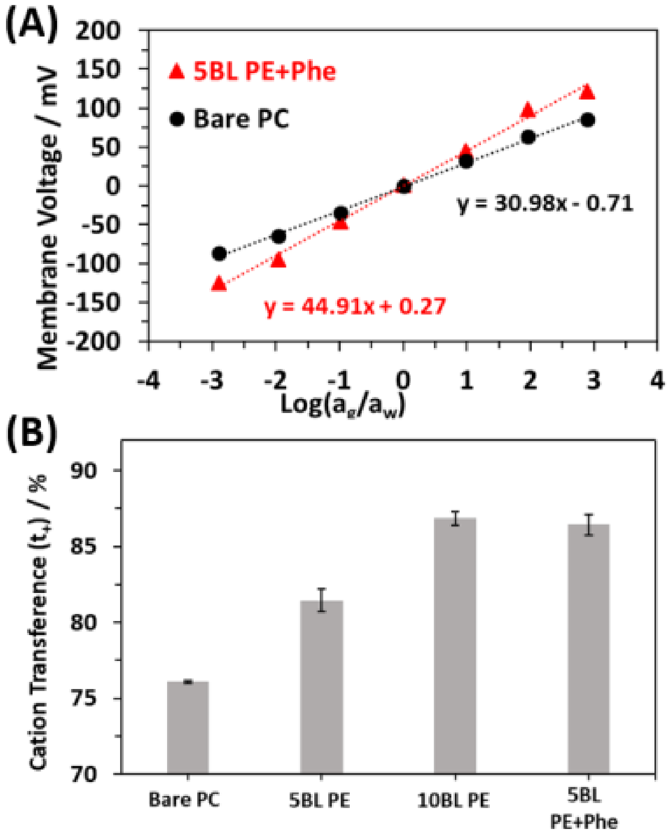
Percival, Rempe, Small, Spoerke, *et al.*. *Soft Matter*, DOI: 10.1039/d1sm00134e (2021).

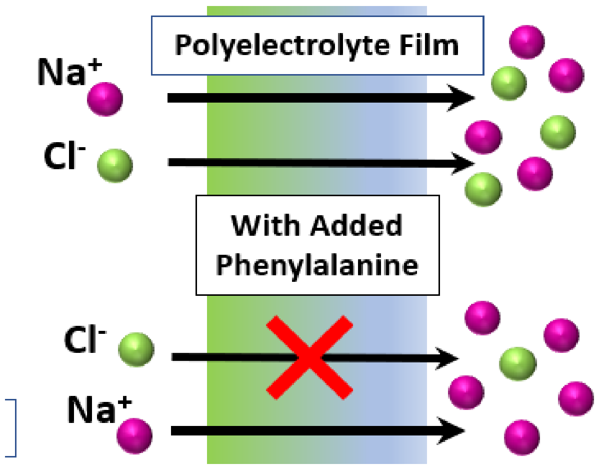
Polyelectrolyte Films Impact Selective Ion Transport

We have previously explored the use of bio-inspired polyelectrolytes to *moderate ion transport* in thin films.



$$V_m = 0.059(t_+ - t_-)\log\frac{a_g}{a_w}$$



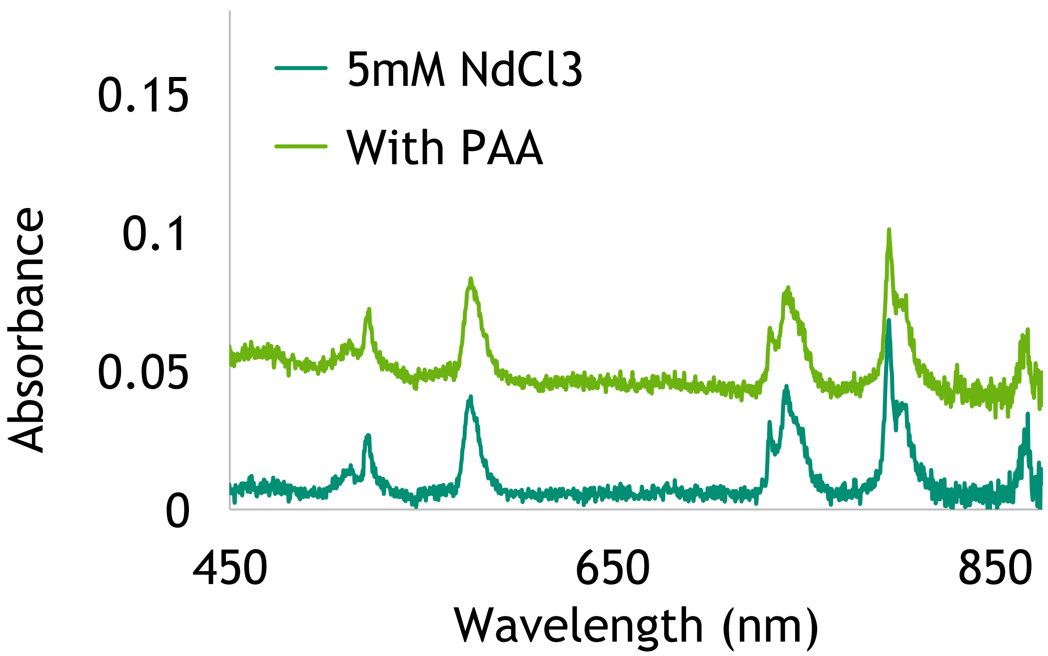


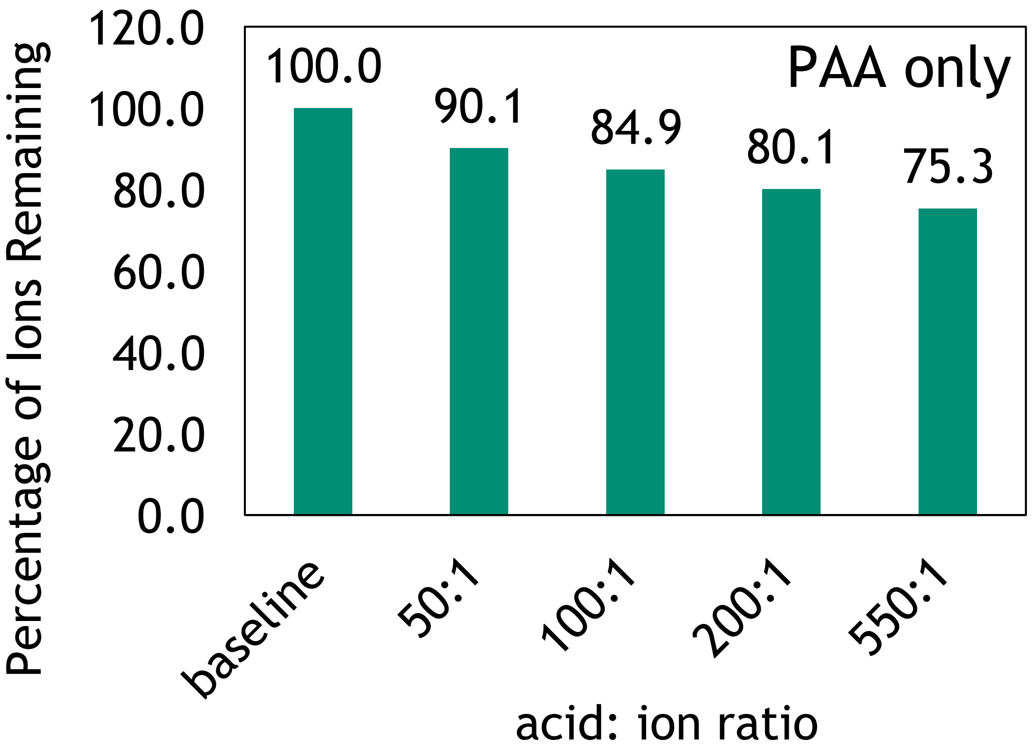
The polyelectrolyte film, modified with a bio-inspired amino acid, resulted in significant improvement in ionic selectivity of polyelectrolyte membranes.

Percival, Rempe, Small, Spoerke, *et al.*. *Soft Matter*, DOI: 10.1039/d1sm00134e (2021).

Can We Capture Rare Earths Using Poly-Acrylic Acid?

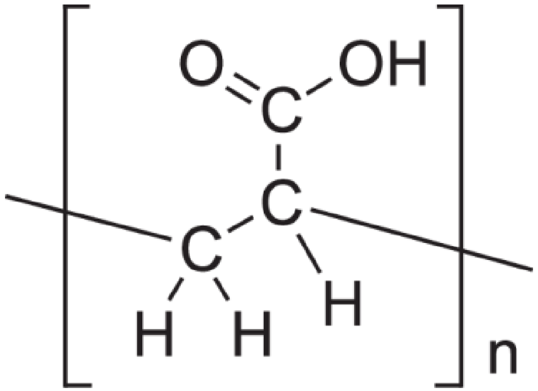
Polyacrylic acid alone is capable of very limited capture



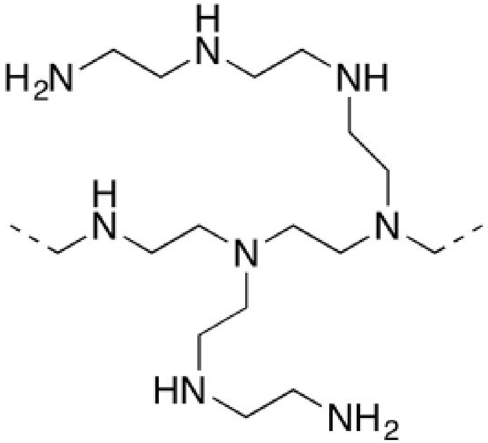


Can We Capture Rare Earths Using a Supramolecular Polyelectrolyte?

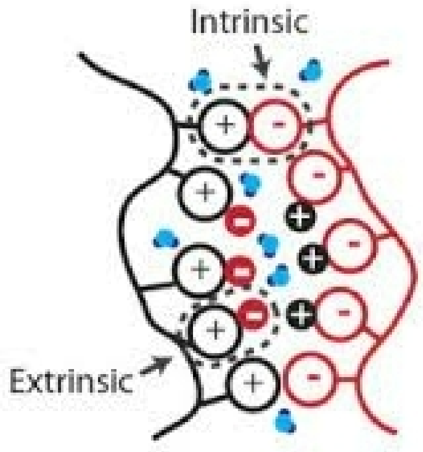
High concentrations of acids and amines in LanM binding pocket motivated polyelectrolyte studies of ion binding.



Poly (acrylic acid) (PAA)



Polyethyleneimine (PEI) (branched)

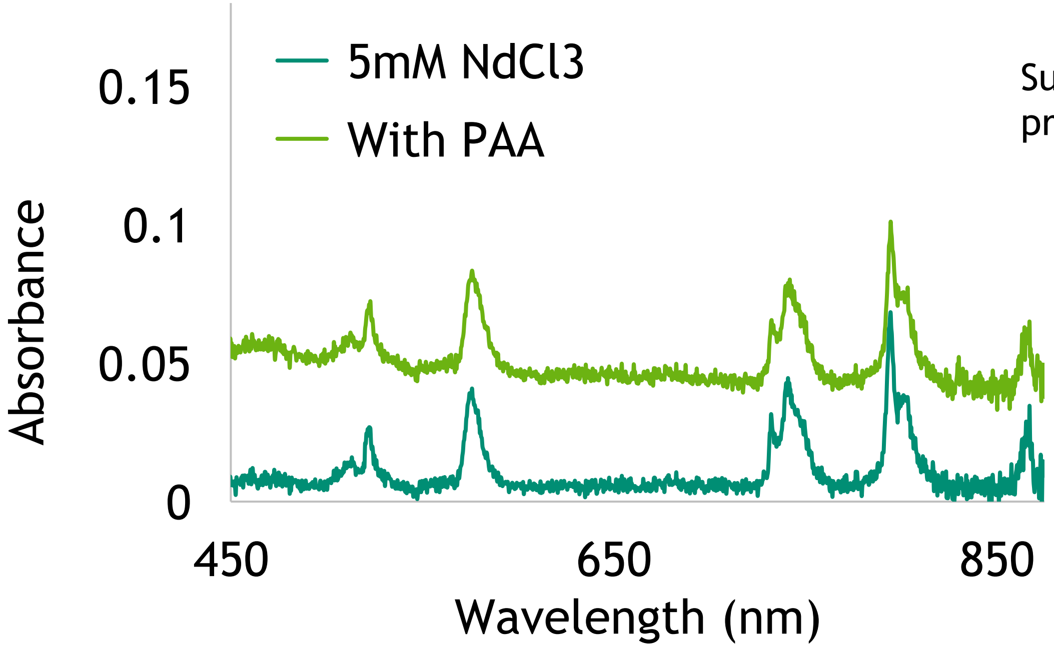


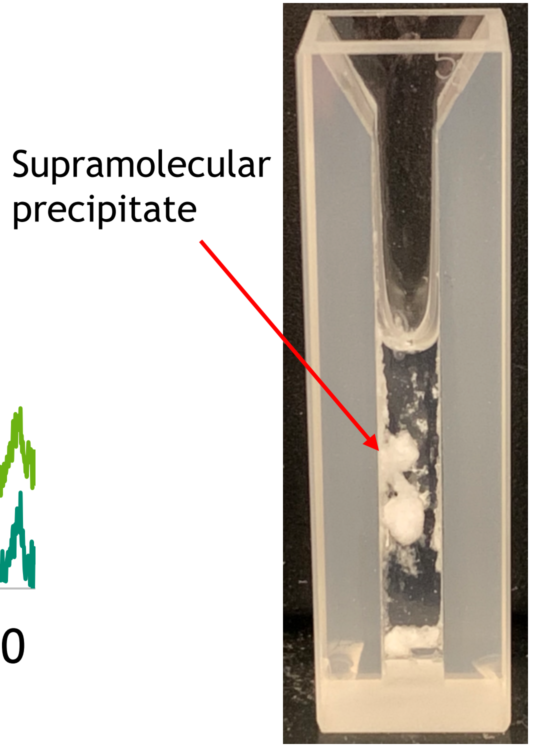
Polyelectrolyte (PE) complex

Objective: simple, inexpensive, non-toxic procedure to extract REM's

Slimed! Forming a Polyelectrolyte Precipitate

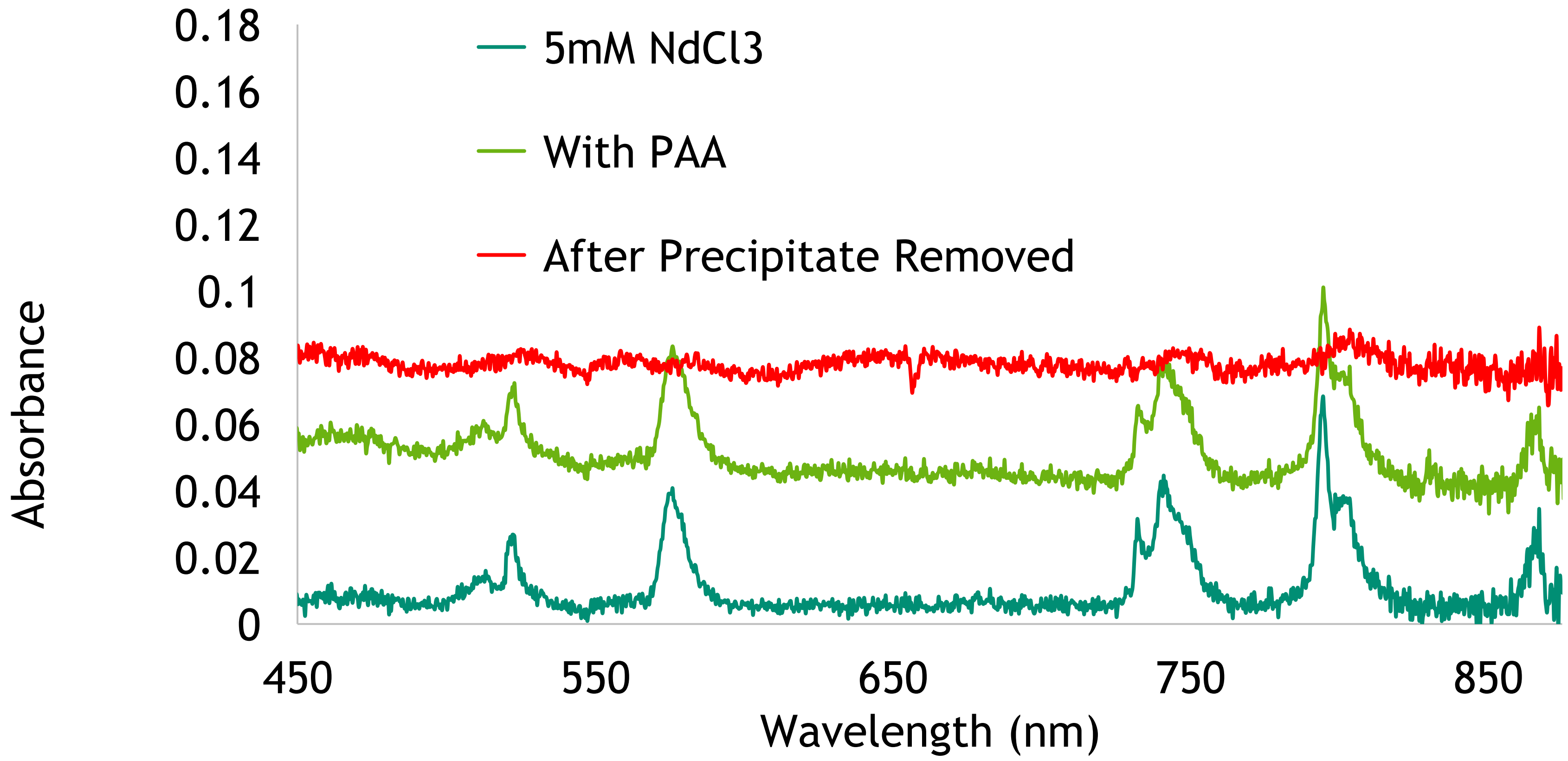
Adding PEI to the solution leads to the rapid formation of a coherent, viscous precipitate.



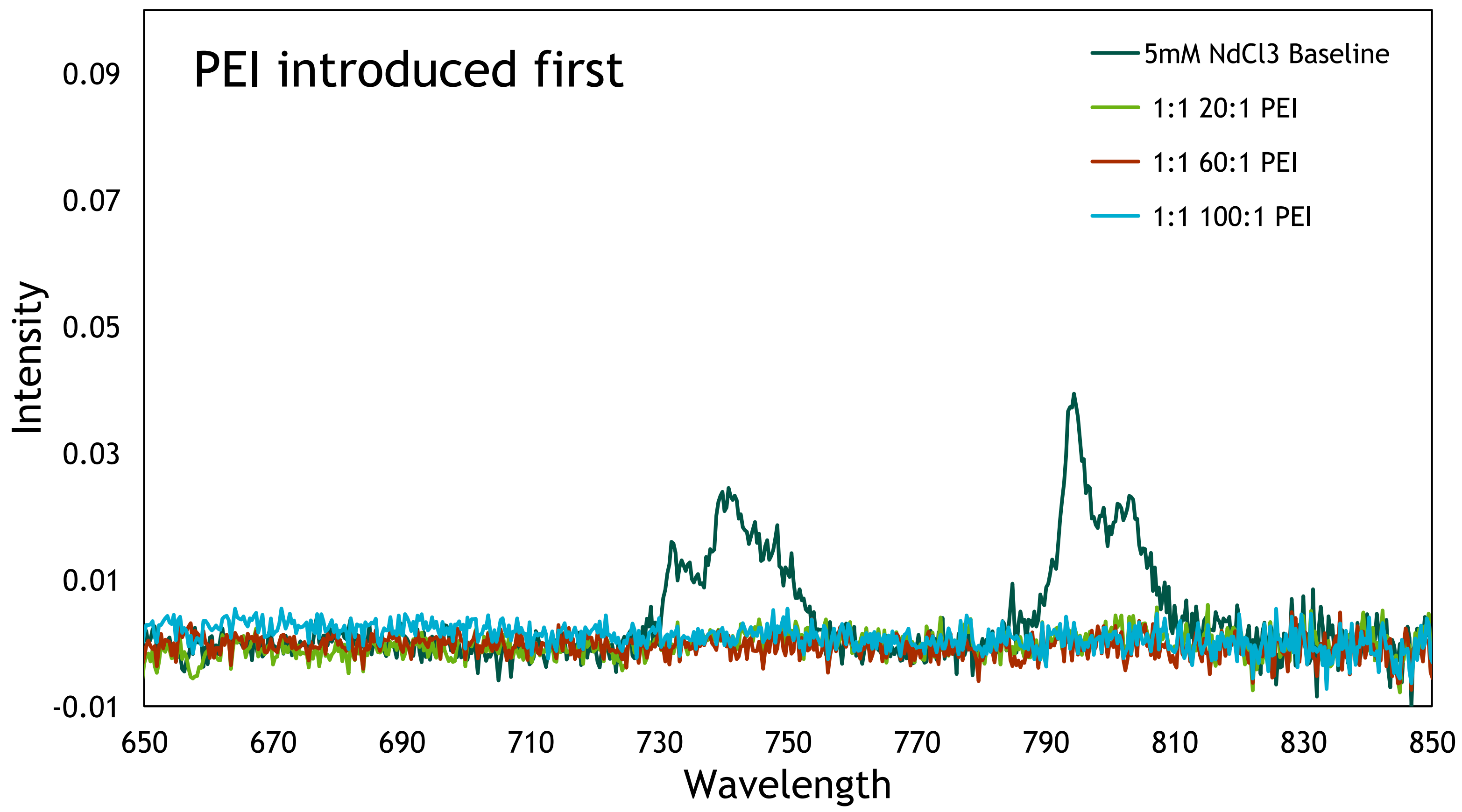


Capture of the Ions in a Supramolecular Aggregate!

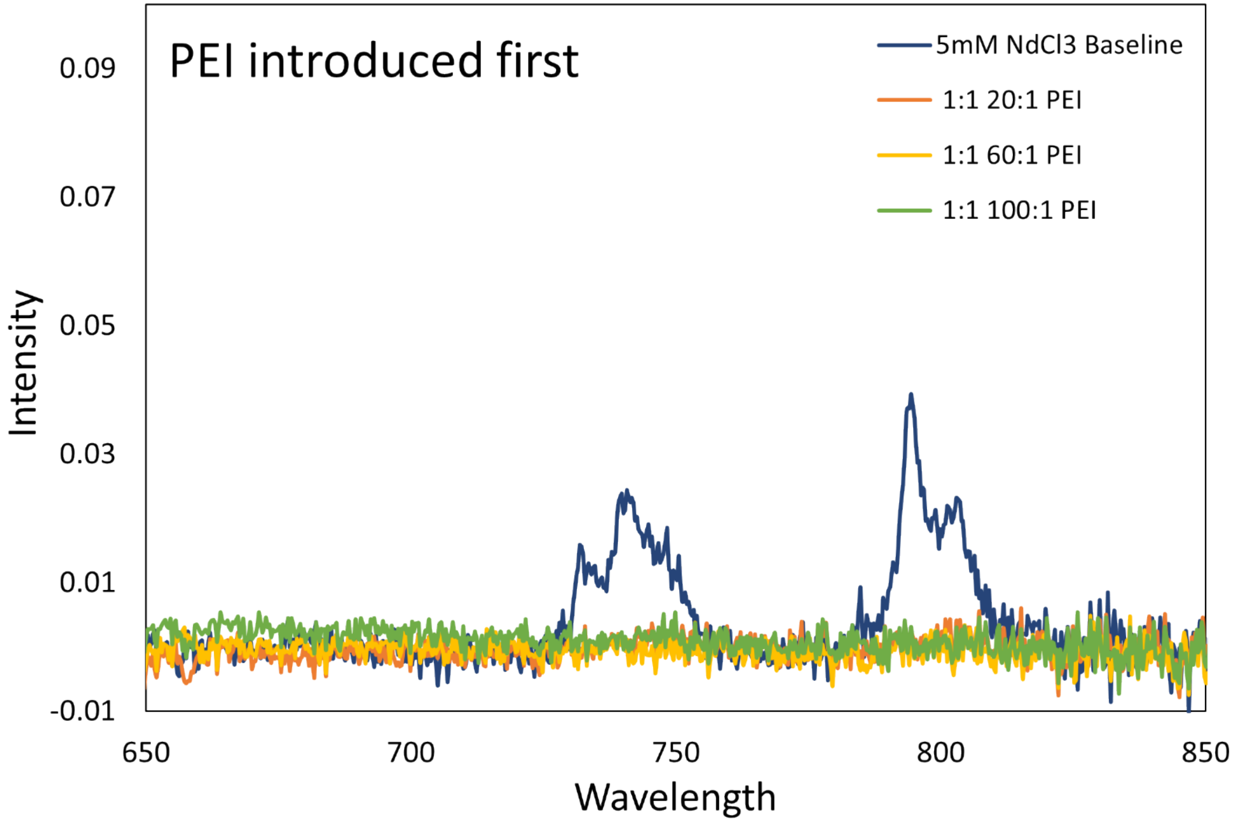
Removal of the precipitate leads to removal of the Nd^{3+}

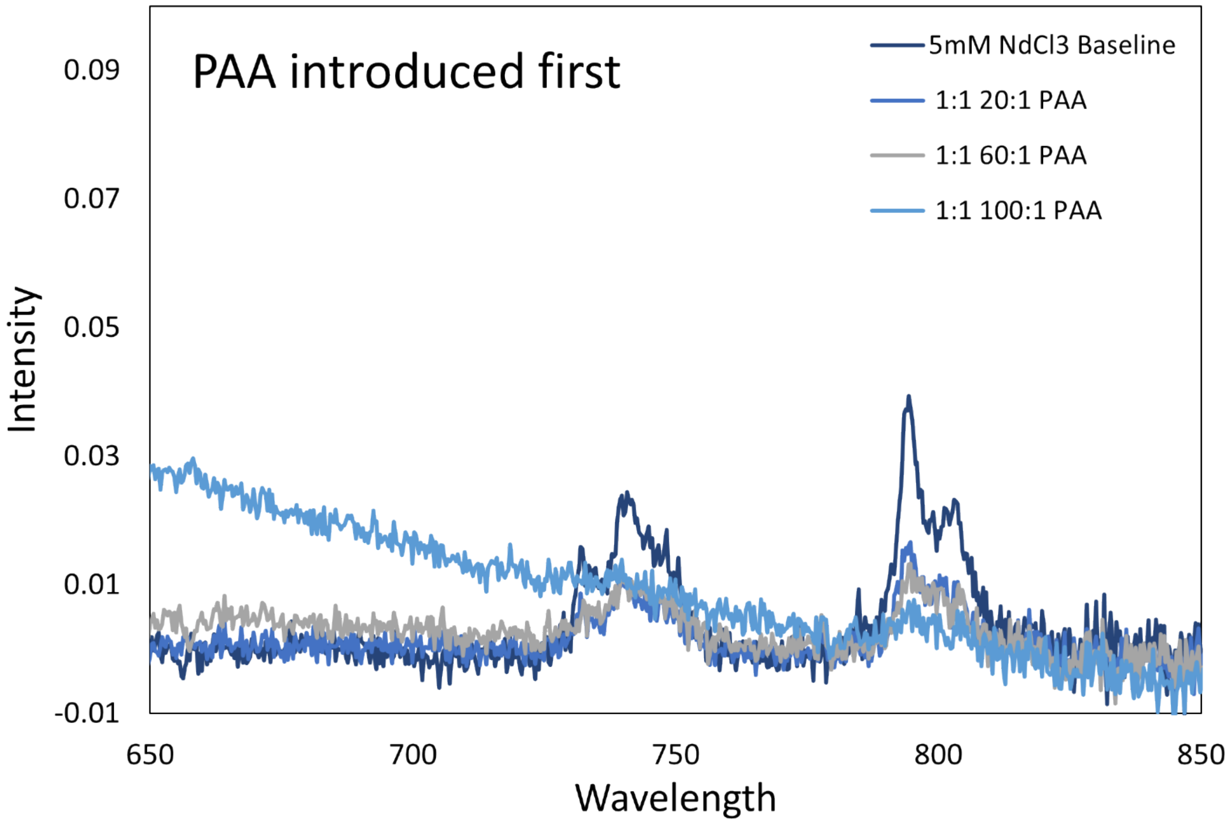


What if We Reverse the Order of Addition?



The Order of Introduction of Polymers Matters

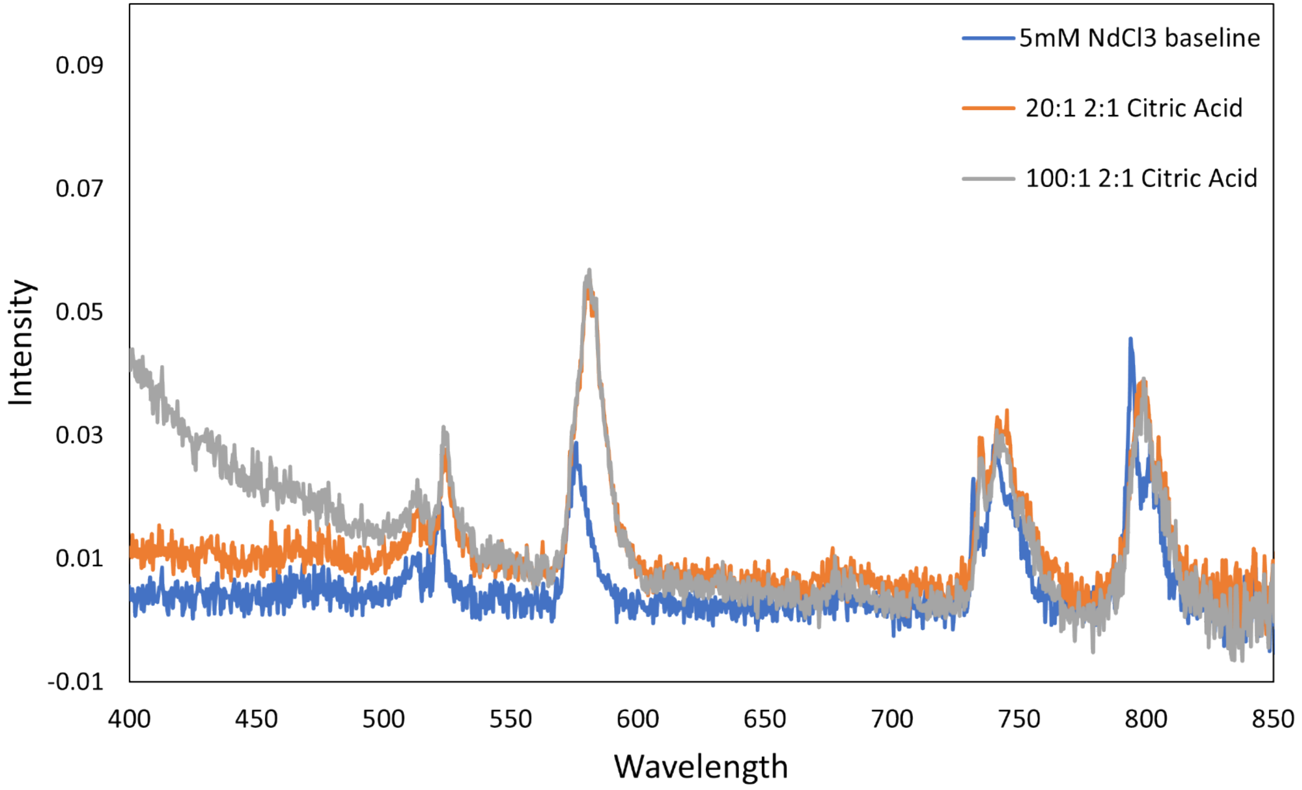




- ➢ Nd concentration decrease by 4.9-5mM (99-100%) in all trials of $NdCl_3$ introduced to PEI first.
- ➢ **PEI interaction with ions first results in a greater capture of ions w/ lower quantity of materials**

- ➢ Nd conc. decreased by 2.9mM (59%) for 20:1 acid to ion ratio
- ➢ Nd conc. decreased by 3.3mM (67%) for 60:1 acid to ion ratio
- ➢ Nd conc. Decreased by 4mM (81%) for 100:1 acid to ion ratio

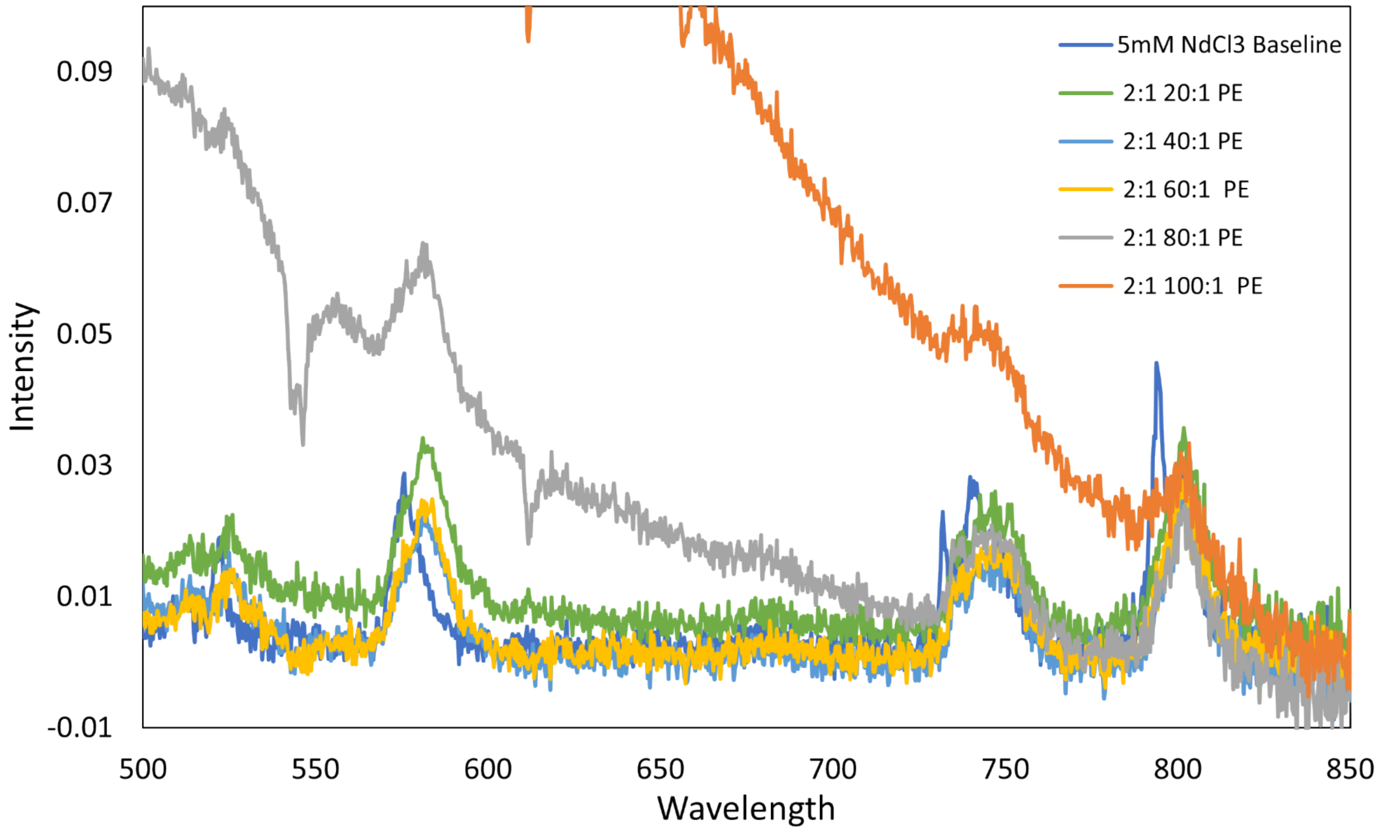
PEI Complex Formation Matters



- Citric Acid substituted for PAA results in peak shifts and failure to fully capture ions
- Peak shifts observed due to alteration of environment around ions.
- Polymeric form of acids crucial for formation of the PE complex to capture ions effectively

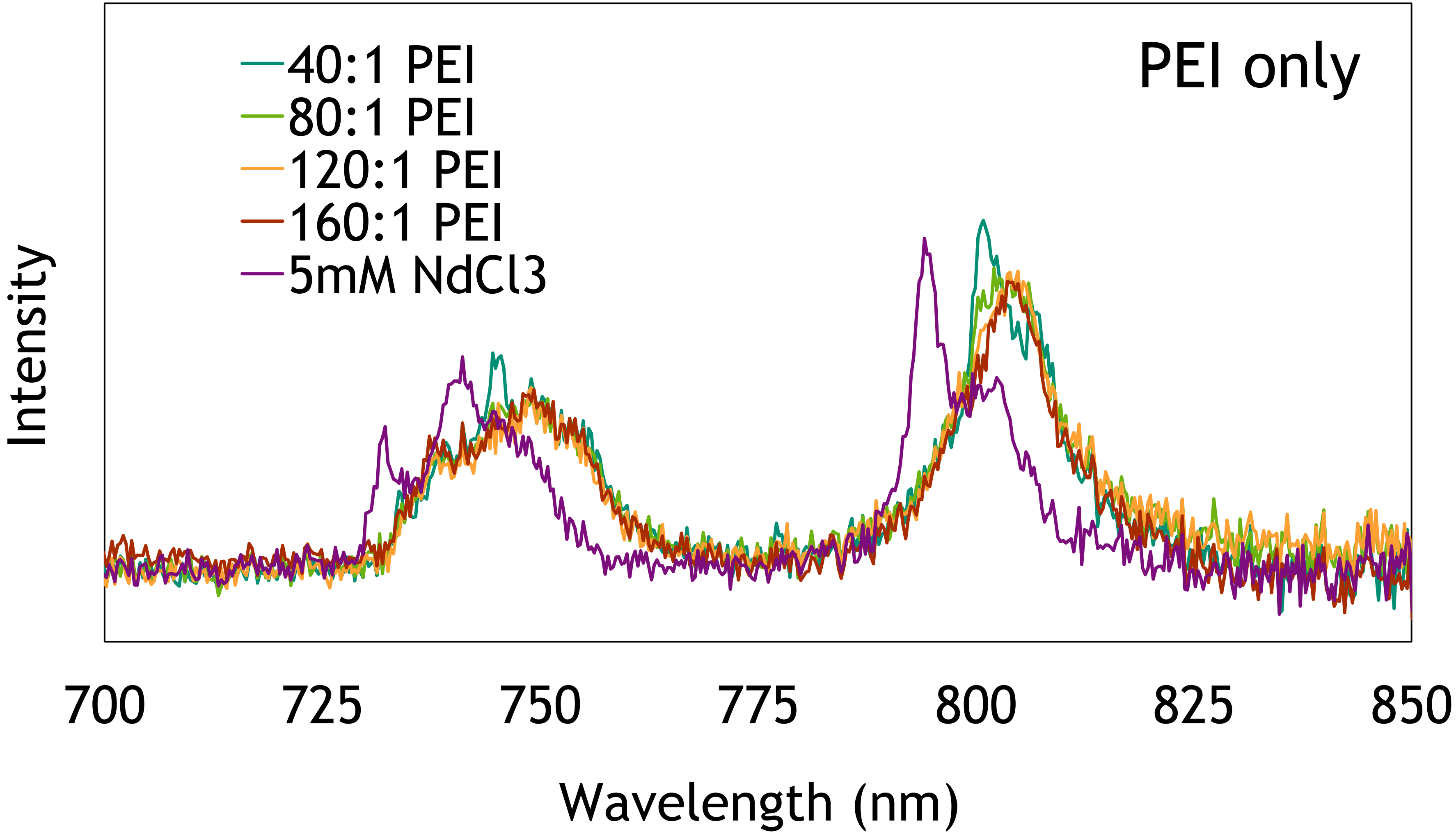
PREformation of Polyelectrolyte Complex is Not Effective

PE complex made prior to exposure to ions results in diminished capture



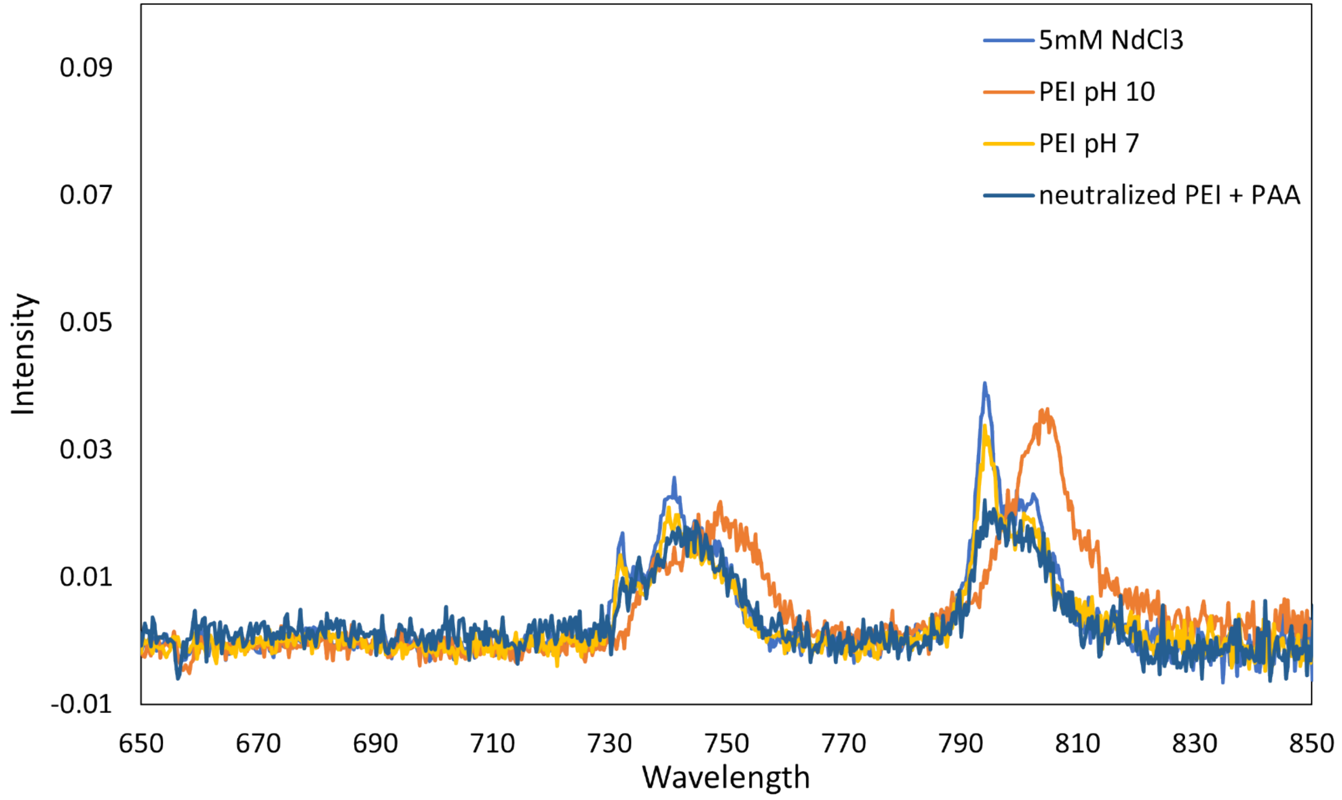
- Peaks shifted and only saw a decrease of 1.47-2.52 mM (29.4-50.3%) between 20:1 and 100:1 acid:ion ratios
  - Necessary to introduce ions to environment pre formation of PE complex
- Harder to separate larger volume PE complex from ions

What Happens with PEI Only?



Testing Impact of pH: Neutralized PEI

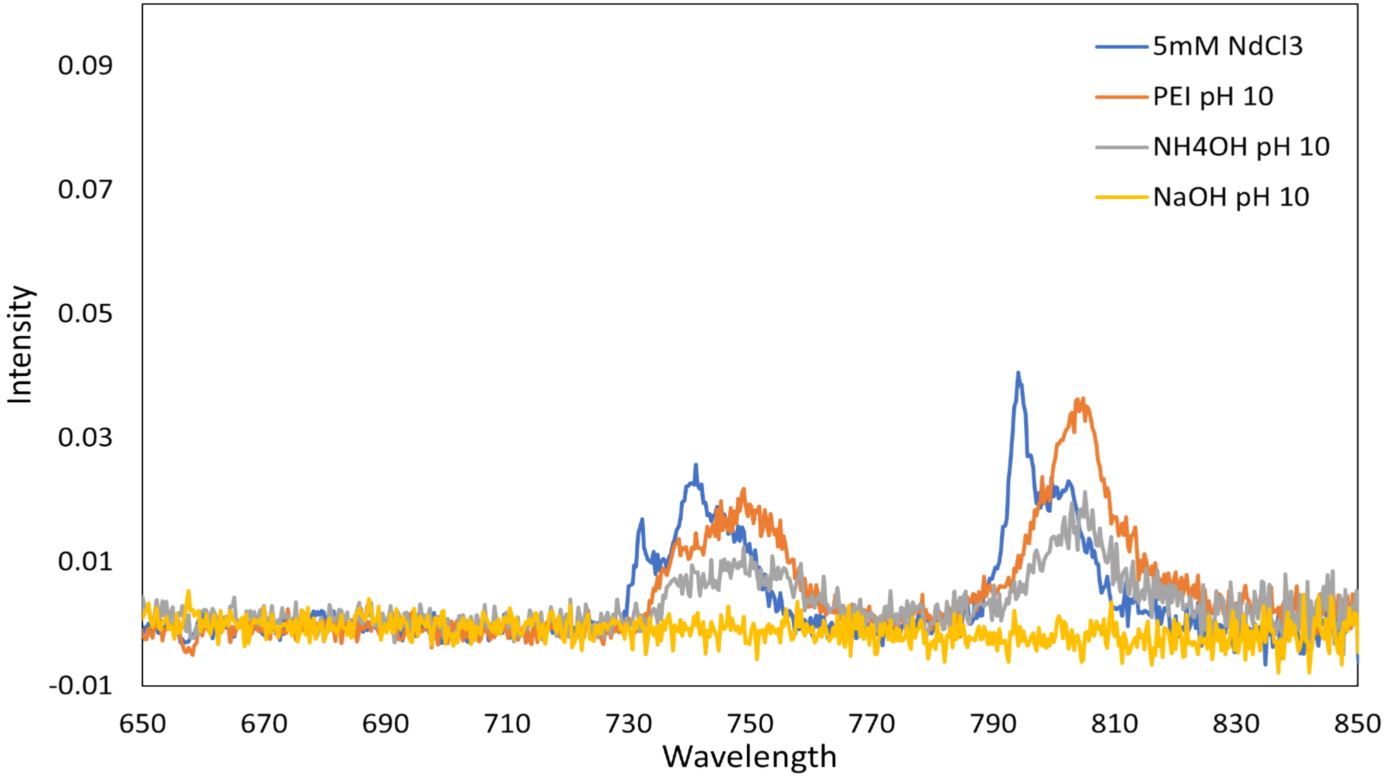
Hydroxyls affect water environment around Nd^{3+} ions.



- ➢ Neutralized PEI shifts back to original peak placement.
- ➢ Hydroxyls drive water off of Nd^{3+} ions, making it easier for PAA to capture them.
- ➢ PAA with neutralized PEI (2:1 ratio) only yields ~45% capture.

pH AND Amines are Important

Amine presence stabilizes ions in presence of hydroxyls.



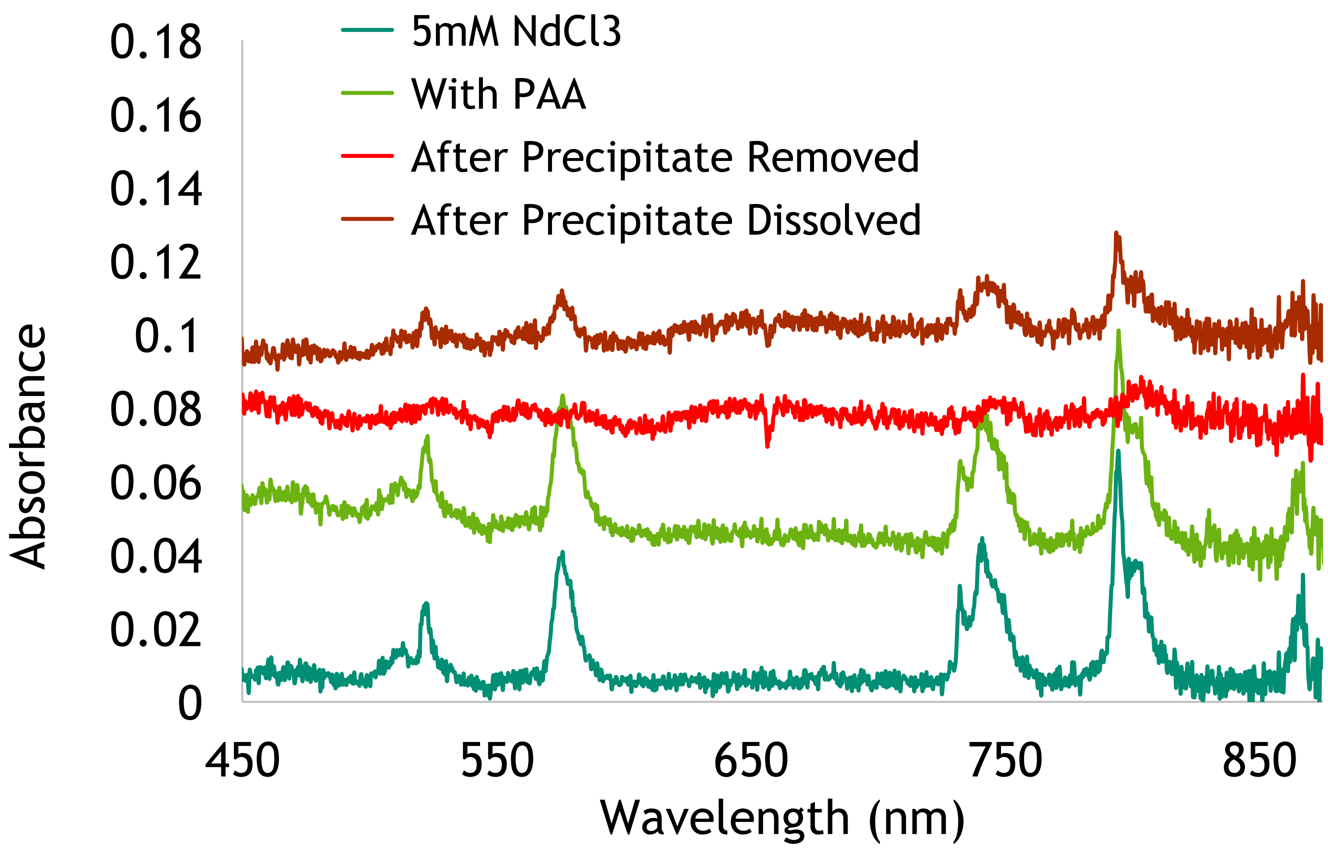
- High pH without amines (NaOH) crashes out system (inorganic precipitate)
- PEI and NH_4OH don't crash out at high pH
  - addition of amines help stabilize formation of hydroxides and oxides

What Do We Know?

- PE complex formation is necessary for ion capture
  - PAA alone limited capture ability (<25% of ions)
  - Non-polymeric form of acid won't capture ions effectively
- Order of Polymer Introduction Matters
  - PAA first reduces ions >98% at a 20:1 acid:ion ratio and 2:1 PEI:PAA ratio
  - PEI first reduces ions >98% at a 20:1 acid:ion ratio and 1:1 PEI:PAA ratio
  - PE complex first has limited capture
- PEI interacts with ions to improve capture conditions
  - High pH plus amines matter for full capture

Can We Recover the Ions?

Acidification to disrupt the supramolecular aggregate leads to controlled release of the REM!



Take Home Messages

- There is an important need to develop domestic sourcing of Rare Earth materials.
- Biological systems are powerful inspiration for sustainable, selective Rare Earth harvesting.
- PE complex captures Nd^{3+} ions out of solution
  - Polymeric form of both acid and base essential for capture
  - Non-selective between divalent and trivalent ions
- PEI interaction with ions first results in best capture
  - Hydroxyls drive off water, making it easier for PAA to capture Nd3+ and exclude water from PE complex
  - Amine presence important to stabilize ions

Thank You!

Bio-Inspired Harvesting of Rare Earth Metals

Erik Spoerke*
George Bachand
Stephen Percival
Amanda Peretti
Susan Rempe
Krista Hilmas
Naat'anii Castillo

Pengyu Ren (UT Austin)
Justin Gourary (UT Austin)

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

THE UNIVERSITY OF TEXAS AT AUSTIN

U.S. DEPARTMENT OF ENERGY
National Nuclear Security Administration

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