Portable Fiber Optic Sensors for Critical Metal Ions

FWP-1022420

Scott E. Crawford, PhD

National Energy Technology Laboratory (NETL) Support Contractor

U.S. Department of Energy

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Author and Contact Information

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Project Overview

2022	2023	2024	Total Task Value (2022 – 2024)
$127k	$0k	$0k	$127k

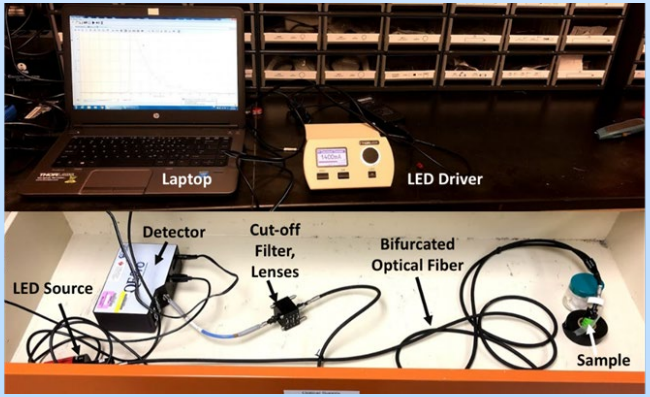
Task Team Members

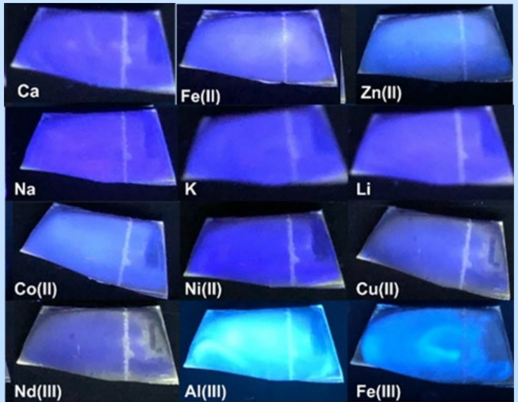
Principal Investigator: John Baltrus

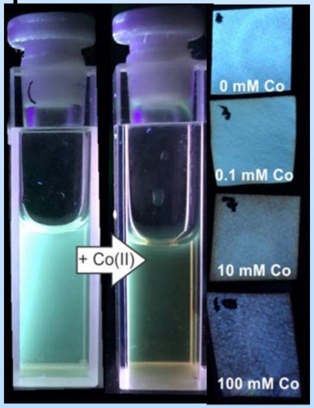
Other Key Personnel: Scott Crawford

End Product:
Optically based inexpensive, portable, and rapid detectors for REEs and other critical metals

Plan Overview: Demonstrate a device for measurement of REEs and other critical elements in liquid streams at low part-per-million (ppm) or part-per-billion (ppb) levels using an optical probe by identifying, synthesizing, and incorporating novel photoluminescent sensing materials targeting specific critical elements. This EY will focus on Co and Al detection, testing of field samples, and includes development of other detection platforms, such as test strips and sensitizers specific to other critical elements, as time permits.

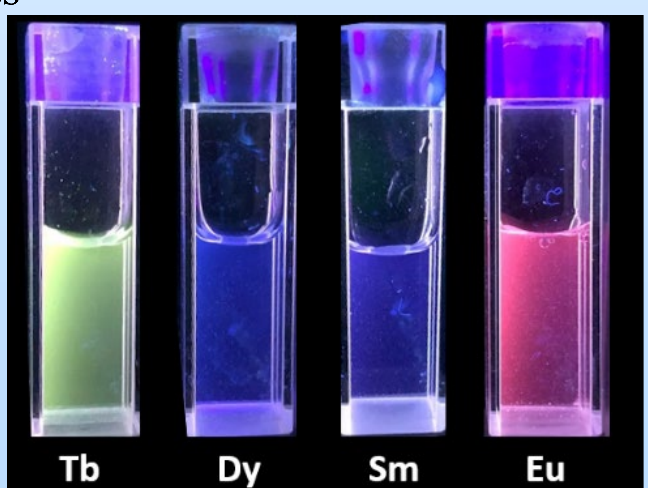


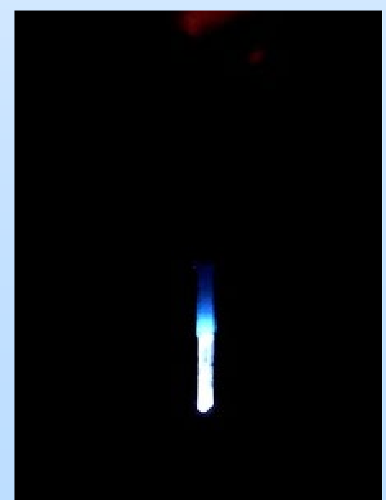




Historical Overview

- Showed possibility of sensitizing rare earth element (REE) detection
  - Designed a simplified setup for a portable spectrometer (US Patent 11,170,986)
  - Measurements taken with sensitizer in solution (cyanide-based sensitizer)
- Moved from cyanide sensor to metal-organic frameworks (MOFs)
- Demonstrated a modular device incorporating early elements of a portable spectrometer
- Demonstrated detection by immobilizing sensitizers on the fiber optic
- Optimized detection of select REEs based on MOF structure
- Explored materials, other than MOFs, and mechanisms to detect additional critical elements





Importance of Characterization

Prospecting:

Coal

~70 to 140 ppm REE
DOI: 10.1016/j.coal.2016.04.005

Acid Mine Drainage
(0.07-7 ppm)

DOI: 10.1016/j.coal.2006.01.009

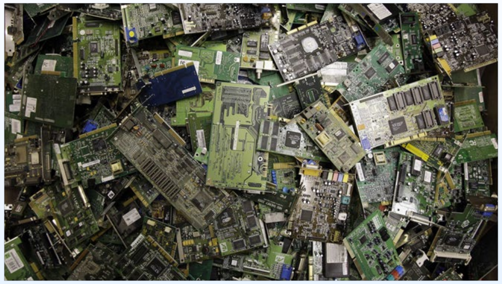
Coal Rock Refuse
(~250 ppm REE)

DOI: 10.1016/j.coal.2011.05.006

Coal Fly Ash
(~450 ppm REE)

DOI: 10.1007/s11356-015-4111-9

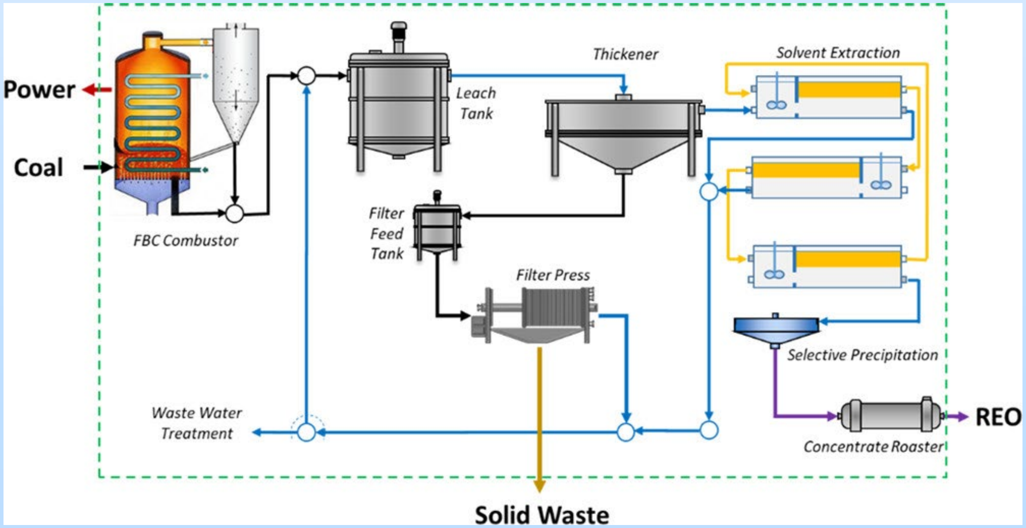
E-Waste



The Atlantic

- **Circuit Boards**
- **Phosphors**
- **Magnets**
- **Batteries**
- **Other sources being explored**

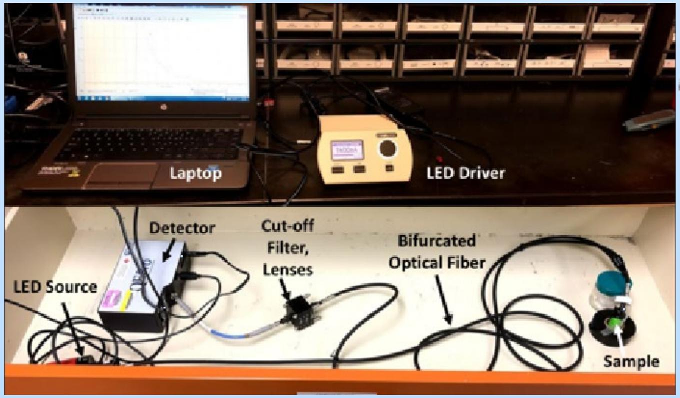
Process Monitoring:



DOI: 10.1021/acs.energyfuels.9b00295

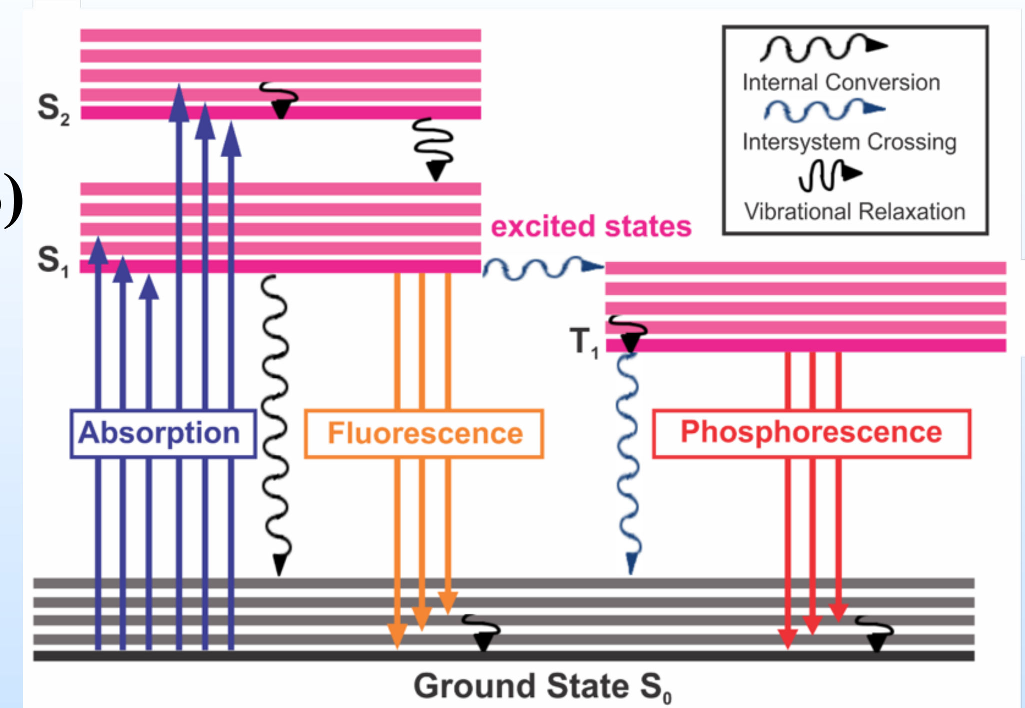
State-of-the-Art is Costly and Slow

Technique	Instrument Cost	Detection Limit	Portable?
Inductively-Coupled Plasma Mass-Spectrometry	~$180k	Part-per-trillion	No
X-Ray Fluorescence Spectroscopy	~$13-17k	10s of part-per-million	Yes
Laser-Induced Breakdown Spectroscopy	~$30-50k	10s of part-per-million	Yes
Luminescence Spectroscopy	~$18-35k	10s of part-per-billion	Yes

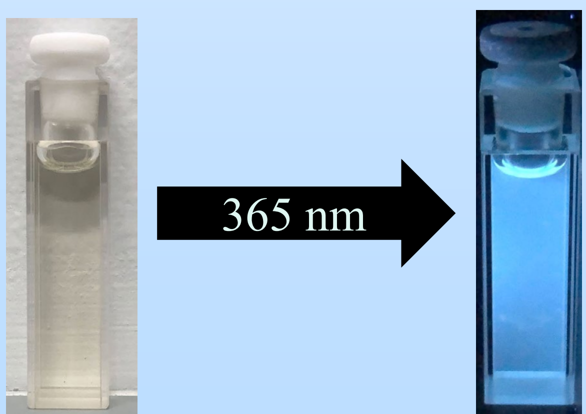


Advantages of Luminescence

- ✓ **Portable**
- ✓ **Inexpensive (rel. to ICP-MS)**
- ✓ **Rapid (seconds/minutes)**
- ✓ **Sensitive/quantitative**
- ✓ **Ease-of-use**

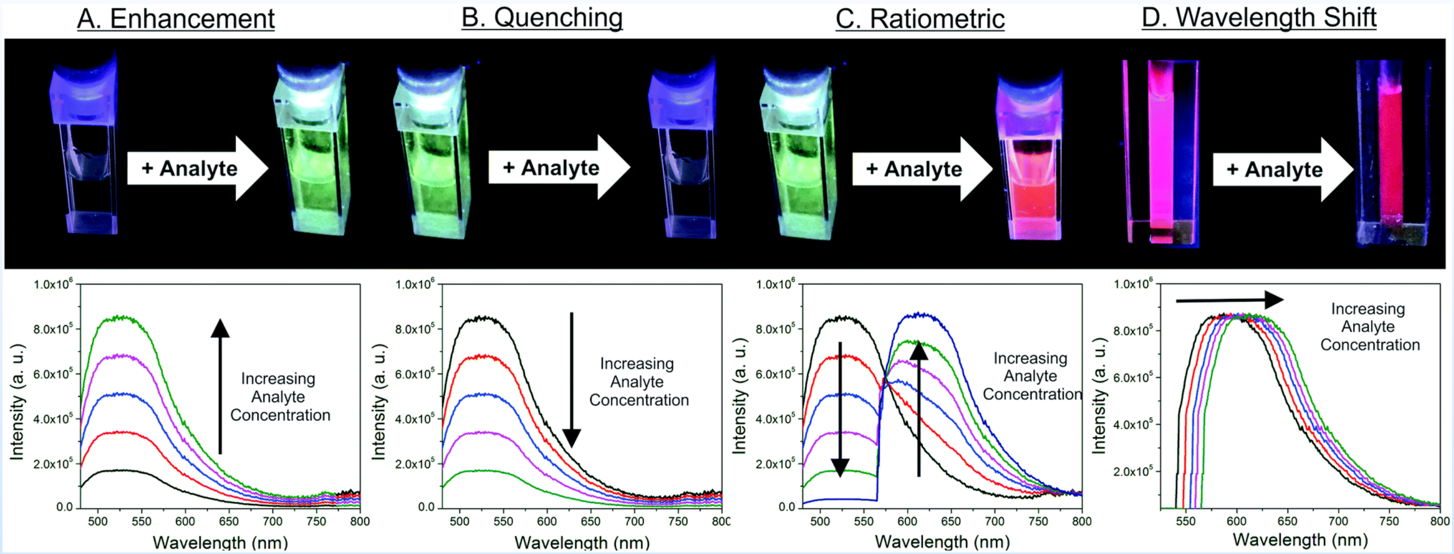


DOI: 10.1039/c3cs60232j

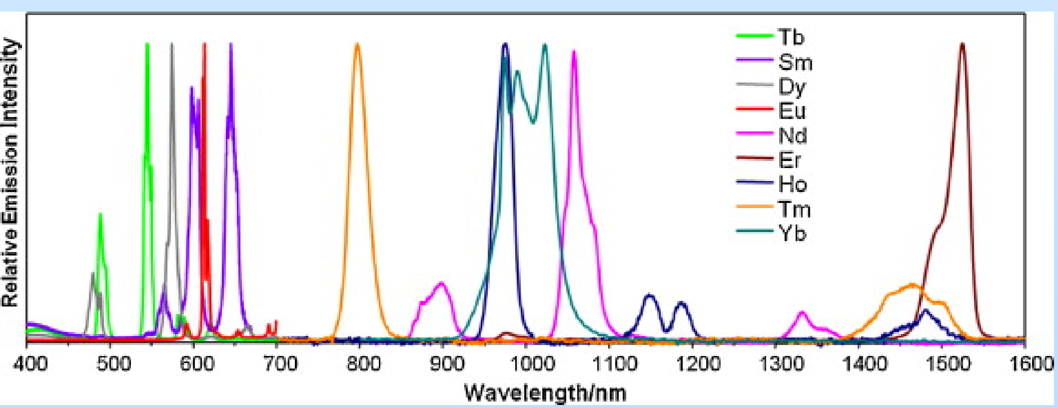


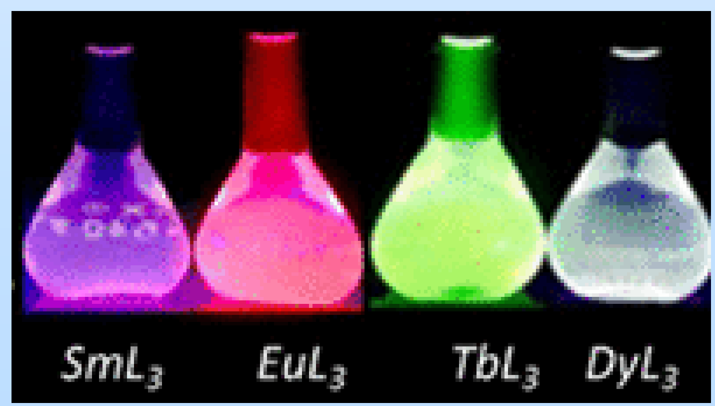
Luminescent Sensing of Metals

Traditional Approaches:



Lanthanide/Rare Earth Sensitization:

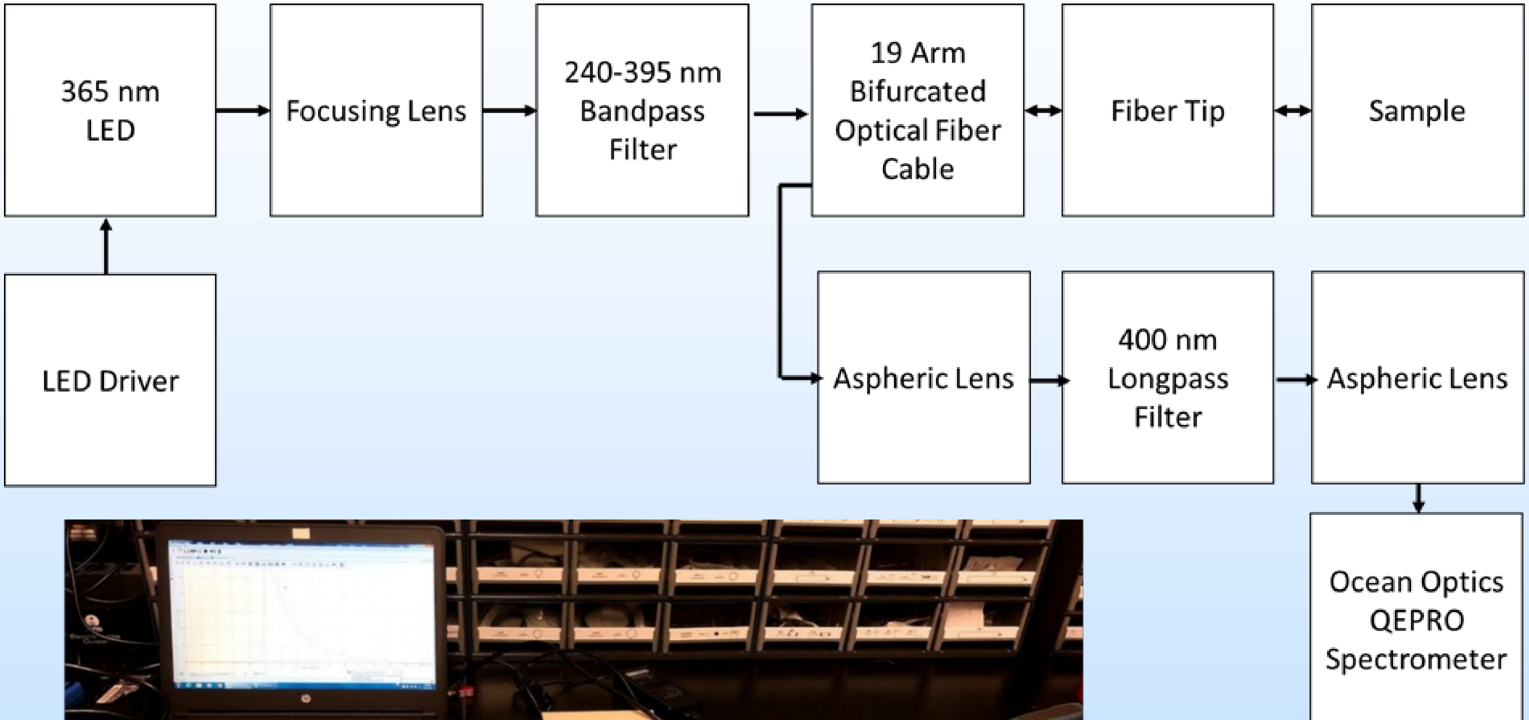


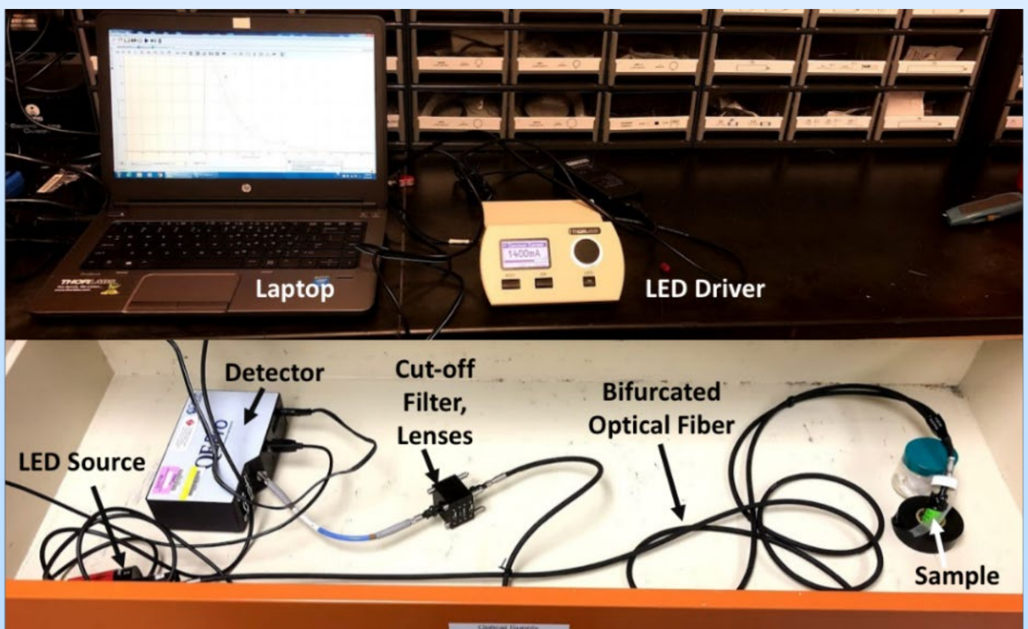


DOI: 10.1016/j.crci.2010.05.007

DOI: 10.1021/acs.inorgchem.7b02861

Compact Fiber Optic Spectrometer





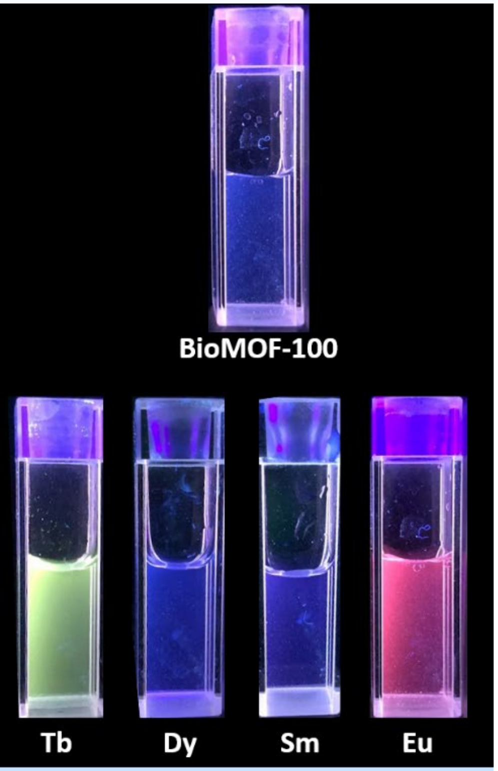
J. C. Ahern, P. R. Ohodnicki Jr, J. P. Baltrus and J. L. Poole, "Luminescence based fiber optic probe for the detection of rare earth elements." U.S. Patent 11,170,986, Nov. 9, 2021

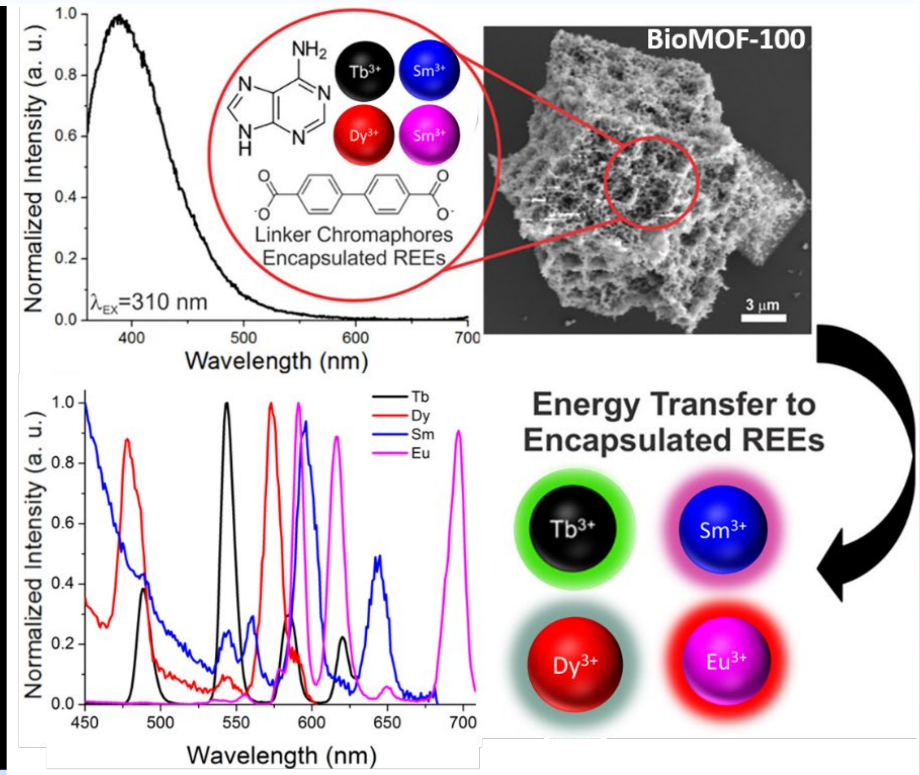
Technical Approach

- **Material Science:** discover and synthesize materials exhibiting a *selective* and *sensitive* response to target metals
- **Platform Development:** continued optimization of compact spectrometer capable of integrating different sensing materials
- **Evaluation (risk):** test materials in real or simulated samples, accounting for factors such as *low pH*, *interfering metals*, and *high ionic strength*

End Product:
Optically based inexpensive, portable, and rapid sensing platform for REEs and other critical metals, capable of detecting part-per-million or lower concentrations of critical metal ions in process streams and/or environmental samples

Initial Studies: Rare Earths



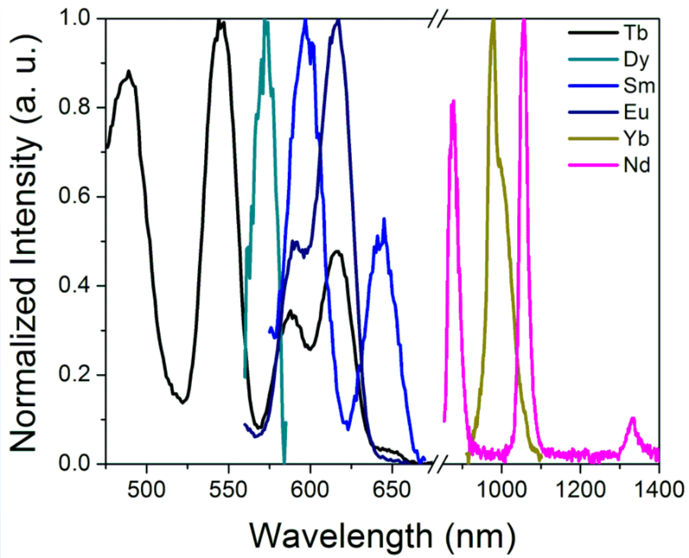


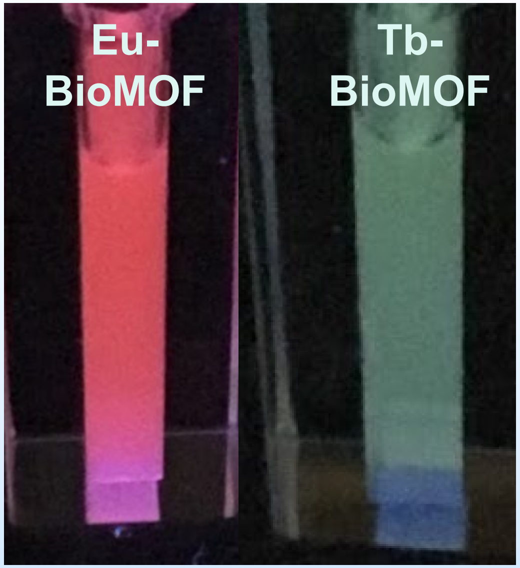
1. REE encapsulation
2. Excitation of MOF
3. Energy transfer
4. REE-centered emission

Metal-Organic Frameworks (**MOFs**): well-ordered microscopic crystals comprised of metal clusters linked by organic molecules, forming porous structures with tunable properties (*e.g.,* pore size, chemical functionality)

Crawford*, Gan, Lemaire, Millstone, Baltrus, and Ohodnicki, *ACS Sensors* **2019**, *4*, 1986

One Material Senses Six REEs

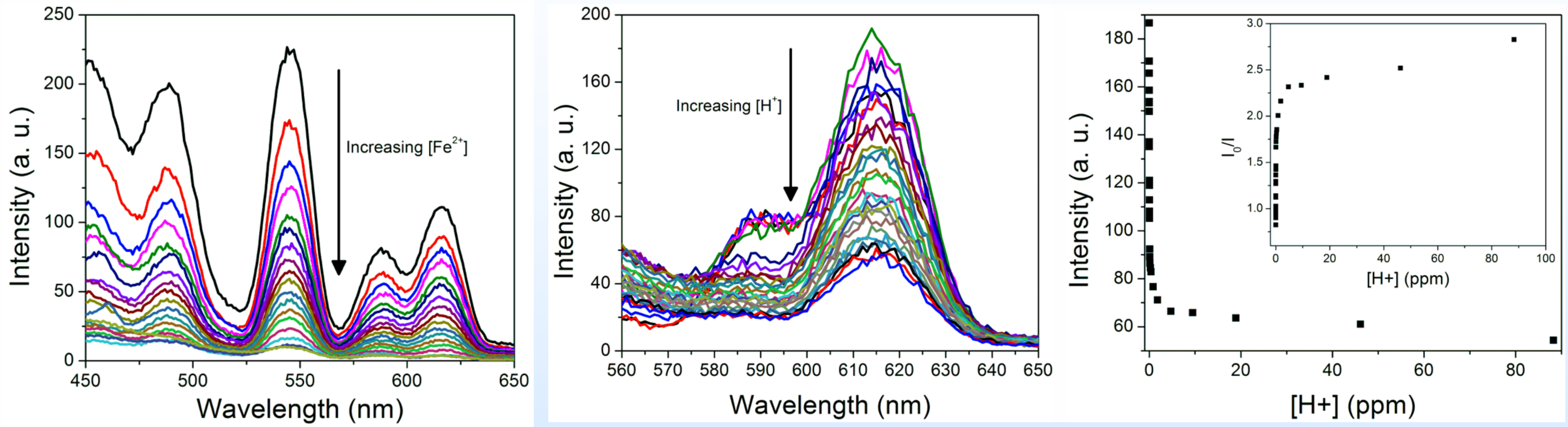




Part-per-billion (ppb) scale detection limits of six REEs with the same material!

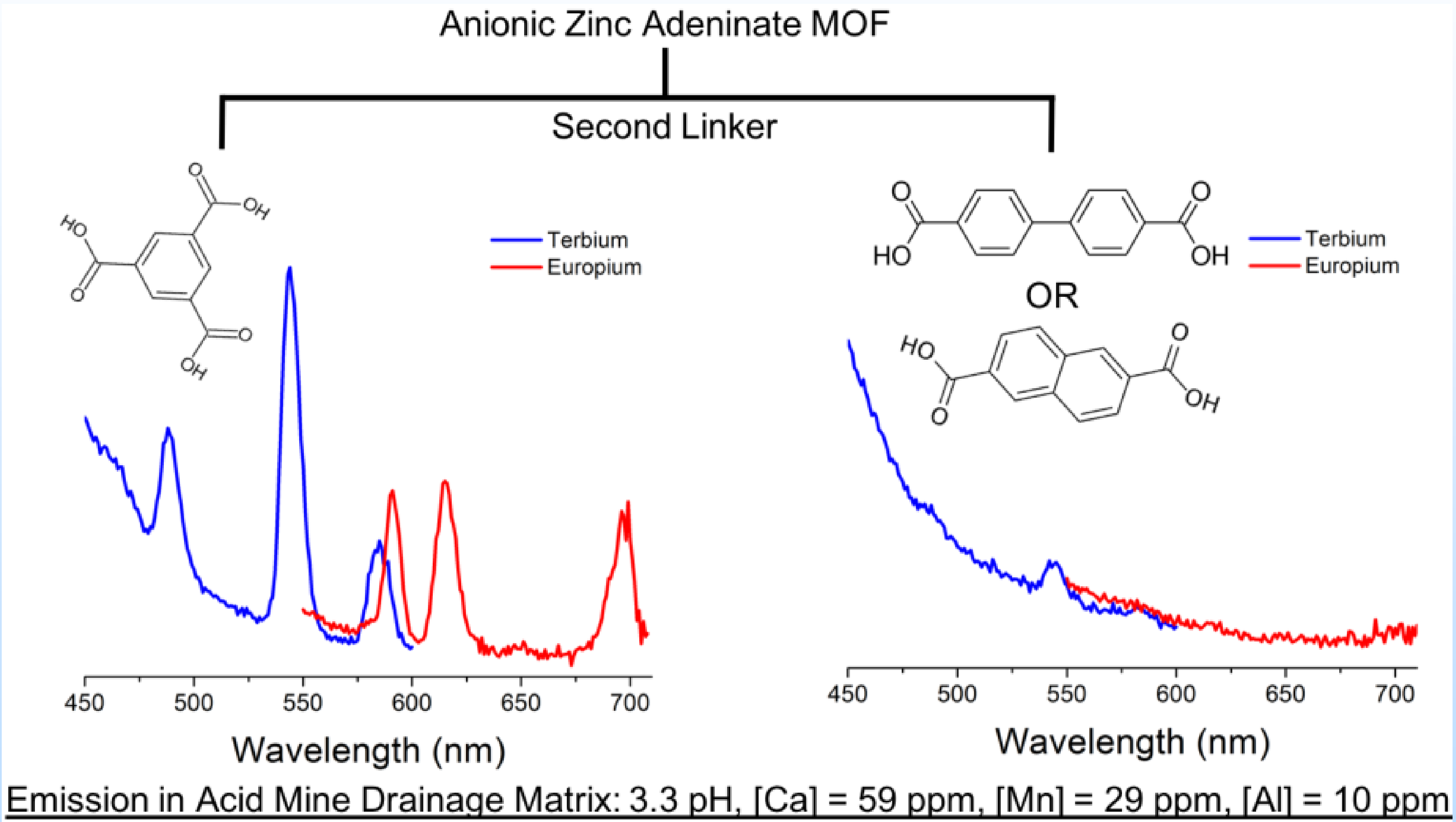
REE Sensitized	Limit of Detection (ppb)	Limit of Quantification (ppb)
Tb	5.7 ± 0.6	18 ± 2
Dy	170 ± 10	550 ± 30
Sm	184 ± 6	600 ± 100
Eu	18 ± 4	60 ± 10
Yb	260 ± 6	900 ± 20
Nd	100 ± 2	340 ± 7

Challenge: Acid and Other Metals



Location	pH	Total REE (ppm)	Fe (ppm)	Al (ppm)	Ca (ppm)	Mg (ppm)
Sitai Mine, China	3.61	**.0612**	4.73	8.83	249	1.03
Clarion, PA	4.4	**1.134**	385	9.1	149	236
Pittsburgh, PA	6.3	**0.00029**	22	0.1	66	20.1
Germany	4.8	**0.073**	0.01	4.01	405	193
Germany	3.8	**4.7**	404	88.2	57.8	1,139
Romania	3.0	**1.58**	1500	237	402	88.3
Romania	3.0	**0.38**	538	74.8	386	141
Sweden	3.2	**0.035**	6.3	1.10	396	57.4

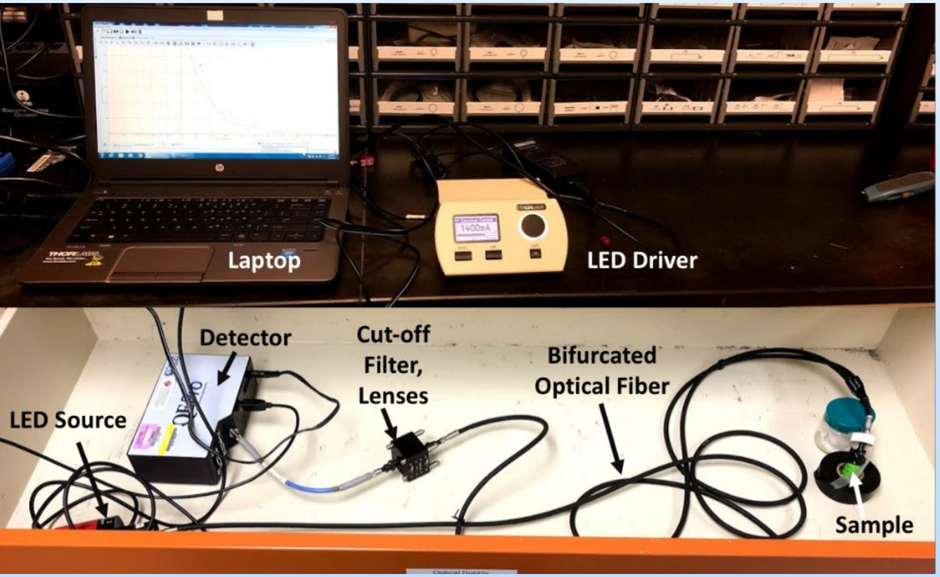
Structure Influences Performance

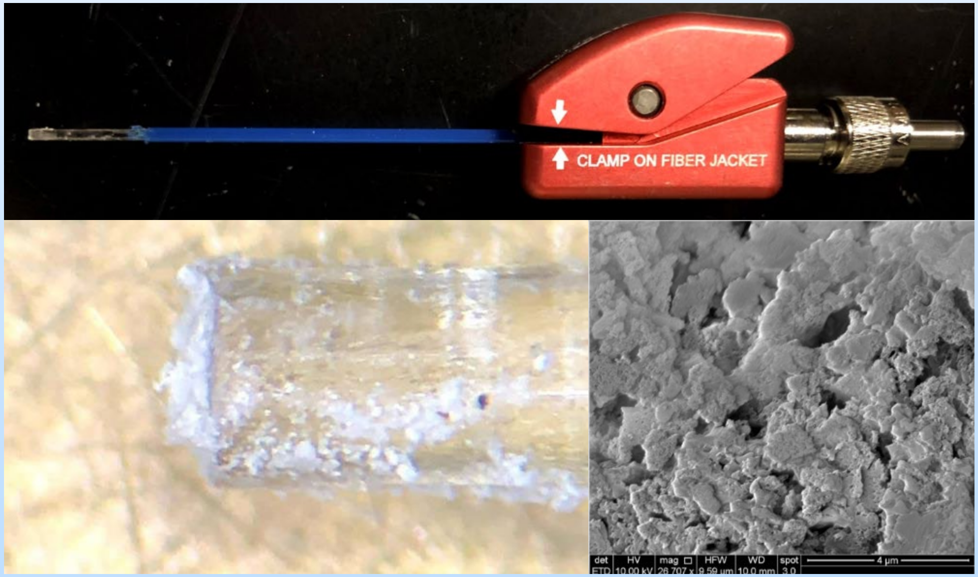


Crawford, S.,* Ellis, J., Ohodnicki, P., Baltrus, J., *ACS Applied Materials & Interfaces* **2021**, *13*, 6 7268

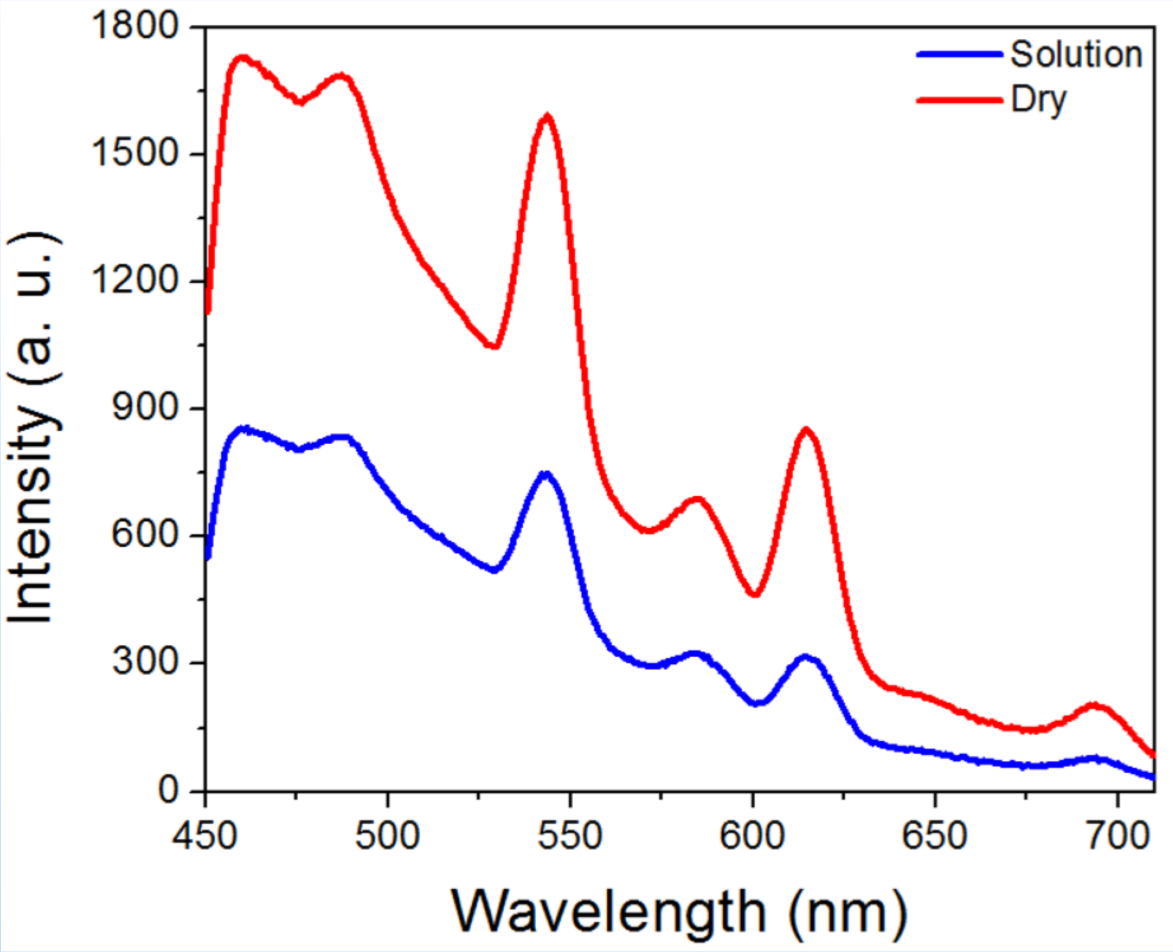
Integration onto Optical Fiber

- Rapid detection (**minute time-scale**)
- Detection limits in the **tens of ppb** range for Tb, Eu
- Reusable tip/Inexpensive tip replacement (**$0.06**/MOF-coated tip)
- Enables solvent removal to **improve signal** and **sensor re-use**



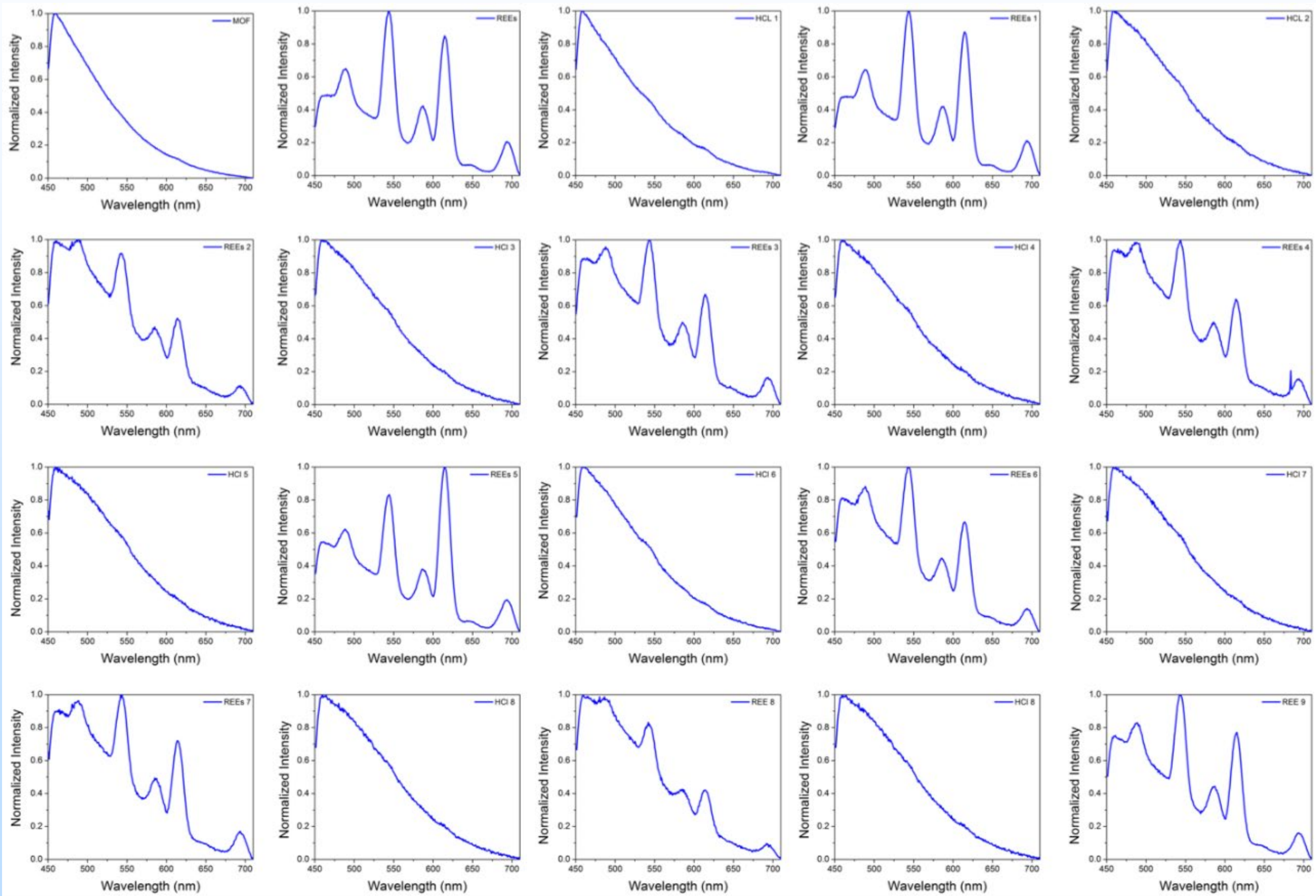


Enhanced Emission Signal



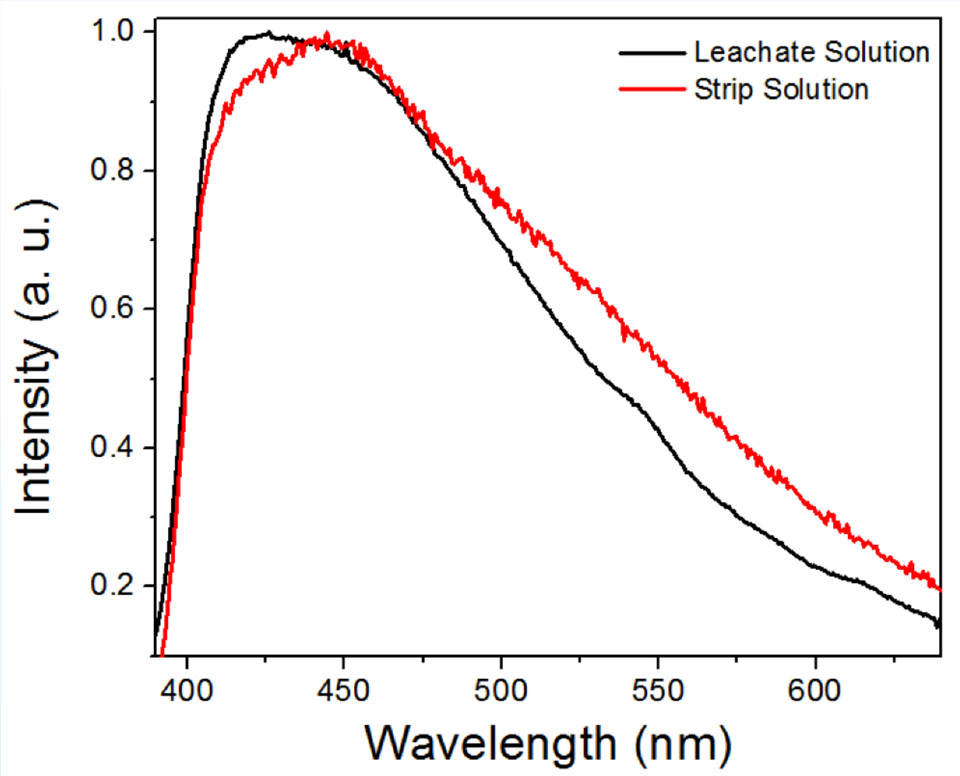
- Drying sensor tip reduced vibronic quenching from solvent, **improving signal**
- Can reduce the detection limit by **~a factor of 2**

Sensing Material Regeneration

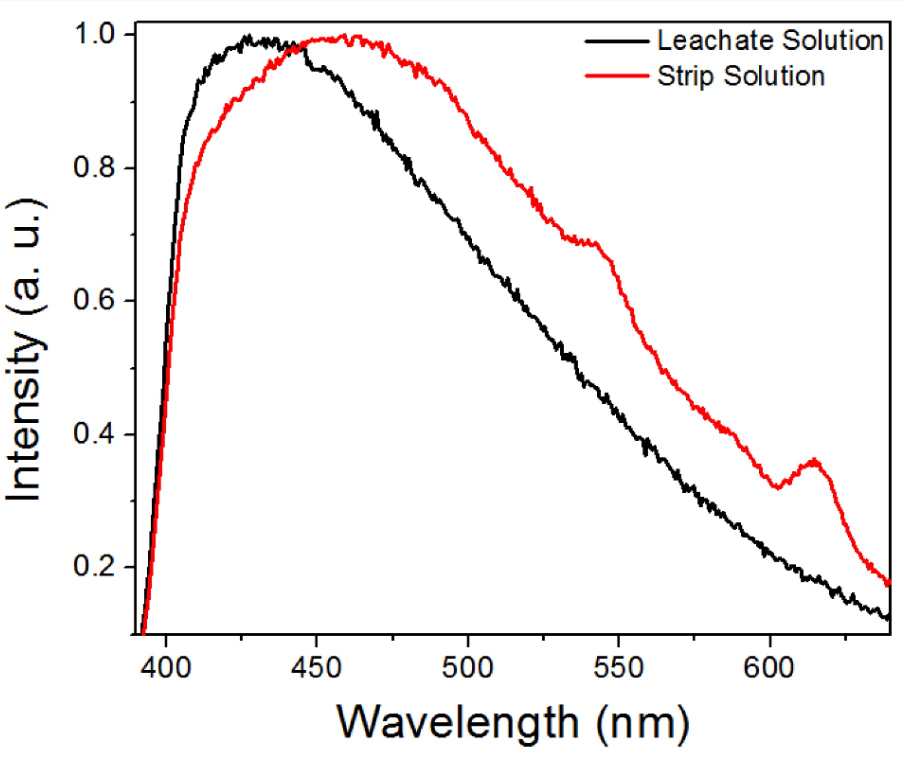


Performance in a Process Stream

T = 0 hours

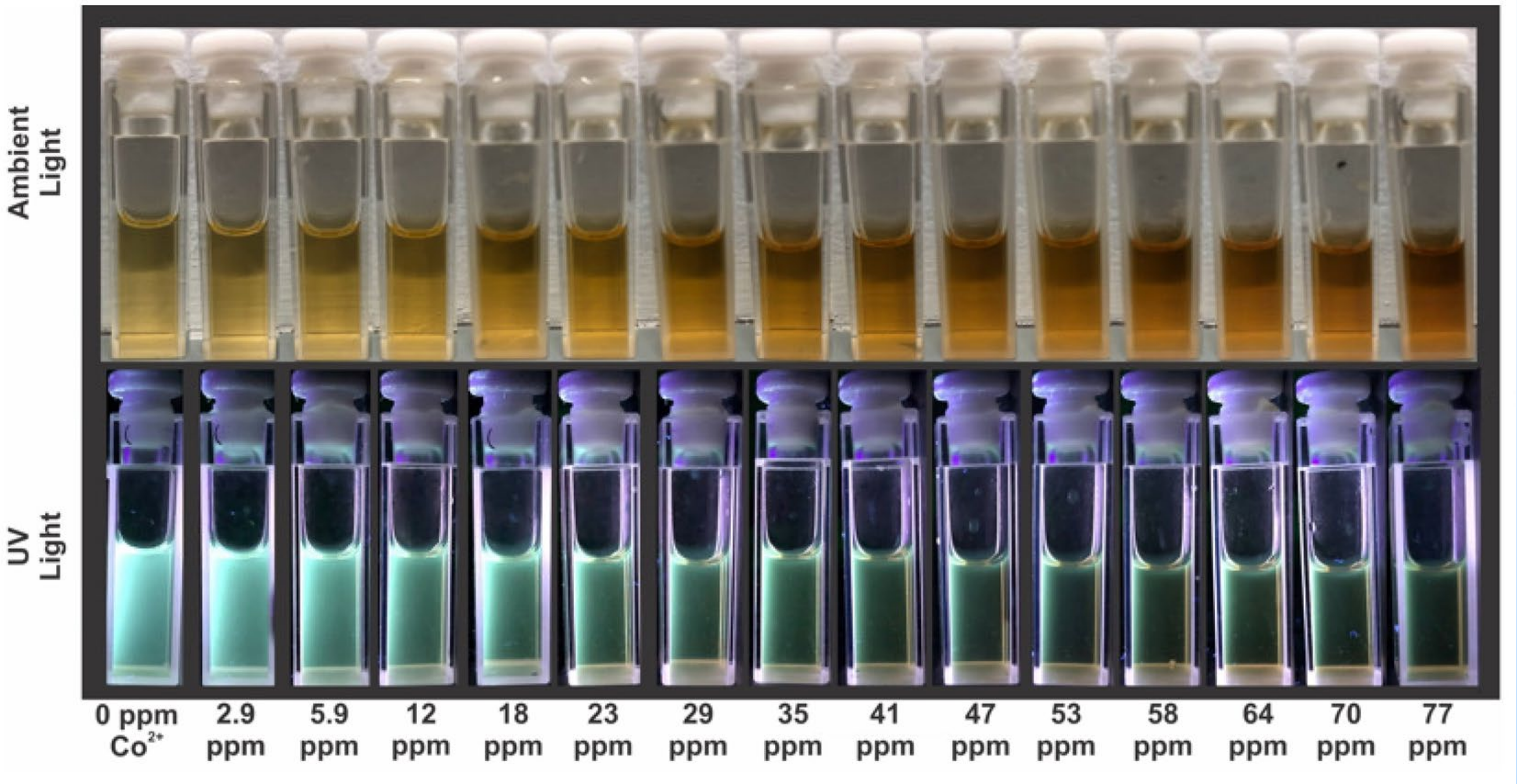


T = 27 hours



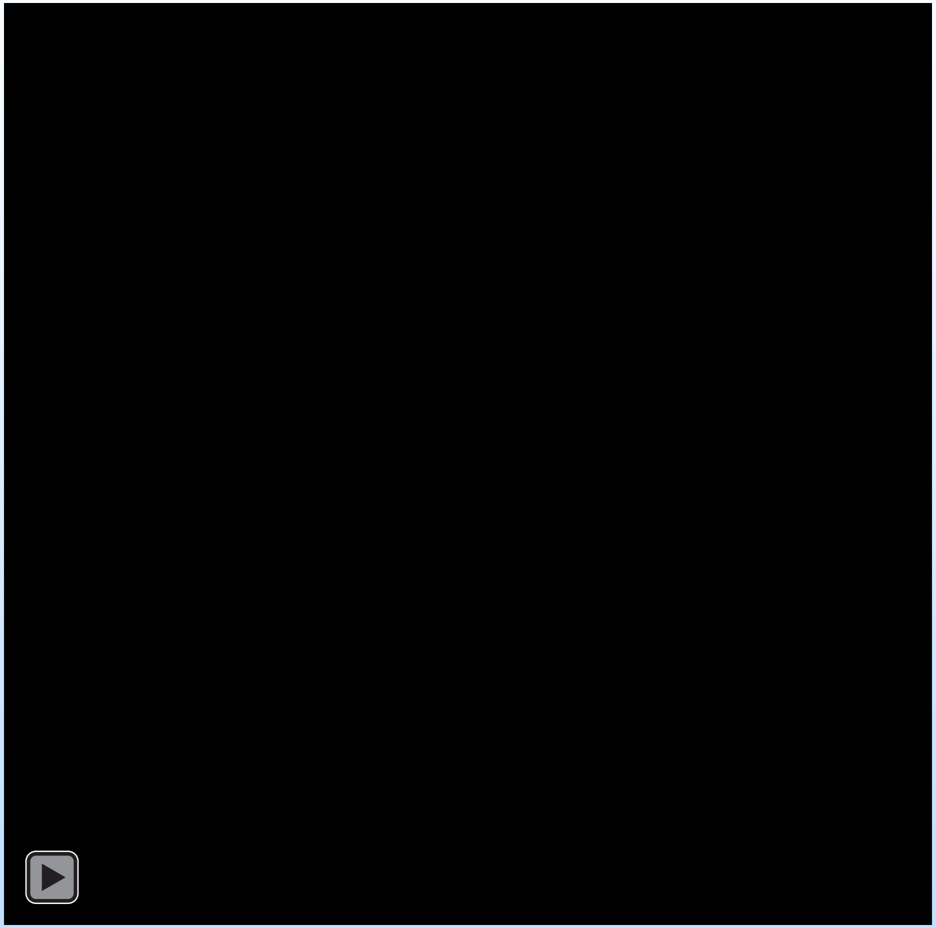
Initially, REEs are in ~pH 3 leachate stream with >1000 ppm Al, Ca, and other metals. REEs are selectively leached into 1 M sulfuric acid strip solution. Qualitative agreement with inductively-coupled plasma mass spectrometry was observed

Other Targets: Cobalt



Material exhibits a selective, sensitive luminescent quenching response to cobalt

Other Targets: Cobalt



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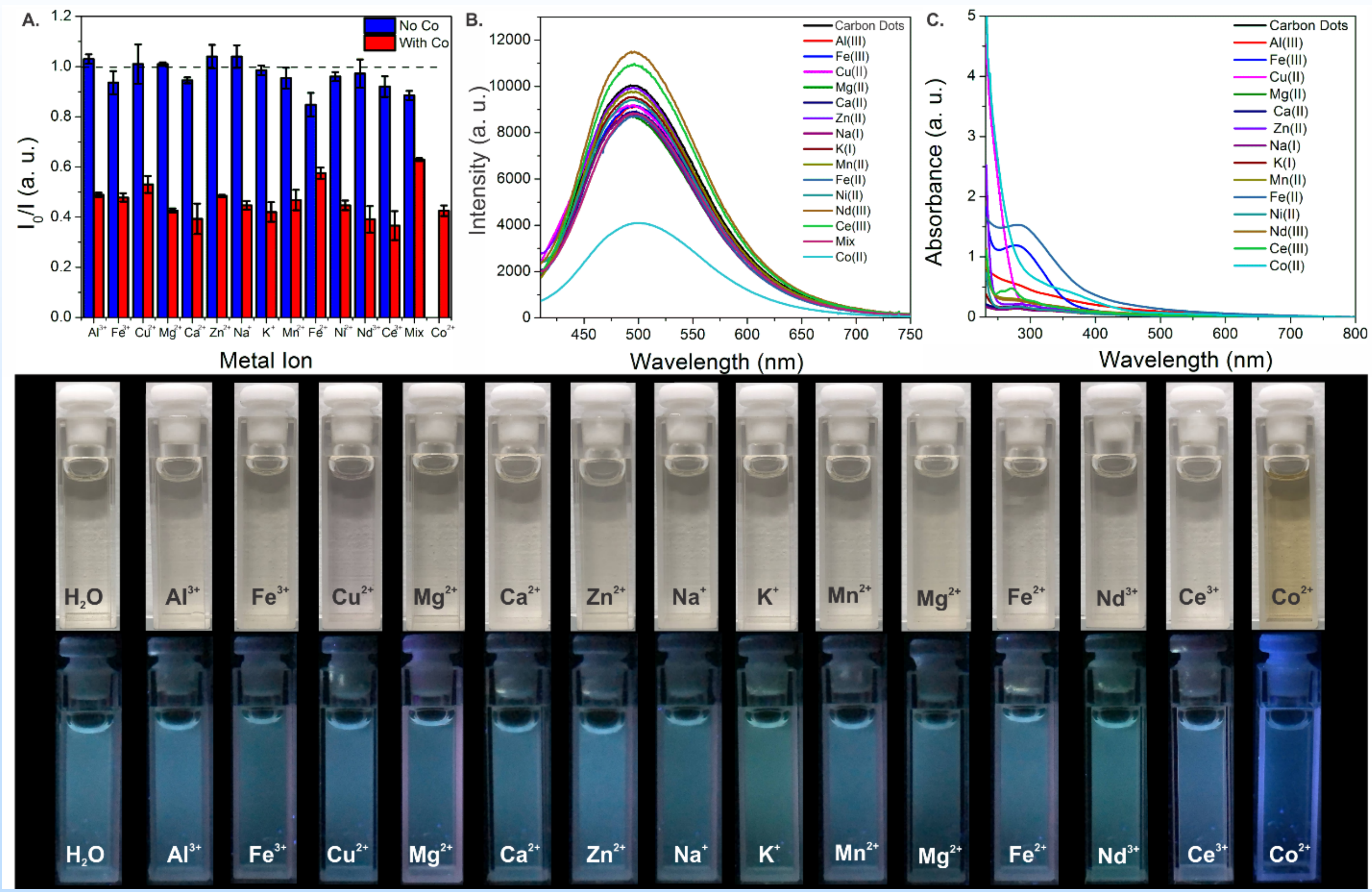
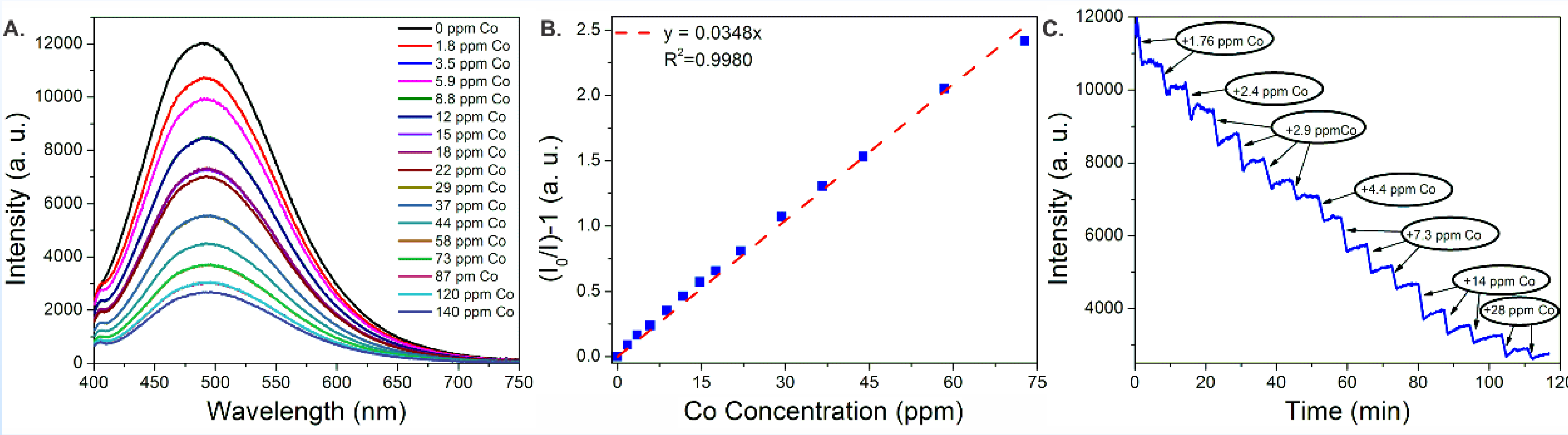


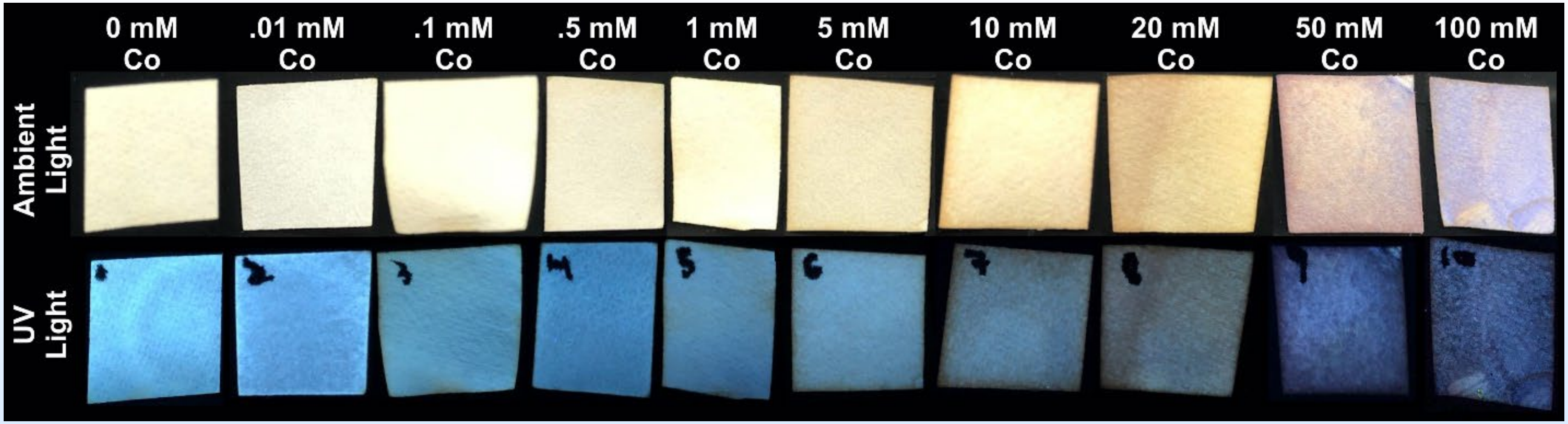
Material exhibits a selective, sensitive luminescent quenching response to cobalt

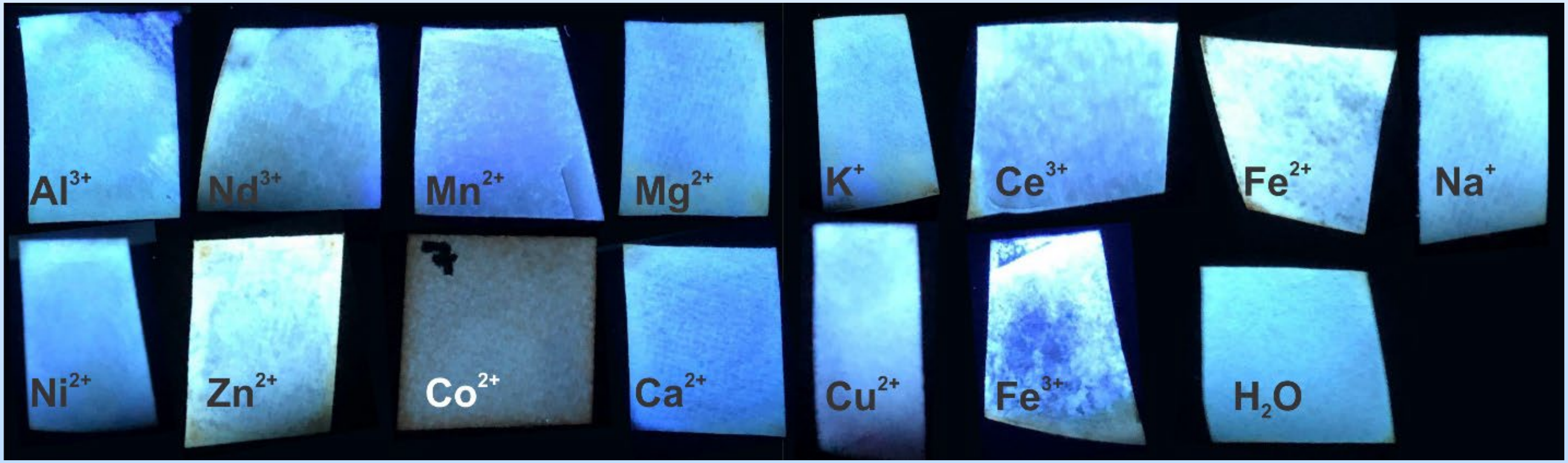
Rapid, Sensitive Co Response



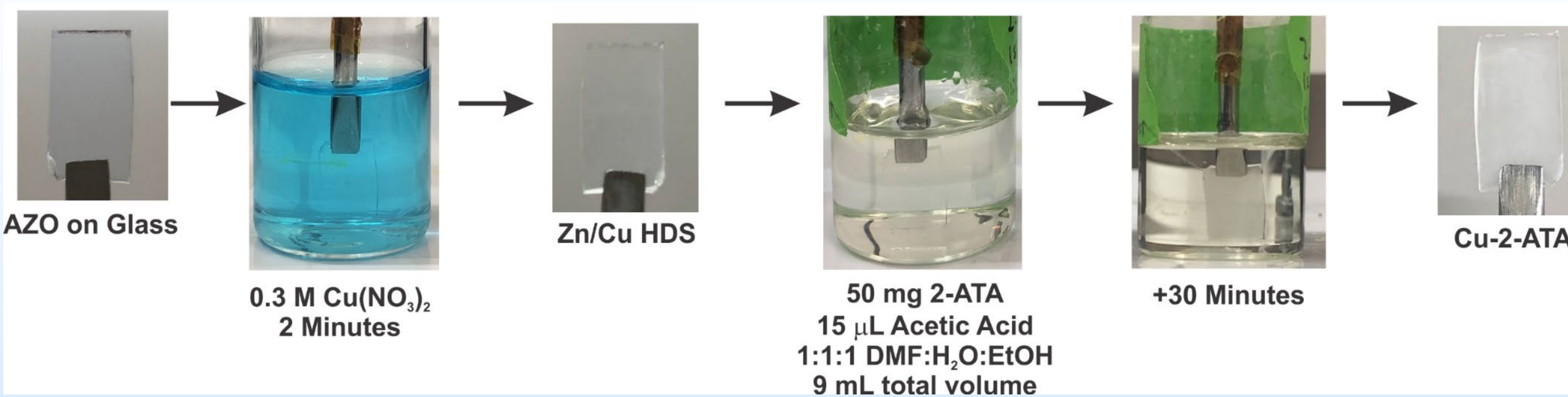
The portable sensor is capable of 0.6 ppm detection limits in water and 3.5 ppm detection limits in pH 1.68 buffer. The response to cobalt addition is nearly instantaneous.

Preparation of Test Strips for Co^{2+}

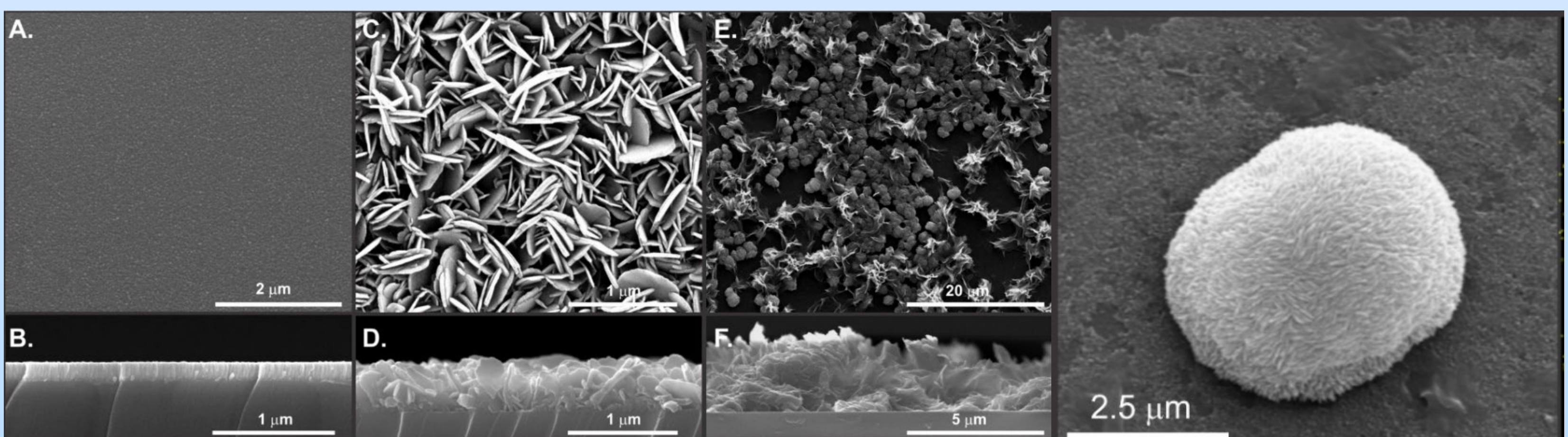




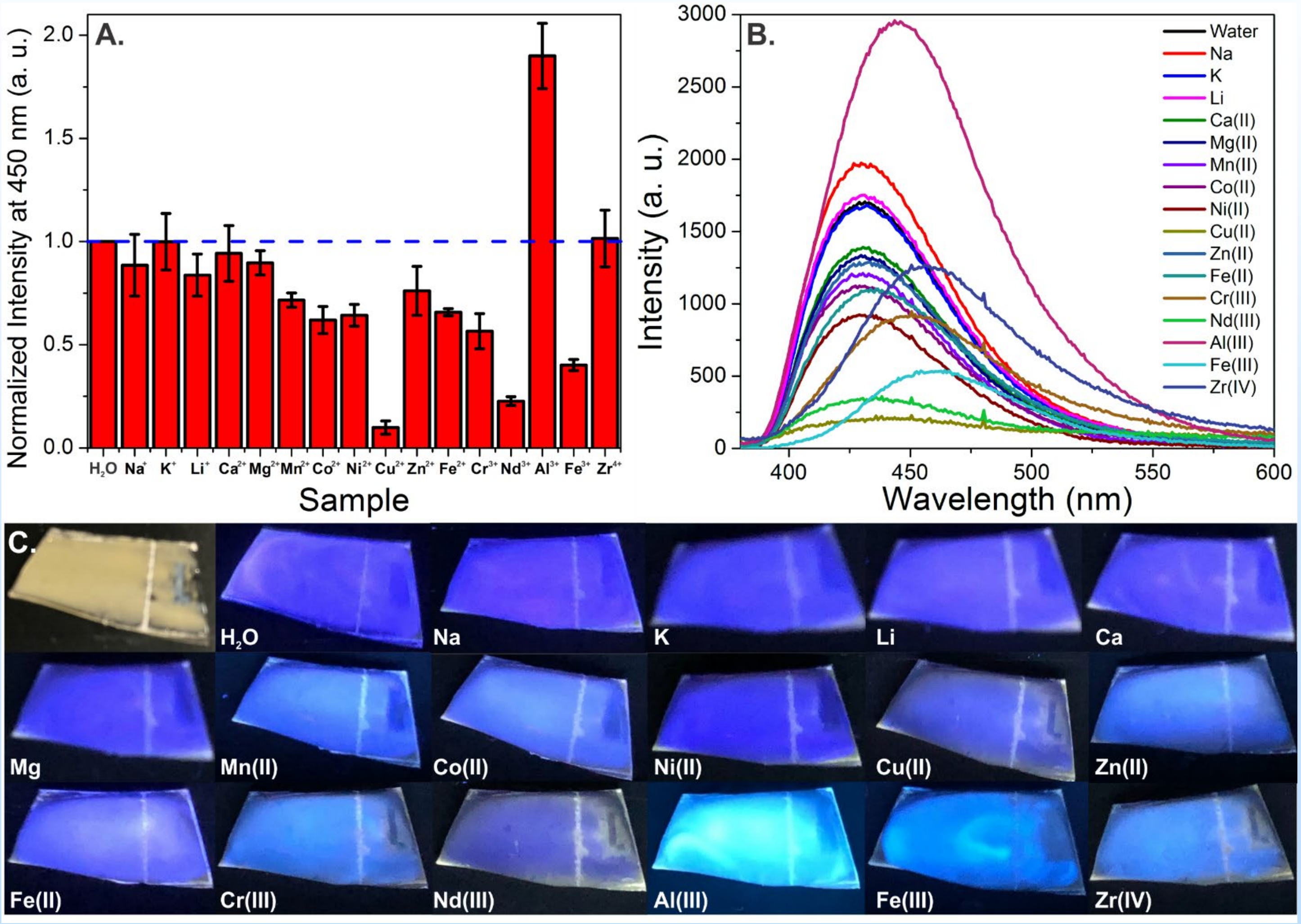
Synthesis of Aluminum Sensor



AZO: aluminum-doped zinc oxide; DMF: Dimethylformamide; EtOH: Ethanol; 2-ATA: 2-aminoterephthalic acid

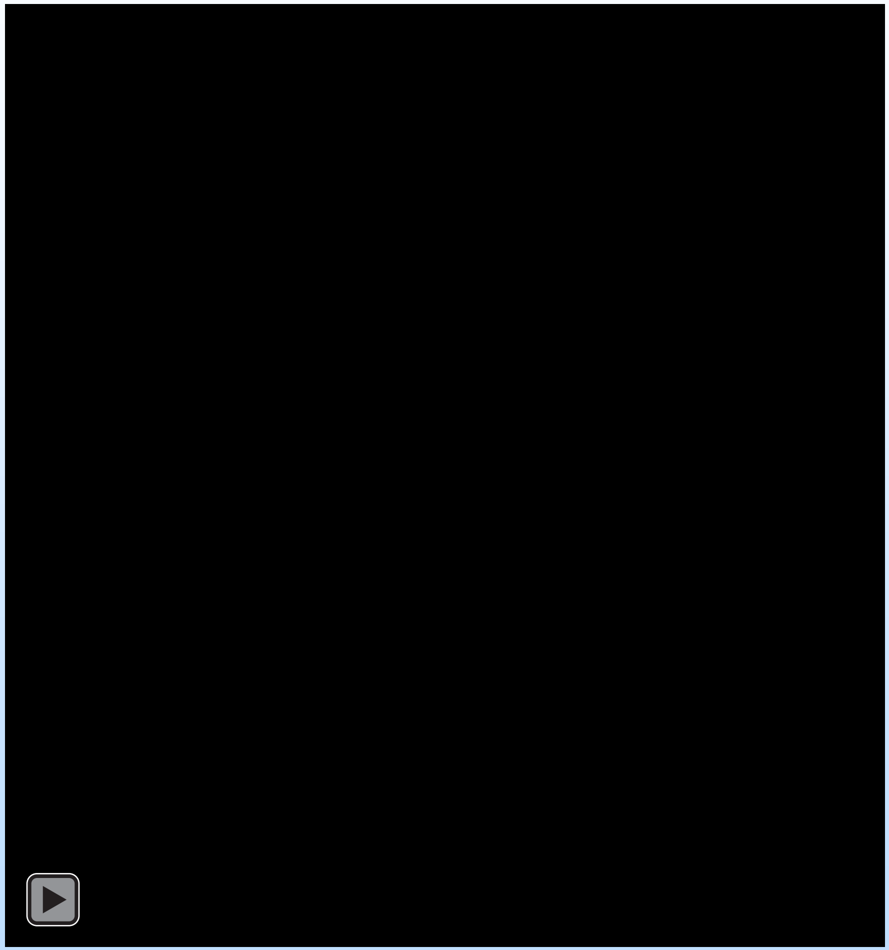


Selective Aluminum Response



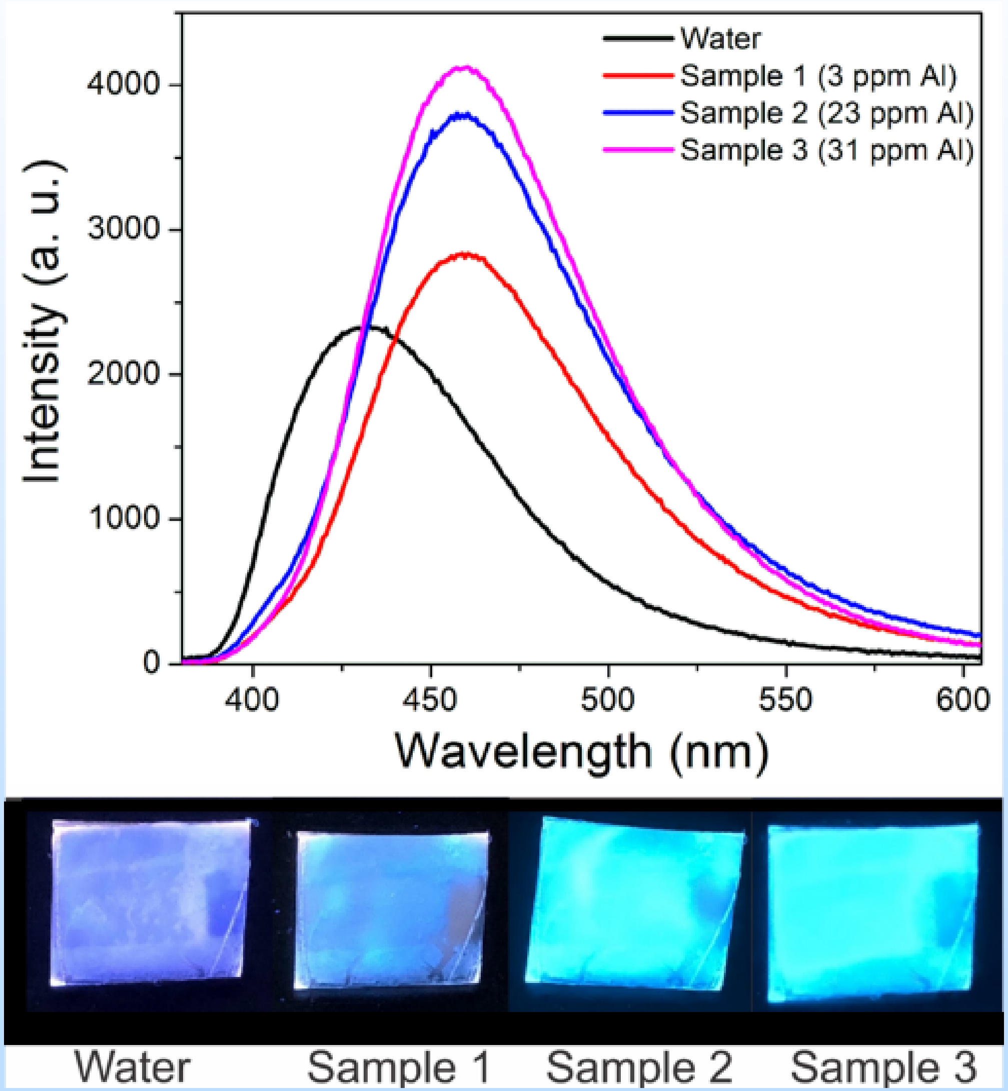
Detection limit: 120 ppb in water for Al

Aluminum Response



Detection limit: 120 ppb in water for Al

Fly Ash Analysis



- Diluted fly ash leachates with a final pH of **3.8**, and at least **40 other metal elements** in solution.
- Good correlation with inductively-coupled plasma mass spectrometry.

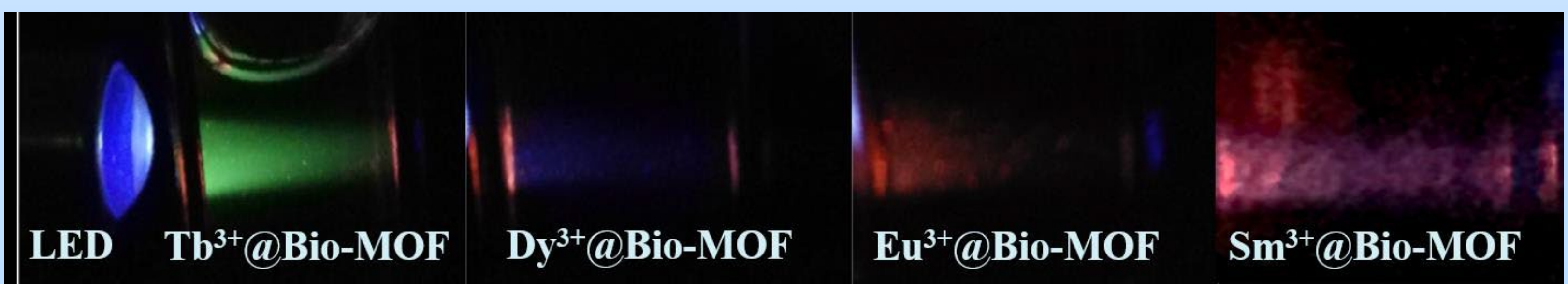
Future Directions

Commercialization: REE-sensing process recommended for patenting by invention review board. Discussions are ongoing with industrial partners regarding potential licensing

Deployment: Sensors are evaluated on samples/processes generated in-house and from external partners

Extension to other priority metals to increase versatility: Mn, Li, Ni, etc.

Collaboration is ongoing to further lower cost of spectrometer



Outreach: Publications

1. Ahern, J. C., Poole, Z. L., Baltrus, J., & Ohodnicki, P. R. (2017). Portable luminescence-based fiber optic probe for REE detection and quantification. *IEEE Sensors Journal*, *17*(9), 2644-2648.
2. Crawford, S. E., Gan, X. Y., Lemaire, P. C., Millstone, J. E., Baltrus, J. P., & Ohodnicki Jr, P. R. (2019). Zinc-Adeninate metal–organic framework: A versatile Photoluminescent sensor for rare earth elements in aqueous systems. *ACS sensors*, *4*(8), 1986-1991.
3. Crawford, S. E., Ohodnicki, P. R., & Baltrus, J. P. (2020). Materials for the photoluminescent sensing of rare earth elements: challenges and opportunities. *Journal of Materials Chemistry C*, *8*(24), 7975-8006.
4. Crawford, S. E., Ellis, J. E., Ohodnicki, P. R., & Baltrus, J. P. (2021). Influence of the anionic zinc-adeninate metal–organic framework structure on the luminescent detection of rare earth ions in aqueous streams. *ACS Applied Materials & Interfaces*, *13*(6), 7268-7277.
5. Ellis, J. E., Crawford, S. E., & Kim, K. J. (2021). Metal-Organic Framework Thin Films as Versatile Chemical Sensing Materials. *Materials Advances, 2*, 6169-6196
6. Crawford, S. E., Kim, K. J., & Baltrus, J. P. (2022). A Portable Fiber Optic Sensor for the Luminescent Sensing of Cobalt Ions using Carbon Dots. *In Revision.*
7. Crawford, S. E., Kim, K. J., Diemler, N. A., & Baltrus, J. P. (2022) Efficient and Rapid Synthesis of a Luminescent, Solvent and Ion-Responsive Copper 2-aminoterephthalate Thin Film. *Submitted*.

Outreach: Presentations

1. August 2022, “Metal-organic Framework Thin Films: From Synthetic Strategies To Critical Metal Ion Sensing,” **International Materials Research Congress 2022**, Cancun, Mexico (Invited, virtual)
2. June 2022, “Development of a Portable Fiber Optic Luminescence Sensor for Rare Earth Elements,” **TechConnect World Innovation Conference & Exposition 2022**, Washington, DC
3. March 2022, “Luminescence-Based Sensing of Rare Earth Elements Using Zinc Adeninate Metal-Organic Frameworks ” **American Chemical Society 2022 Spring National Meeting**, San Diego, CA (Virtual)
4. March 2021, “Metal-Organic Framework-based Luminescent Sensors for Rare Earth Elements,” **Pittcon 2021**, Virtual Conference
5. November 2020, “Rapid, Selective, Ambient Growth and Optimization of Copper Benzene-1,3,5-Tricarboxylate (Cu-BTC) Metal Organic Framework Thin Films on a Conductive Metal Oxide for Sensing Applications,” **Materials Science & Technology 2020**, Virtual Conference
6. November 2020, “Luminescent Metal-Organic Framework-Based Sensors for Rare Earth Elements in Aqueous Streams,” **Materials Science & Technology 2020**, Virtual Conference
7. December 2019, “Metal-Organic Framework - Based Luminescent Detection of Rare Earth Elements,” **Materials Research Society Fall Meeting and Exhibit**, Boston, MA
8. April 2019, “Materials for Rare Earth Sensitization and Photoluminescence-Based Detection,” **Pittsburgh Quantum Institute 2019**, Pittsburgh, PA

Outreach: Sensor Symposium

Description:
Renewable energy technologies such as wind power and electric vehicles are heavily reliant upon a variety of metals, including rare earth elements, cobalt, lithium, and nickel. Ever-increasing global adoption of renewable energy sources has spurred significant demand for these metals, however economic, geopolitical, and environmental challenges threaten to destabilize the supply chain. These factors have incentivized increased domestic production from resources such as coal, its utilization byproducts, and electronic waste. However, tedious and expensive characterization techniques (both for metal prospecting and process monitoring) have been significant barriers towards cost-effective domestic production, and alternative methods for metal characterization are needed that are rapid, portable, sensitive, and cost-effective. This symposium highlights recent progress in the development of state-of-the-art analytical techniques (for example, optical, electrochemical, and bio-inspired methods) that are field-deployable for the characterization of critical metals.

Organizer: Scott Crawford - National Energy Technology Laboratory

Biography: Dr. Scott E. Crawford is currently an Analytical Chemist at Leidos Inc.-National Energy Technology Laboratory, where he develops optical sensors for high value metal cations. He obtained his PhD in Analytical Chemistry from the University of Pittsburgh in 2019 under the supervision of Prof. Jill Millstone, where he studied the impact of surface chemistry on the optical and charge transfer properties of luminescent coinage metal nanoparticles. Notable recognitions include the Mickey Leland Energy Fellowship, the Eastern Analytical Symposium Graduate Student Award, the University of Pittsburgh Andrew Mellon Predoctoral Fellowship, and the Society for Chemical Industry Scholar Award.

Speakers:
Scott Crawford - National Energy Technology Laboratory
Charles Henry - Department of Chemistry, Colorado State University
Juewen Liu - Department of Chemistry, University of Waterloo
Madhavi Martin - Oak Ridge National Laboratory
Joseph Cotruvo - Department of Chemistry, Penn State University

Pittcon 2023: March 18-22nd, 2023 (Philadelphia, PA)

Outreach: CM Article Collection

Research Topic Description

Title: Materials Enabling Sensitive, Portable Detection of Critical Metal Ions

Background

Sustainable energy technologies currently rely heavily on various metals, including rare earth, cobalt, lithium, and nickel. Increased worldwide adoption of renewable energy sources has led to demand spikes for these metals. However economic, geopolitical, and environmental factors have led to concerns about supply chain stability, and these factors have motivated increased domestic production. Metal-rich resources such as coal, coal utilization byproducts, and electronic waste have emerged as environmentally benign sources of critical metals as an alternative to mining. However, slow and expensive characterization techniques (such as inductively-coupled plasma mass spectrometry) for metals prospecting and process monitoring are crucial barriers to production. Thus, there is a critical need for inexpensive, rapid, and sensitive sensing techniques to characterize critical metals. Although portable sensing platforms have been developed that are capable of monitoring luminescent, optical, electrochemical, and other sensing responses, innovations in sensing materials remain a key bottleneck. This Research Topic will focus on both experimental and computational papers on the development of highly selective and sensitive materials for critical metals detection, which will facilitate metal characterization and production by lowering the financial and time costs associated with analysis.

Frontiers in Materials, currently recruiting Guest Editor team

Conclusions and Outlook

- Luminescent sensors offer the potential for part-per-billion levels of sensitivity on a minute time-scale at substantially lower costs than the current state-of-the-art.

- Interferants, including the presence of competing metal ions and low pH, present significant challenges, however materials have shown promise in real streams and processes.

- Potential for real-time sensing and/or swapping coated fiber tips to probe multiple economically critical metals.

For Further Information

NETL RESOURCES

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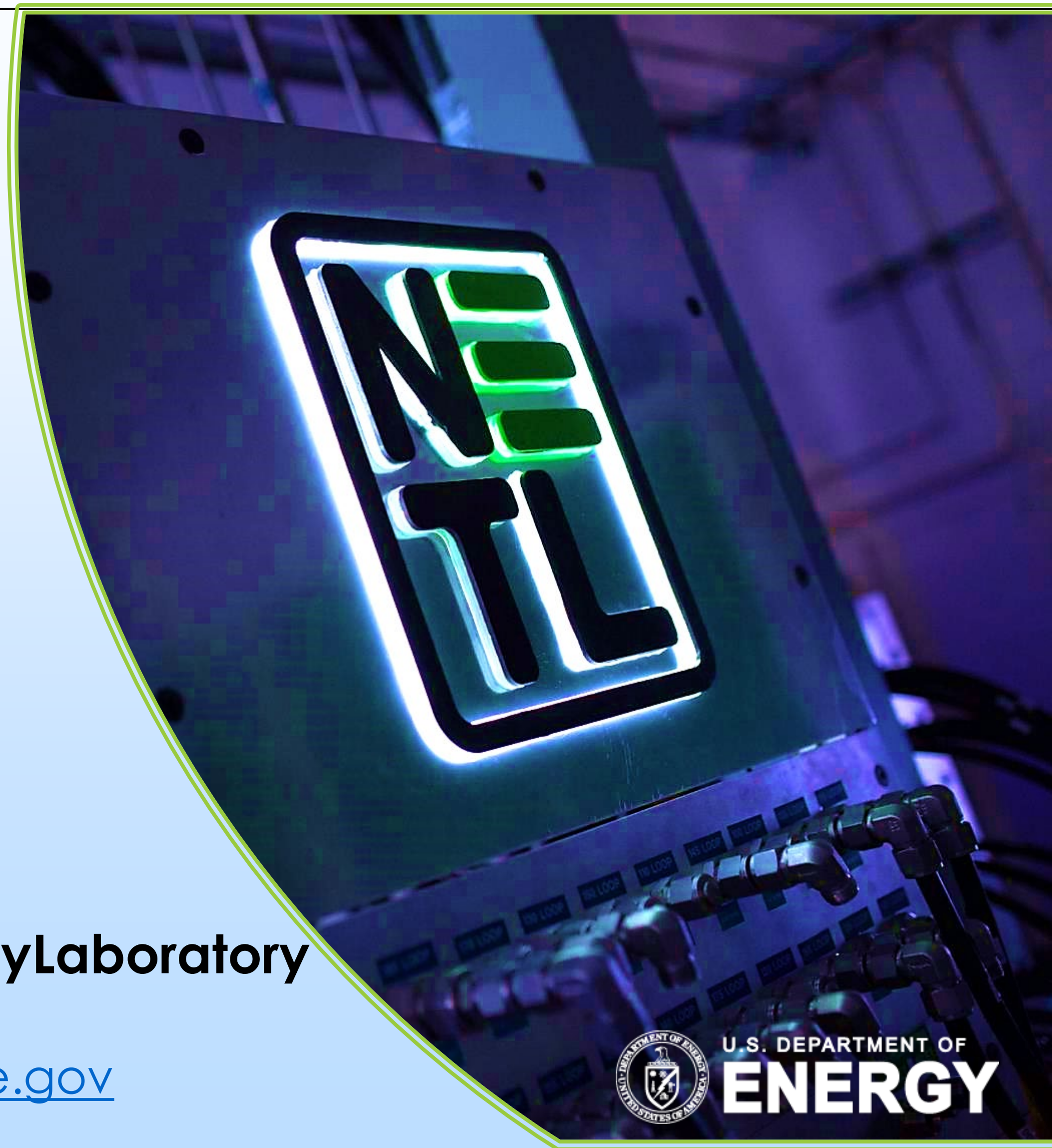
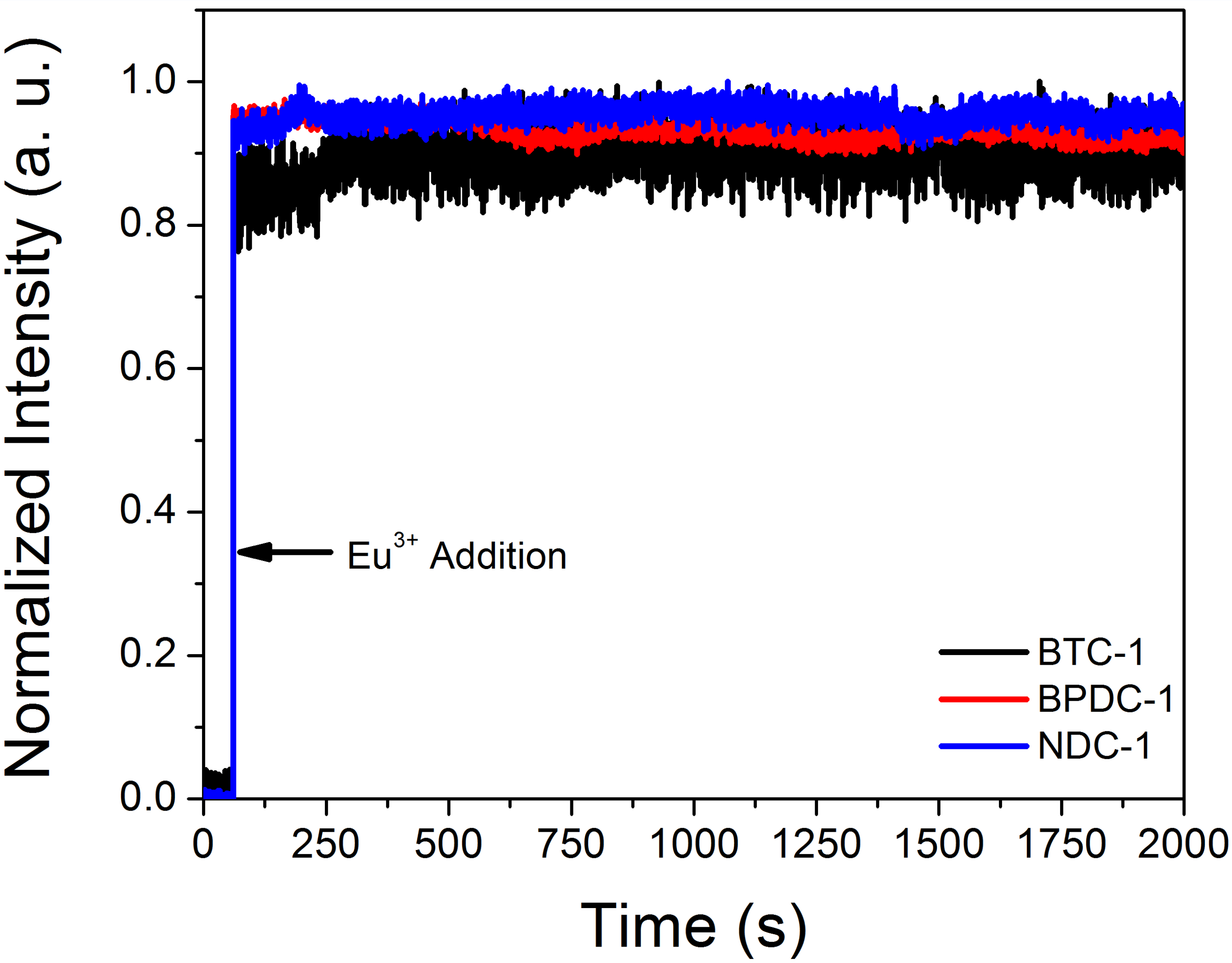
Contact: Scott.Crawford@netl.doe.gov

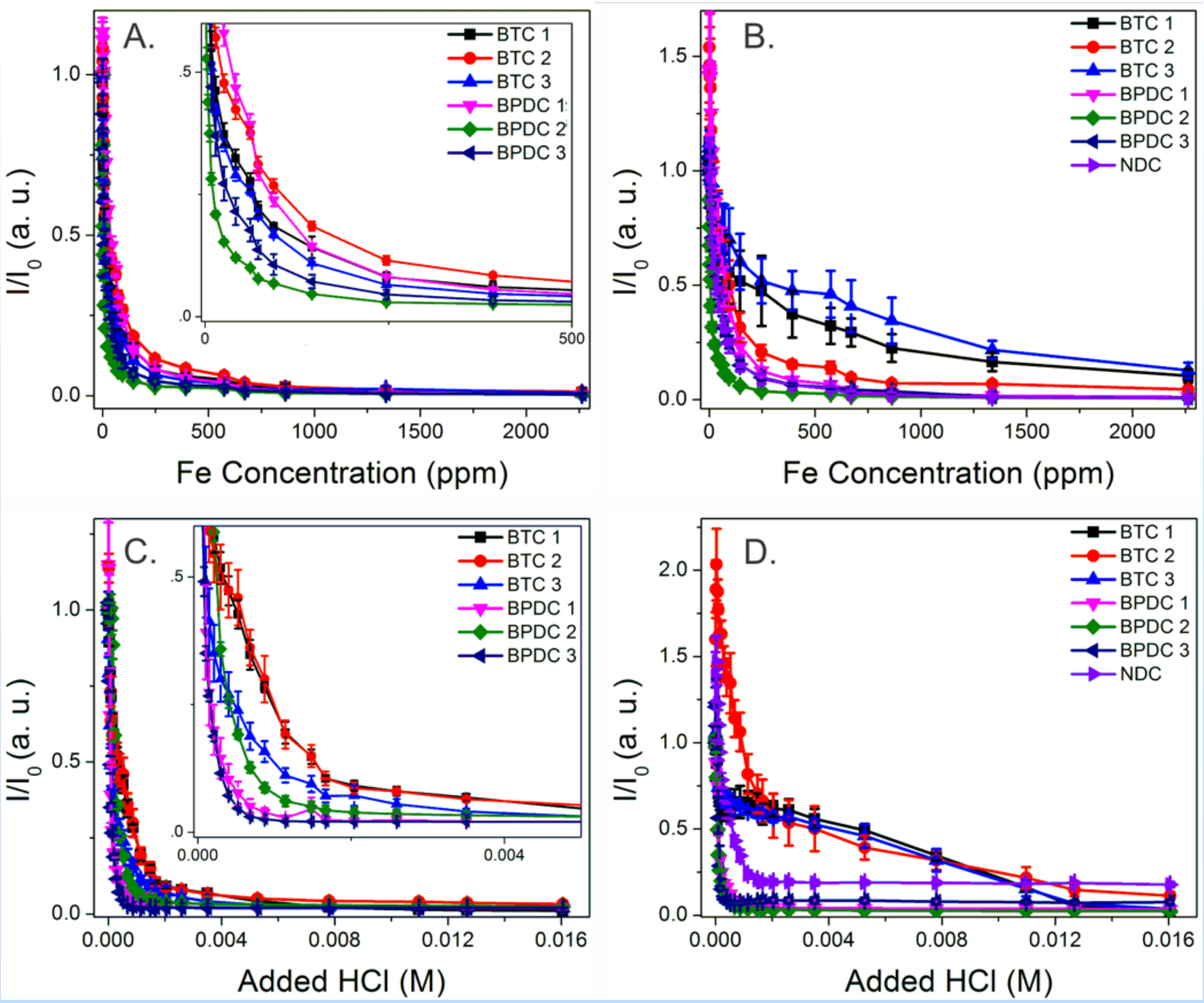


U.S. DEPARTMENT OF ENERGY

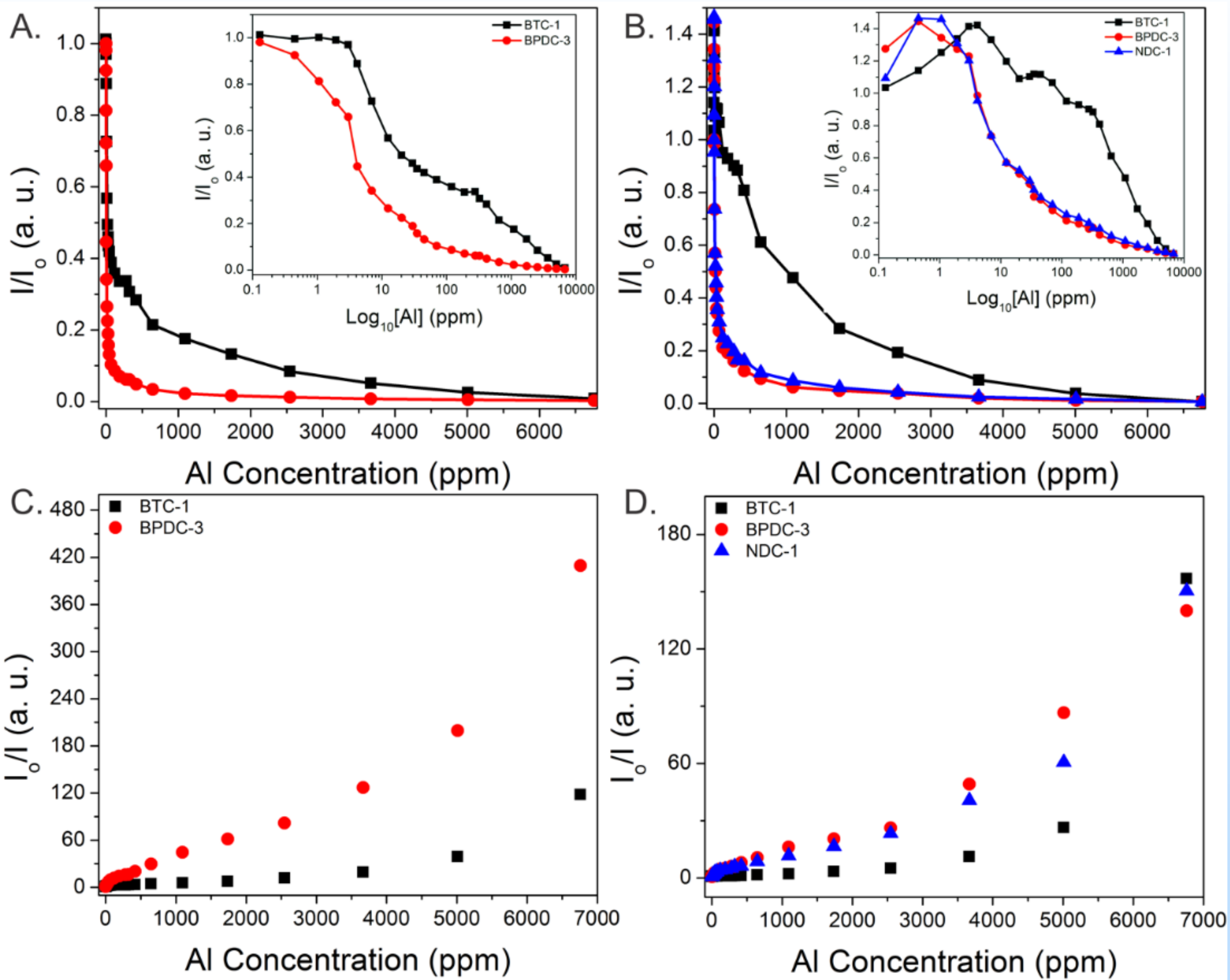
Appendix: Response Time



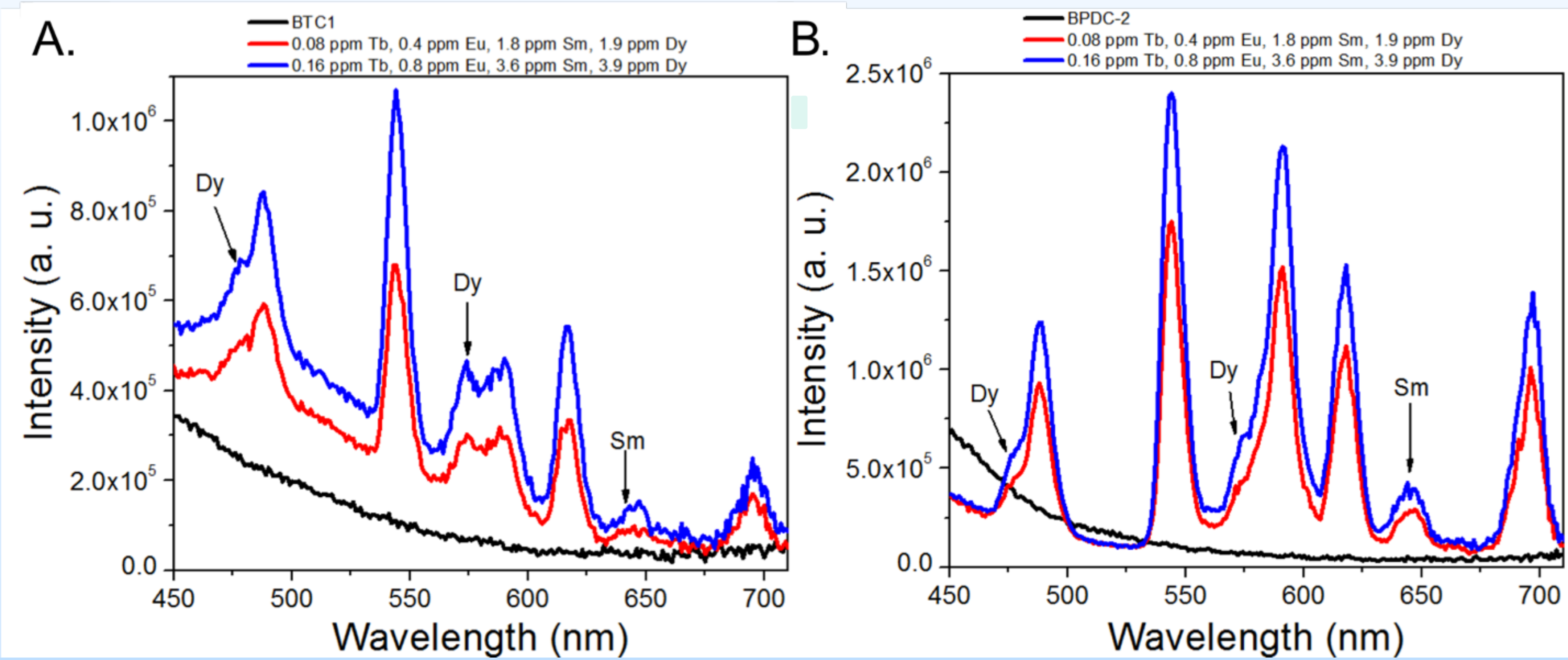
Appendix: Structural Influence



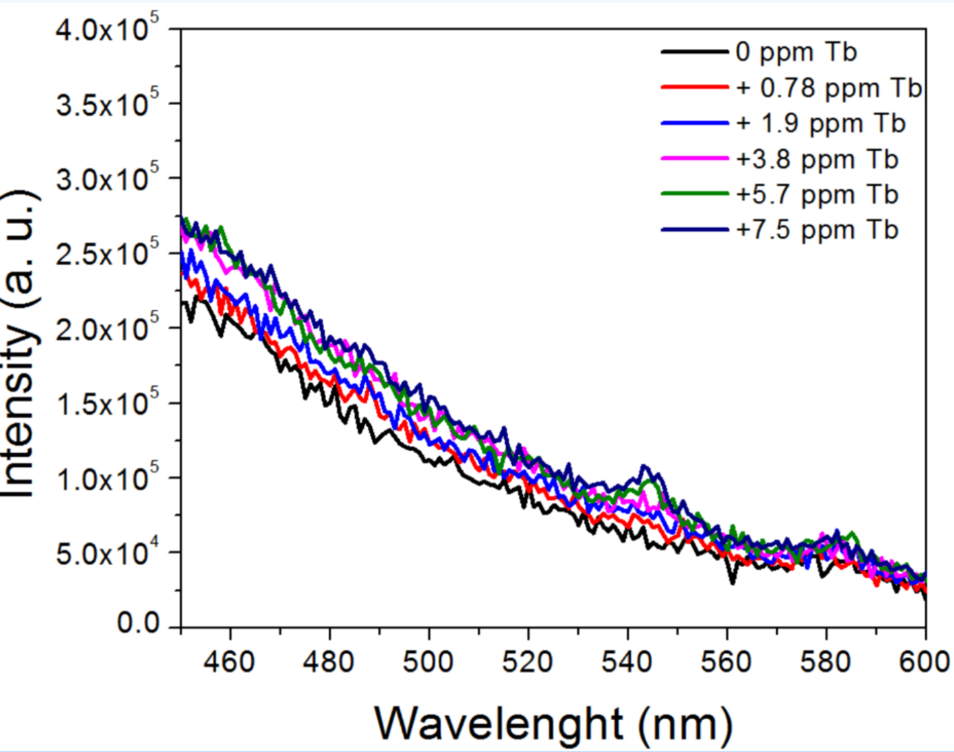
Appendix: Al(III) Interference

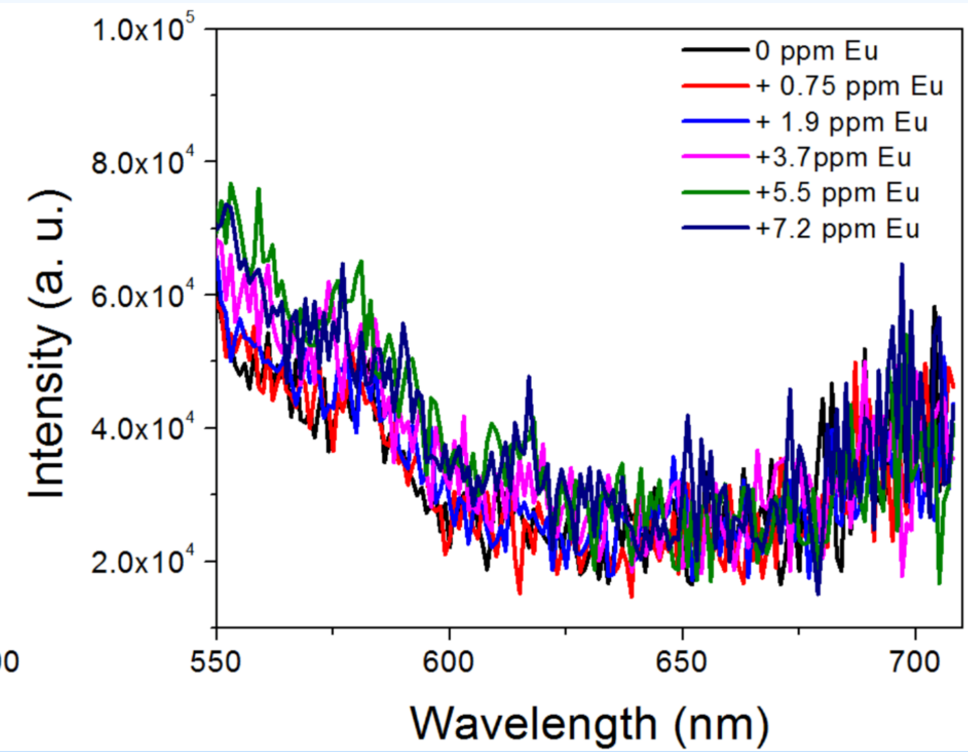


Appendix: Multiple REEs

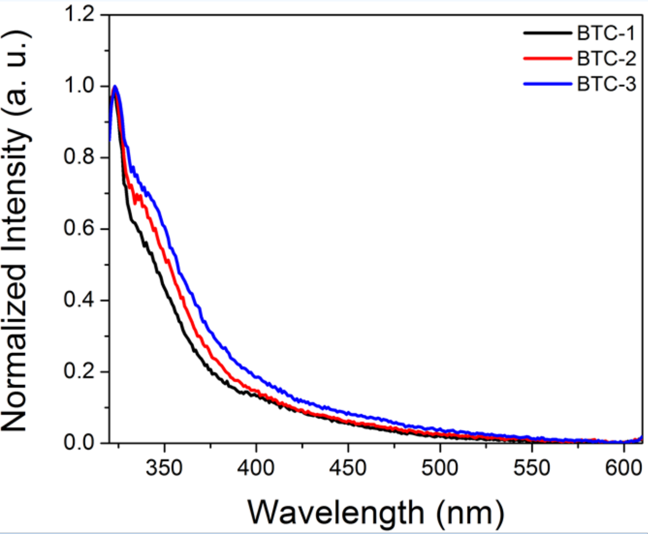


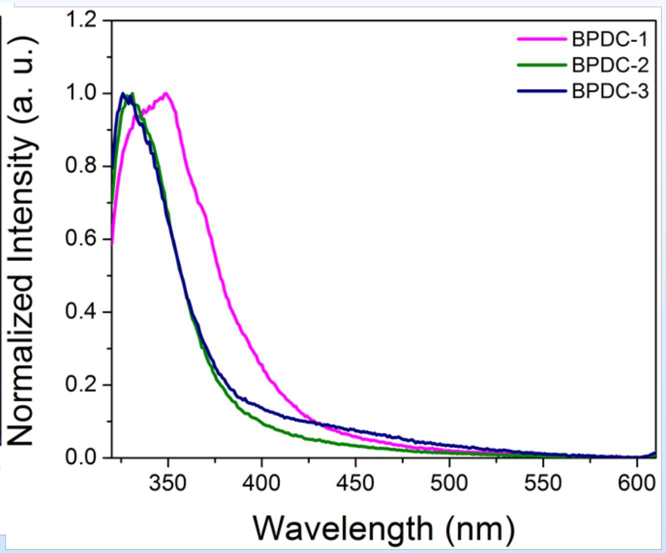
Appendix: No Sensitizer

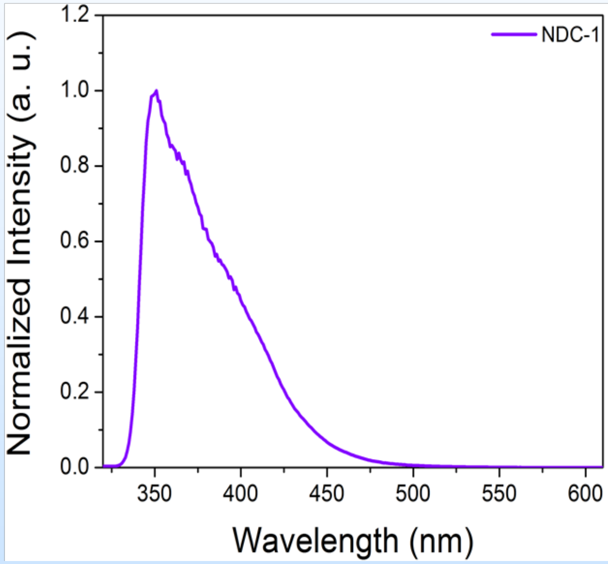




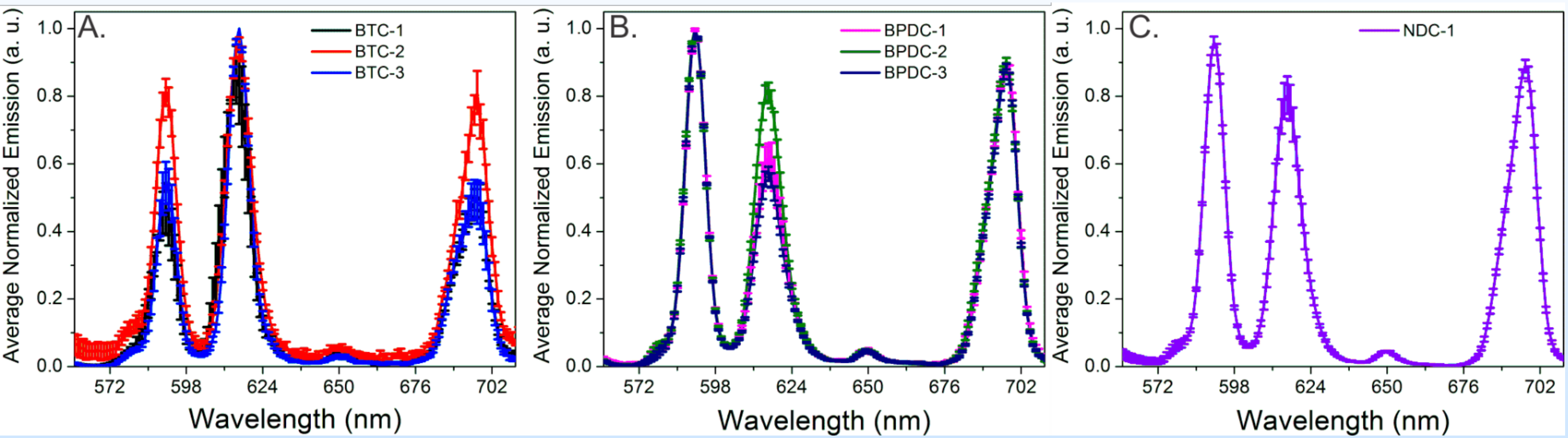
Appendix: Emission of MOF only





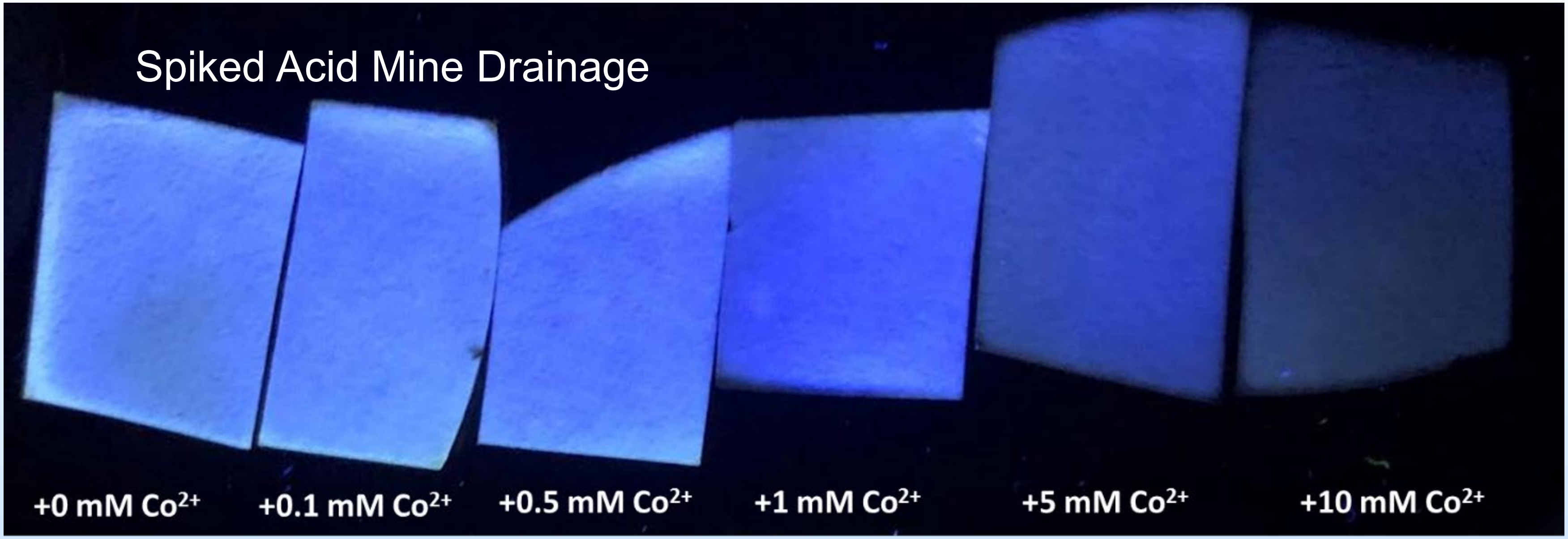


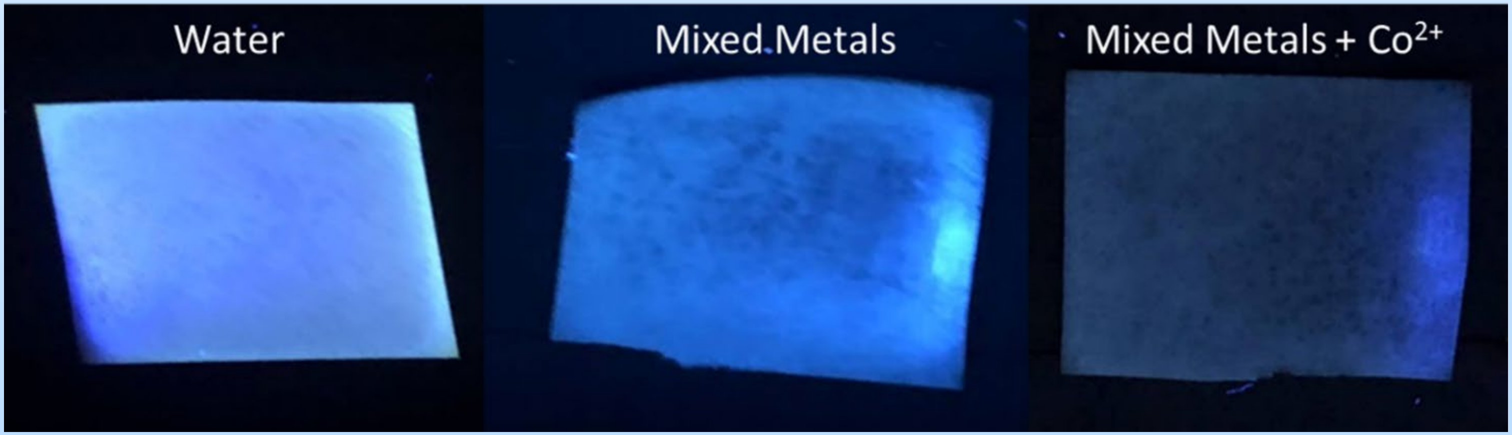
Appendix: Eu Differences



BTC MOFs exhibit enhanced Eu hypersensitive transition peak at 617 nm relative to the BPDC and NDC MOFs, indicating linker-dependent REE coordination.

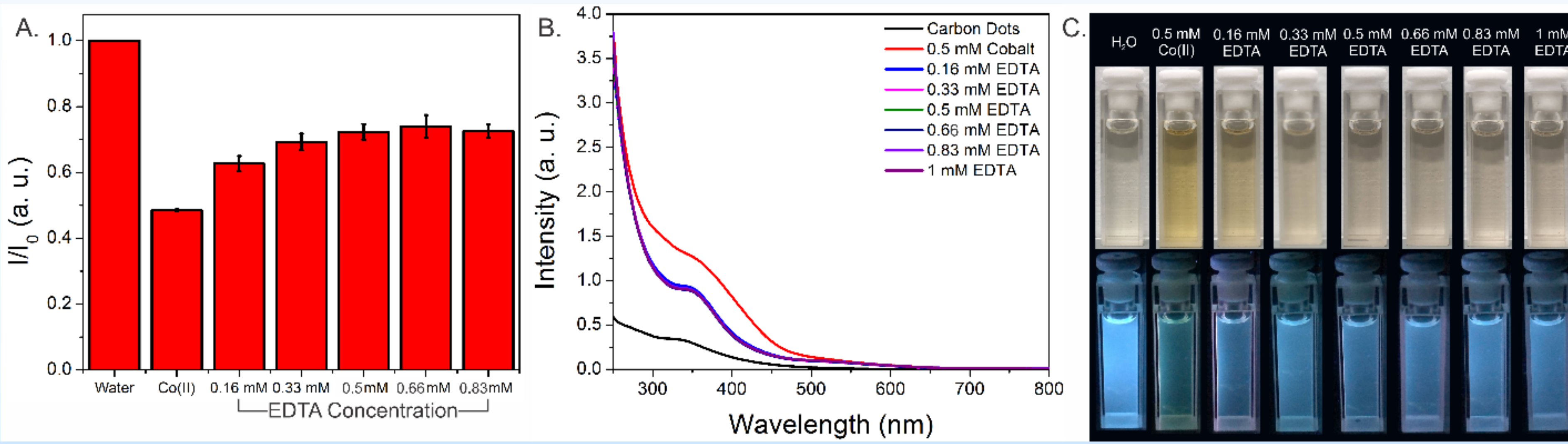
Appendix: Co Performance



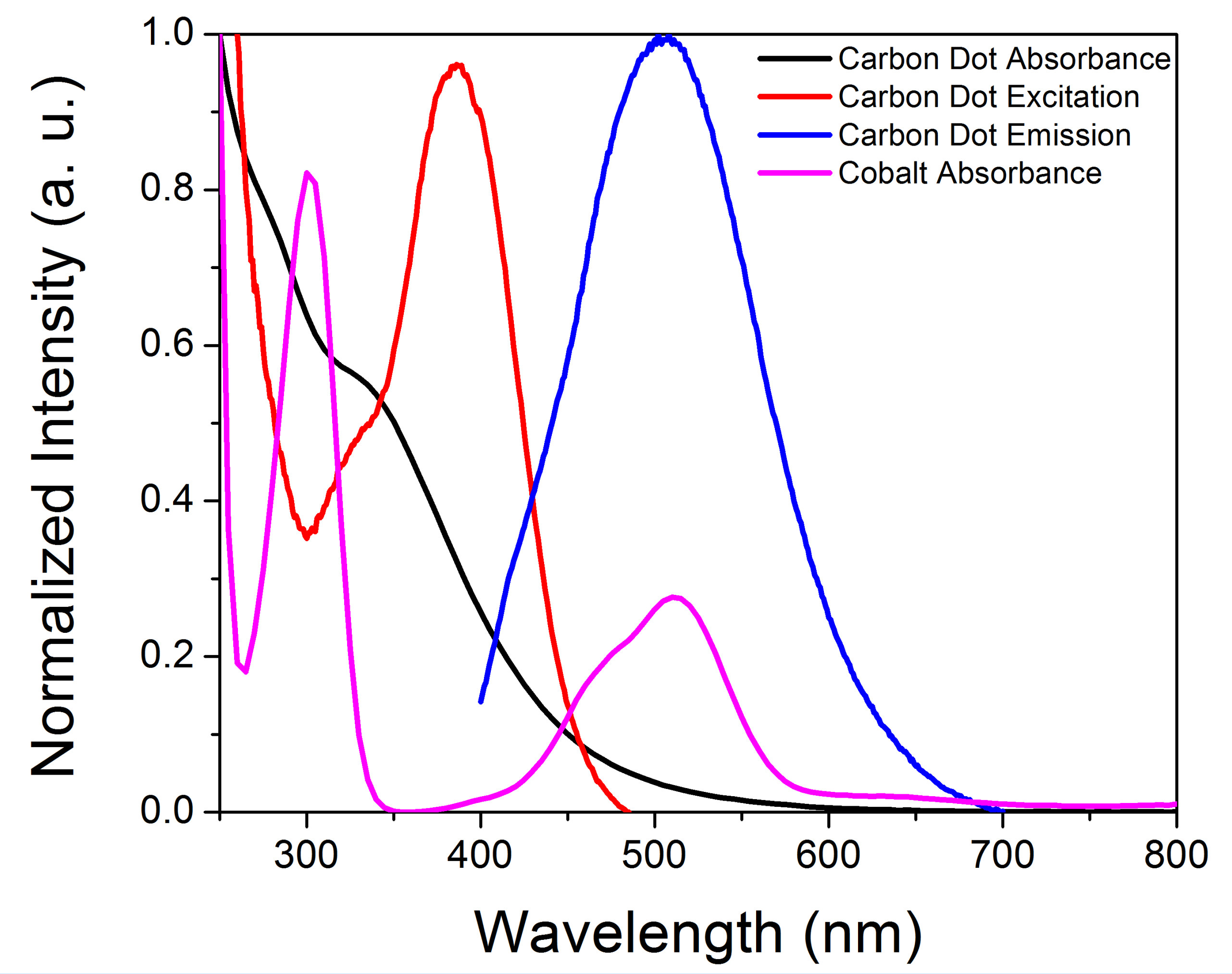


Appendix: Co Reversibility

Spiked Acid Mine Drainage

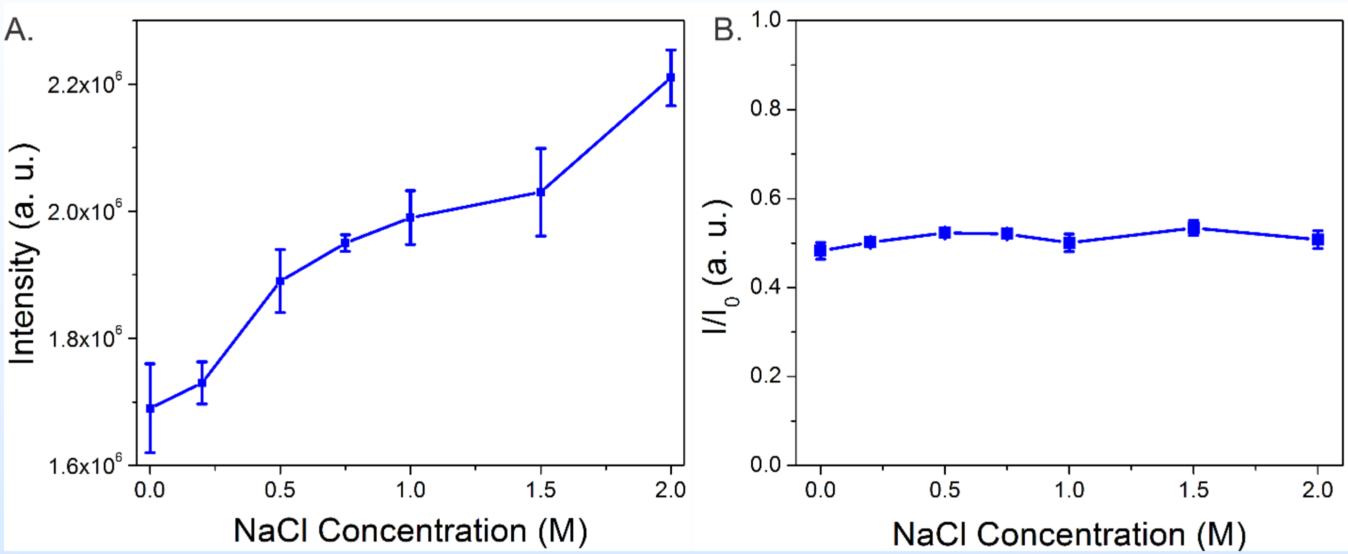


Appendix: Co Mechanism

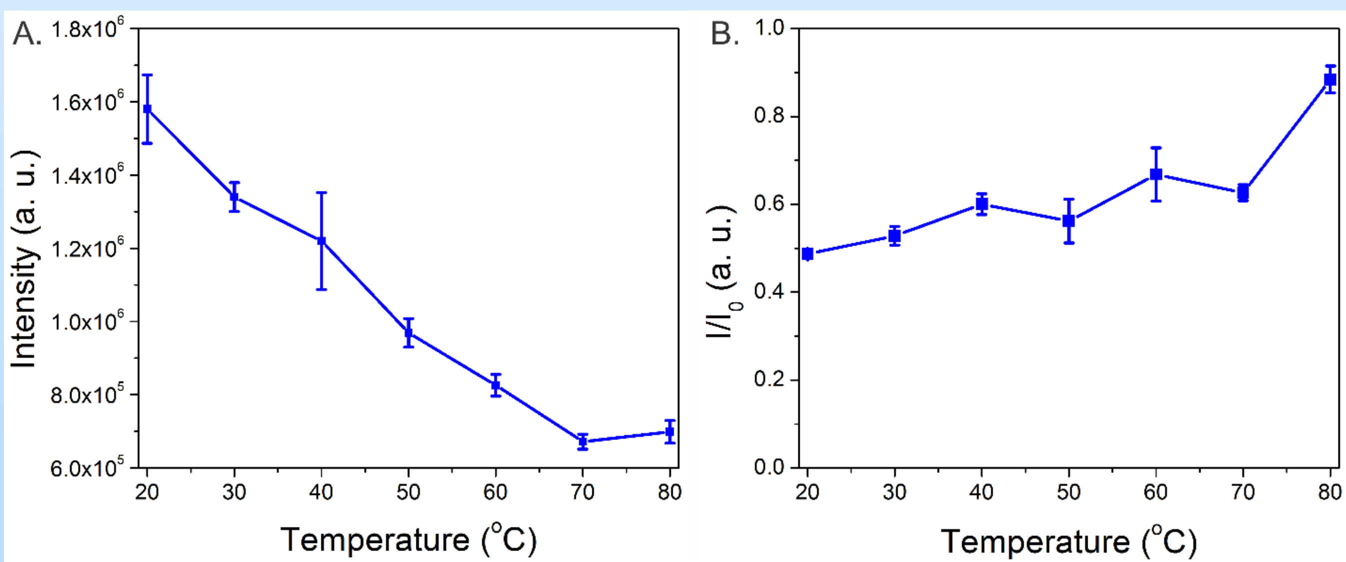


Appendix: Co Controls

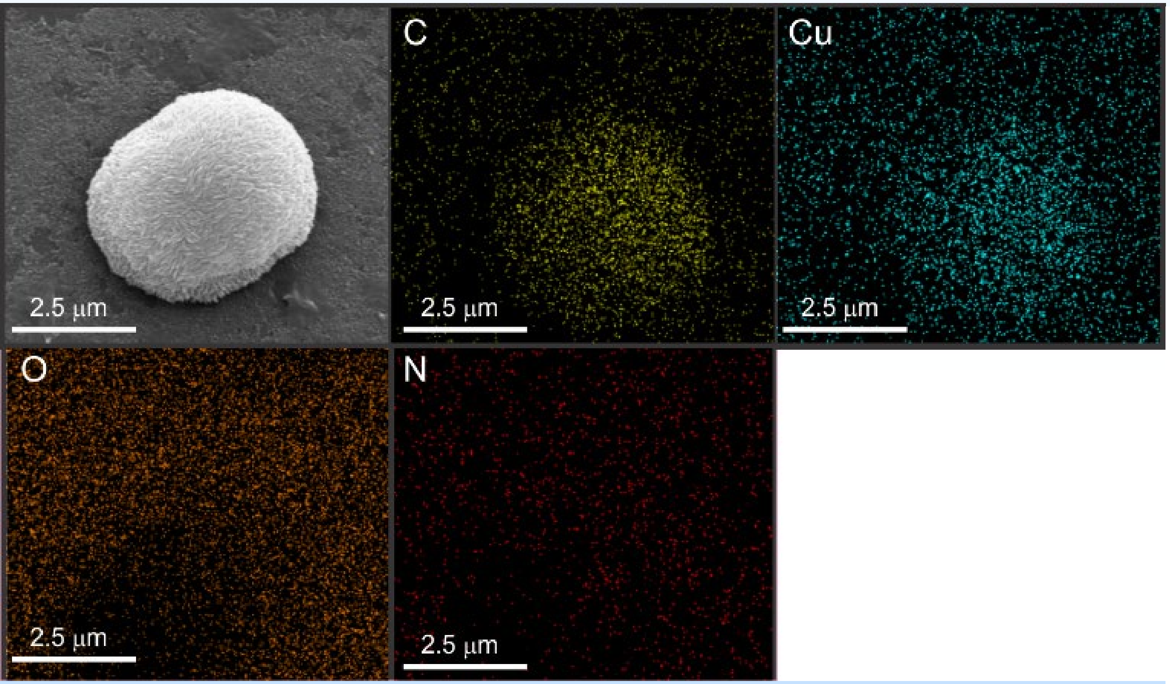
Salinity:

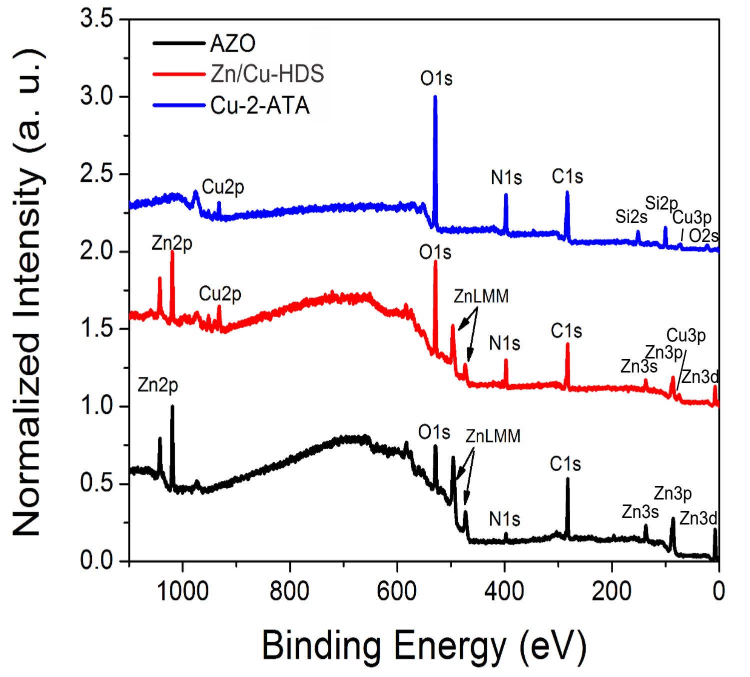


Temperature:

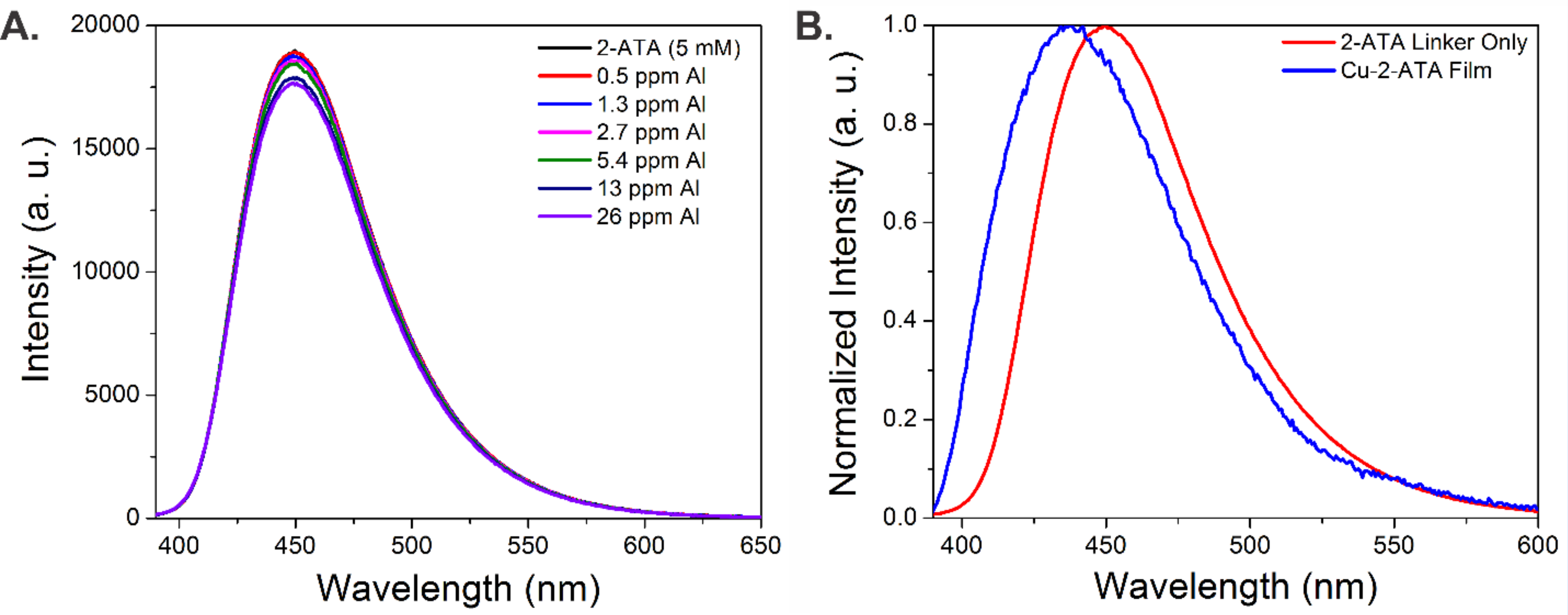


Appendix: Film Characterization

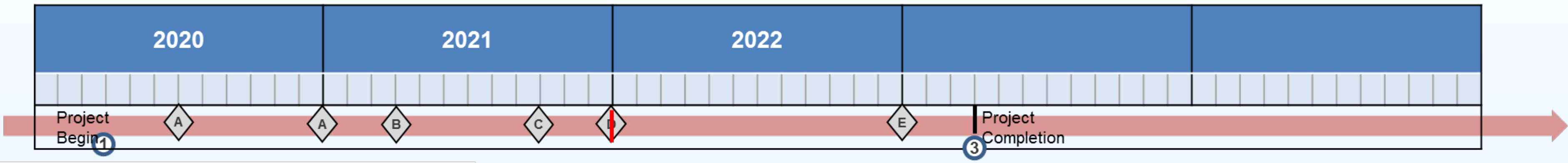




Appendix: Linker Control for Al



Gantt Chart



Milestones Realized & Planned

A. Vetted initial prototypes of optical probes with coated Bio-MOF sensitizers for in situ detection of REEs
B. Demonstrated field or process-related testing for REE detection with prototype of optical probe detection device
C. Demonstrated REE detection in process streams with low initial pH
D. Demonstrated feasibility of extending detection to critical elements including focus on novel materials for sensitizing Co detection
E. Complete optimization of sensitizing materials for Co and other select critical elements and demonstrate detection in field and/or process samples

Impact

Key Accomplishments/Deliverables	Value Delivered
• Demonstrated a device for measurement of REEs in liquids at low ppm or ppb levels using an optical probe • Demonstrated initial application to non-REE critical elements in liquids using an optical probe	• Real-time field or process analysis of REEs and critical elements in liquid streams, eliminating the need for lab analysis with associated higher cost and delays • Addresses Pillar 1 of MSD Multi-Year Program Plan (Oct 2021)

Chart Key

- # TRL Score
- Go / No-Go Timeframe
- Project Completion
- Milestone