Portable Luminescent Sensor Technologies for Economically Critical Metals

FWP-1022420

Scott E. Crawford, PhD

National Energy Technology Laboratory

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Disclaimer

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Author and Contact Information

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Project Overview

Task Team Members

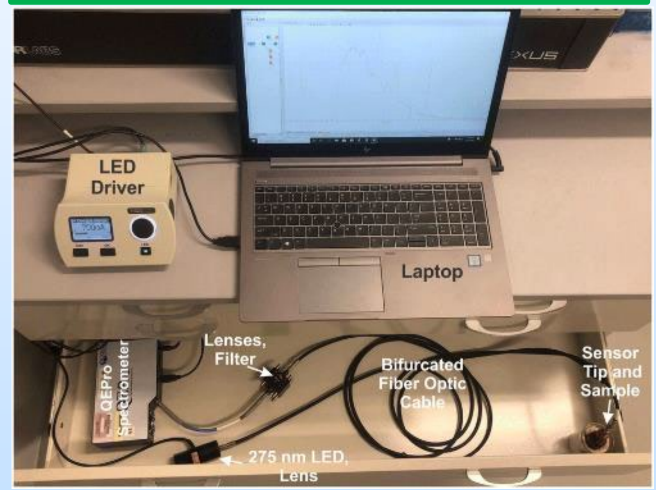
Principal Investigator: Scott Crawford

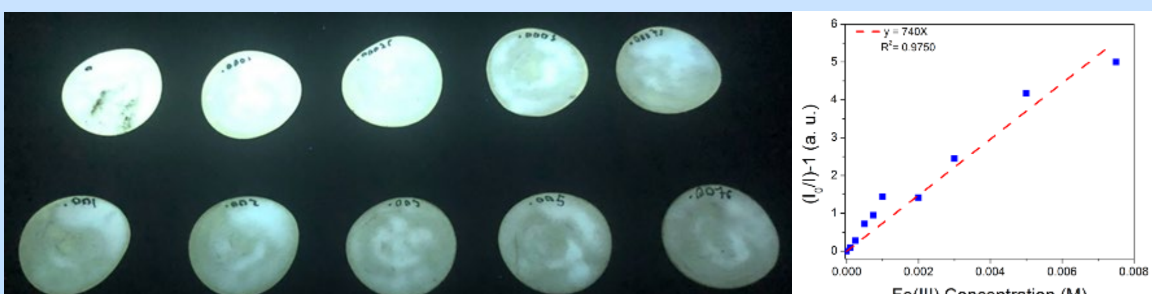
Plan Overview: Refine a device and procedure for measurement of REEs and other critical elements in liquid streams at <u>low ppm or ppb levels</u> using an optical probe. Work with potential commercial partners to identify key concerns that must be mitigated before deploying the optical probe in a commercial device. Develop a patent application, report, and/or manuscript detailing the development and performance of the REE probe with sensing material immobilized on the optical fiber tip. Demonstrate steps to mitigate acids and other interfering metals (iron, aluminum, calcium, etc.) in real time to improve sensor performance in complex environments.

Task Value	2023 $42k

End Product:

Optically-based, inexpensive, portable, and rapid detectors for REEs and other critical minerals.

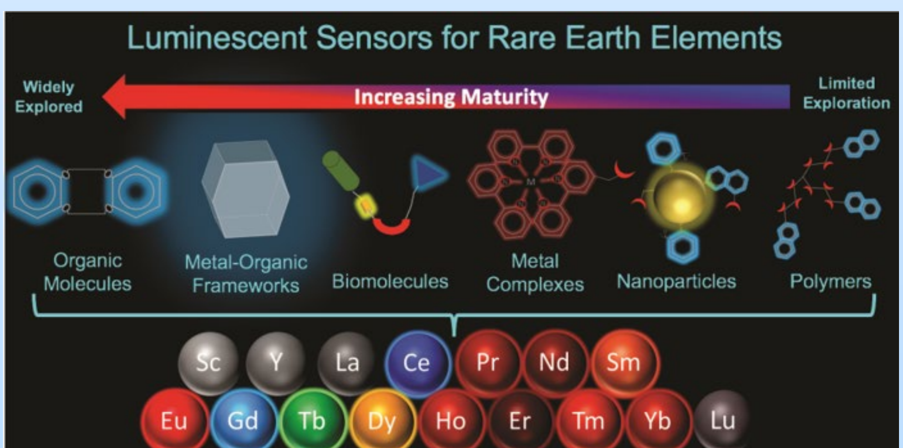




Carbon dot-coated test strips under UV light after exposure to increasing concentrations of Fe(III), a common interferant in critical mineral processing. Luminescence decreases as a function of iron concentration. Right: Calibration curve used to estimate detection limits for Fe(III) using the test strips.

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)
- Published comprehensive review manuscript on sensitizer materials for REEs
- Moved from cyanide sensor to metal-organic frameworks (MOFs)
- Demonstrated detection by immobilizing sensitizers on the fiber optic in portable system
- Optimized detection of select REEs based on MOF structure (Patent Filed August 2023)
- Developed sensor materials for other critical metals (Co, Al) and interferants (Al, Fe)
- Collaborated with external organizations to develop other low-cost compact platforms



Crawford, S., Ohodnicki, P., Baltrus, J.; *J. Mater. Chem. C* **2020**, *8*, 7975

Importance of Characterization

Prospecting:

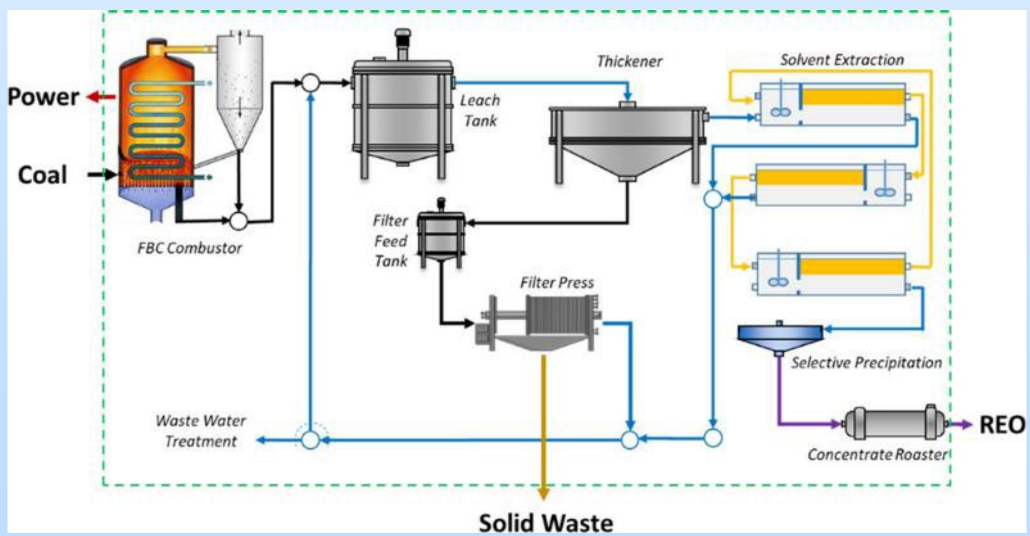
DOI: 10.1016/j.coal.2006.01.009 DOI: 10.1016/j.coal.2011.05.006 DOI: 10.1007/s11356-015-4111-9

E-Waste

The Atlantic

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

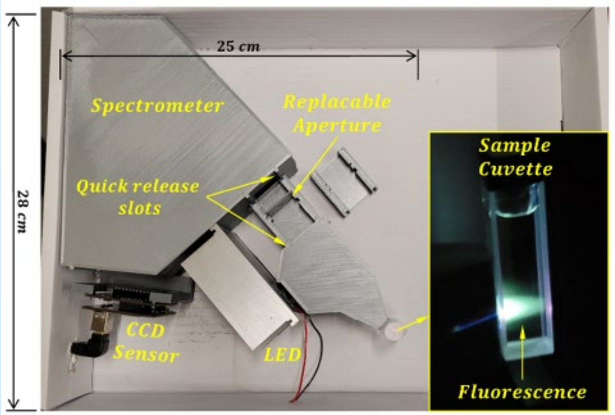
Process Monitoring:



DOI: 10.1021/acs.energyfuels.9b00295

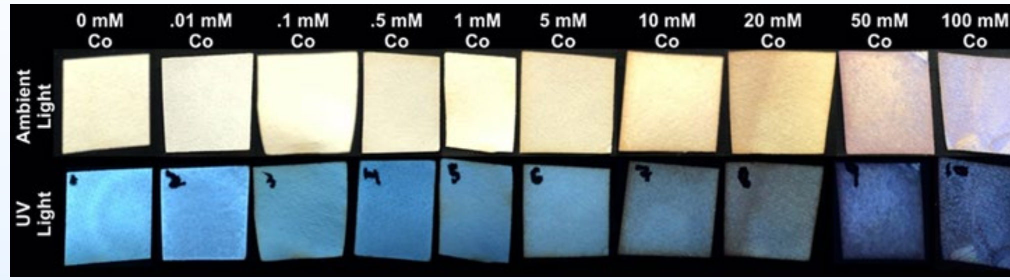
State-of-the-Art is Costly and Slow

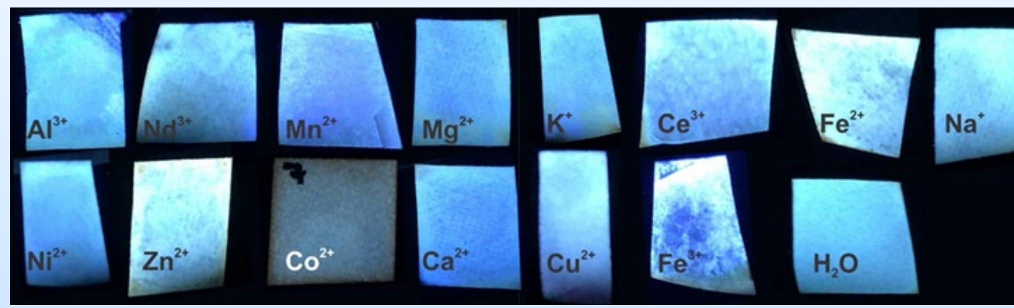
Technique	Instrument Cost	Detection Limit	Portable?
Inductively-Coupled Plasma Mass-Spectrometry	~$180k	Part-per-trillion	No
X-Ray Fluorescence Spectroscopy	~$13-17k	10s of part-per-million	Yes
Laser-Induced Breakdown Spectroscopy	~$30-50k	10s of part-per-million	Yes
Luminescence Spectroscopy	~$18-35k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



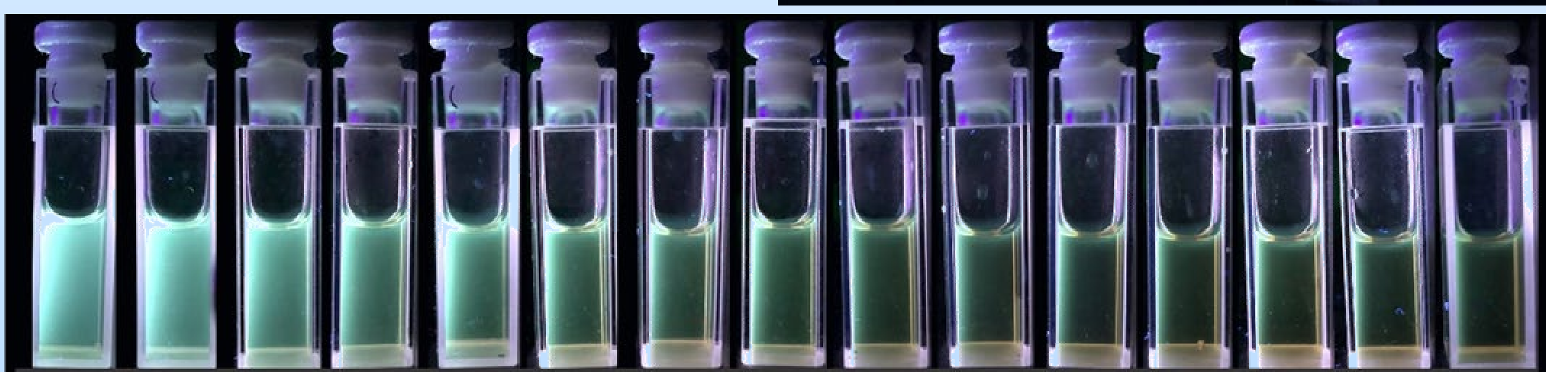
Advantages of Luminescence

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





UV Light



0 ppm Co^{2+} | 2.9 ppm | 5.9 ppm | 12 ppm | 18 ppm | 23 ppm | 29 ppm | 35 ppm | 41 ppm | 47 ppm | 53 ppm | 58 ppm | 64 ppm | 70 ppm | 77 ppm

Technical Approach

- **Material Science:** discover and synthesize materials exhibiting a *selective* and *sensitive* response to target metals

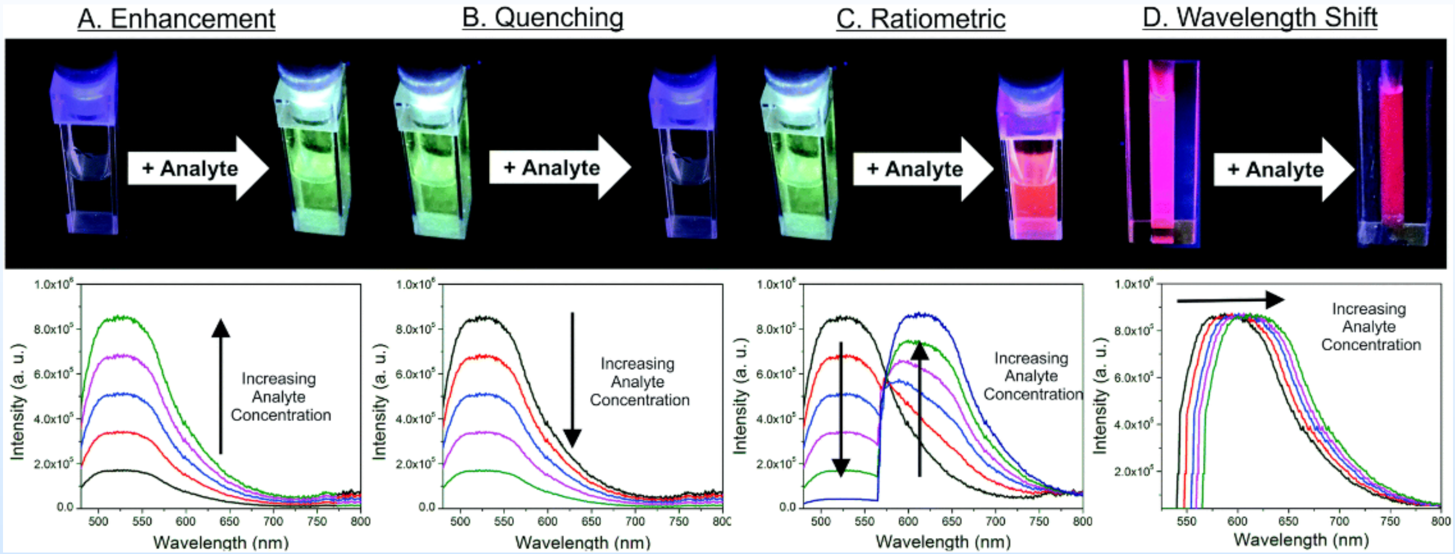
- **Platform Development:** continued optimization of compact spectrometer capable of integrating different sensing materials in solution and solid state

- **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

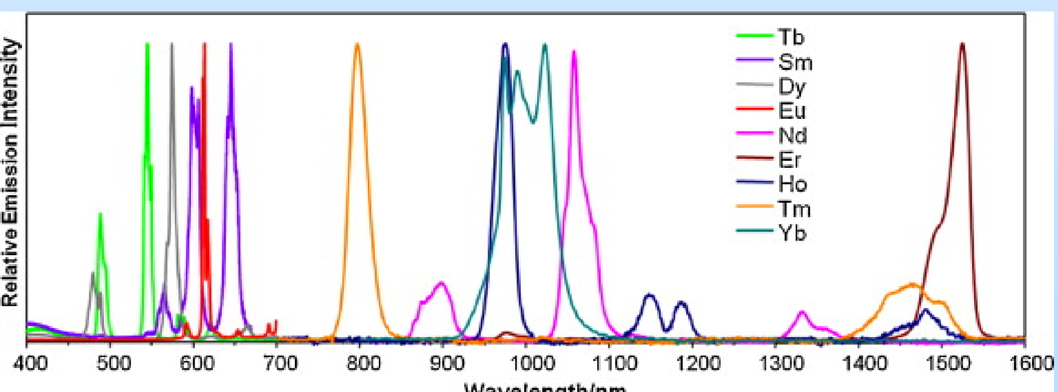
Luminescent Sensing of Metals

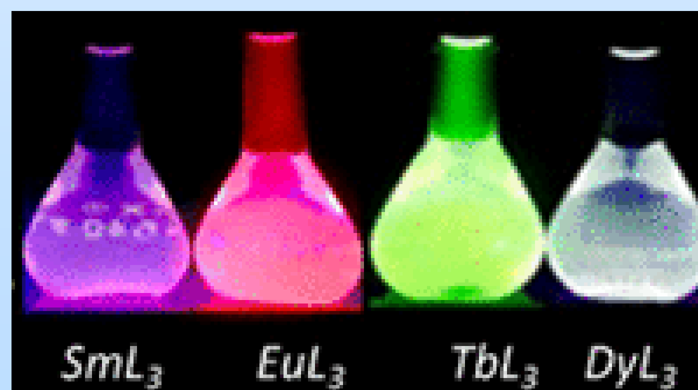
Traditional Approaches:



Ellis, J., Crawford, S., Kim, K.-J., *Mater. Adv.* **2021**, *2*, 6169-6196

Lanthanide/Rare Earth Sensitization:

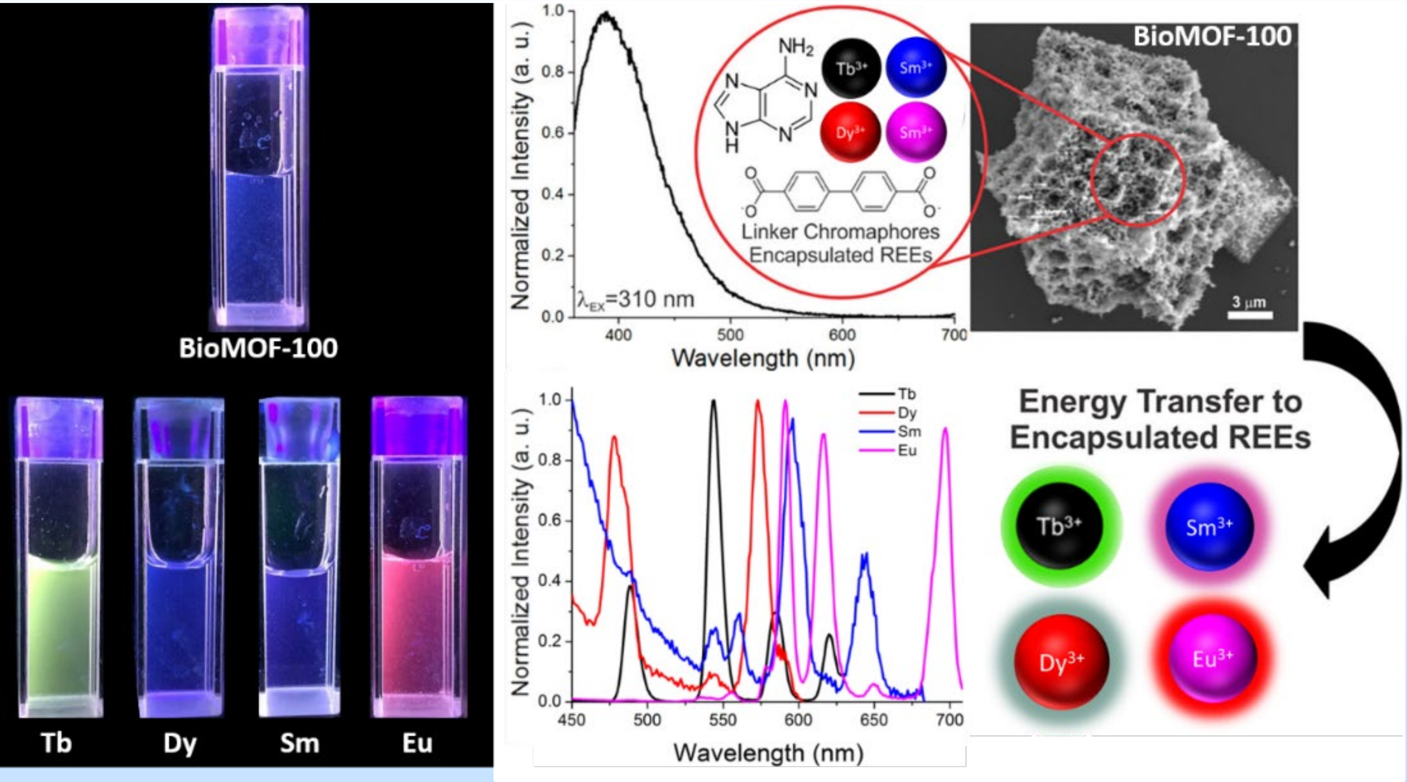




DOI: 10.1016/j.crci.2010.05.007

DOI: 10.1021/acs.inorgchem.7b02861

Initial Studies: Rare Earths

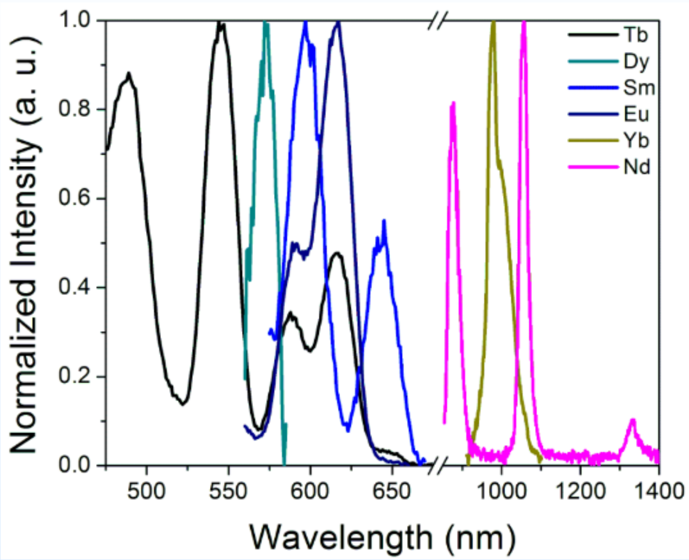


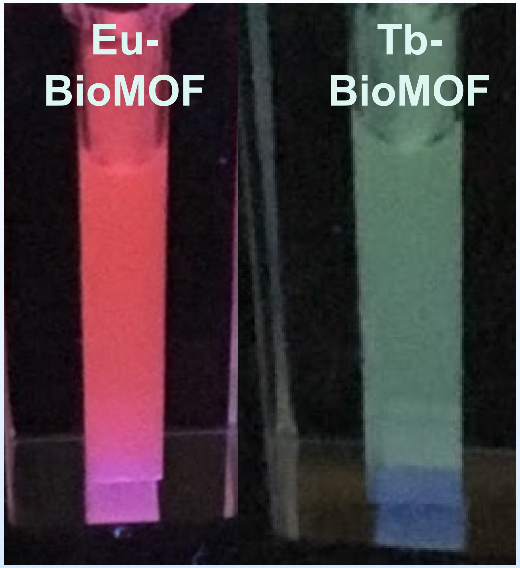
1. REE encapsulation
2. Excitation of MOF
3. Energy transfer
4. REE-centered emission

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, S., Gan X.Y., Lemaire, P., Millstone, J., Baltrus, J., and Ohodnicki, P., *ACS Sens.* **2019**, *4*, 1986

One Material Senses Six REEs

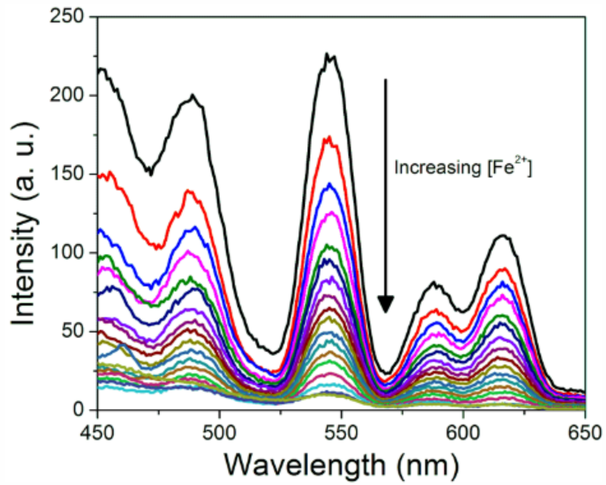


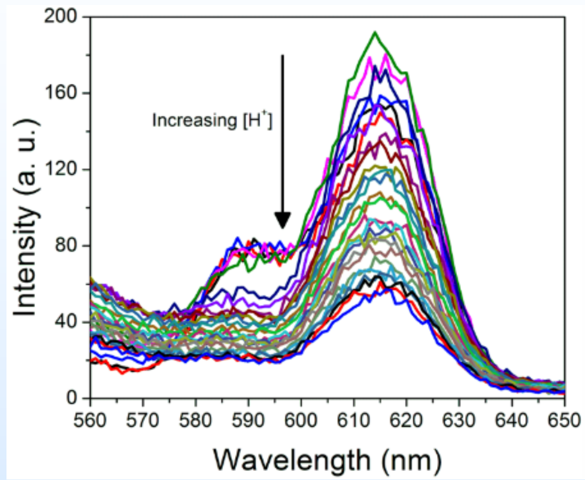


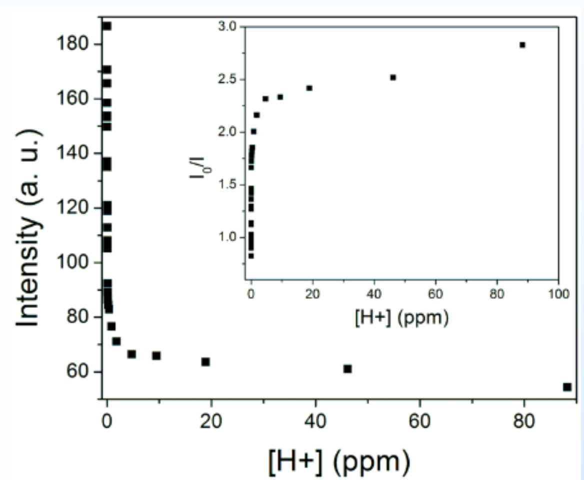
Part-per-billion (ppb) scale detection limits of six REEs with the same material!

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

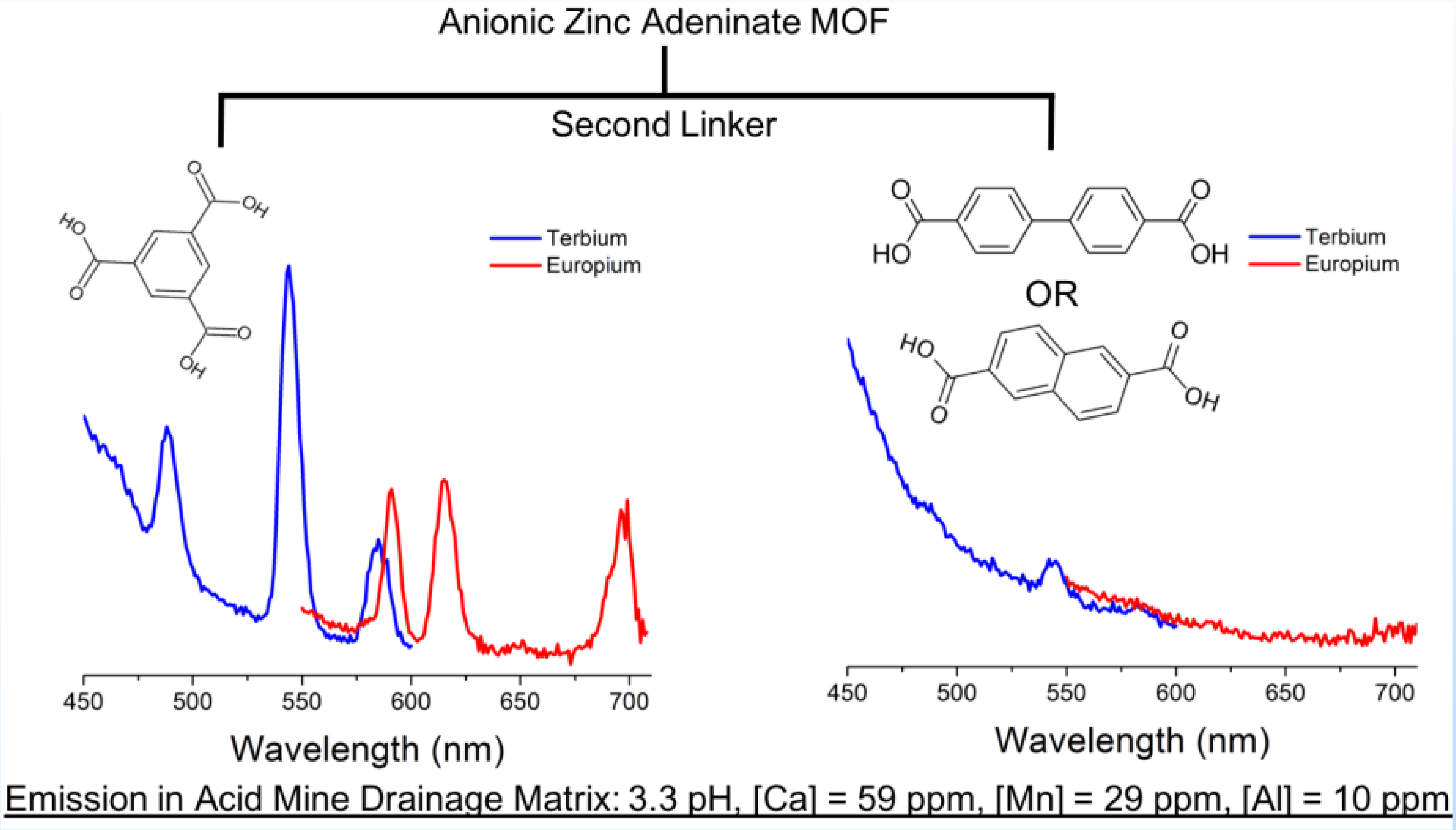






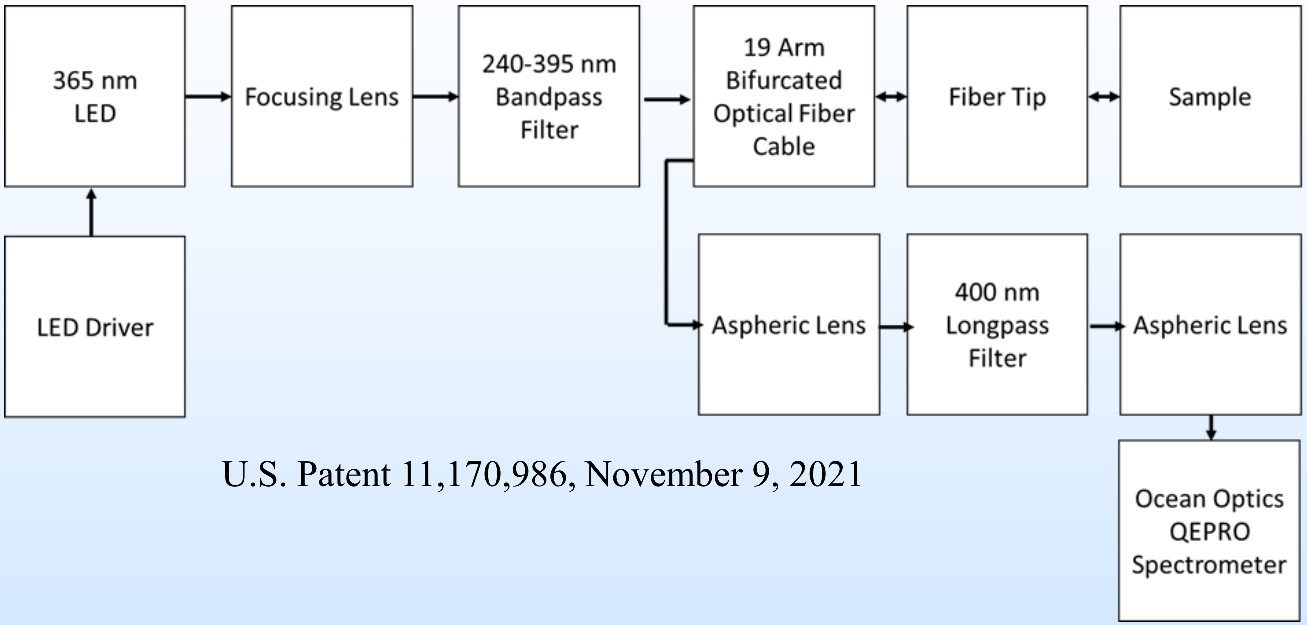
Location	pH	Total REE (ppm)	Fe (ppm)	Al (ppm)	Ca (ppm)	Mg (ppm)
Sitai Mine, China	3.61	**.0612**	4.73	8.83	249	1.03
Clarion, PA	4.4	**1.134**	385	9.1	149	236
Pittsburgh, PA	6.3	**0.00029**	22	0.1	66	20.1
Germany	4.8	**0.073**	0.01	4.01	405	193
Germany	3.8	**4.7**	404	88.2	57.8	1,139
Romania	3.0	**1.58**	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

Compact Analysis Platforms

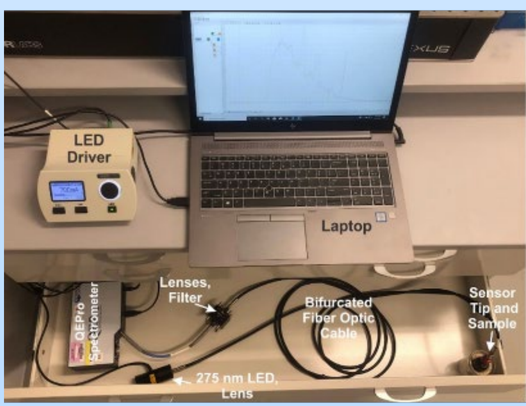


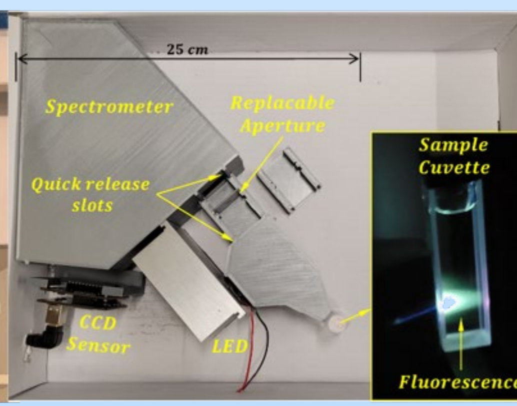
U.S. Patent 11,170,986, November 9, 2021

NETL Fiber Optic
~$20K

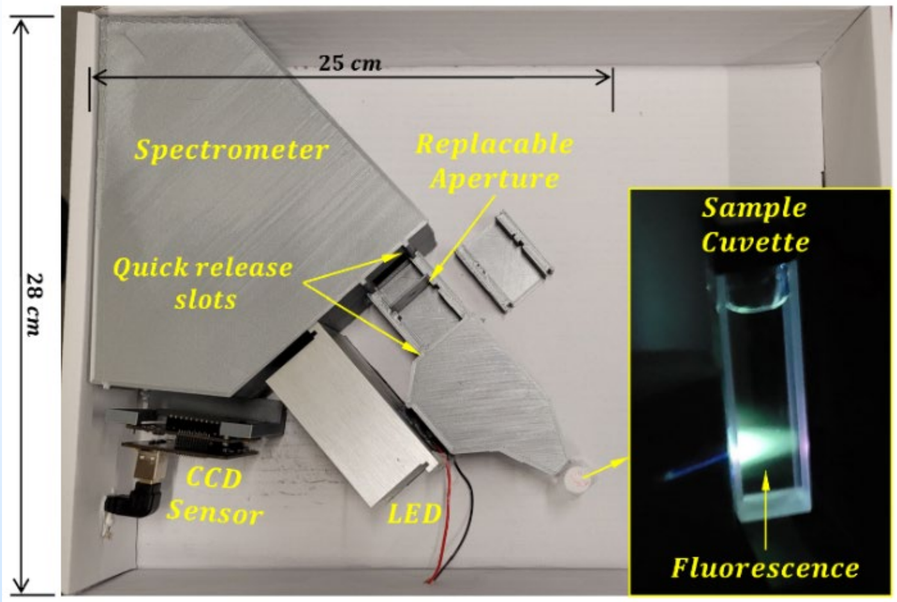
UPitt 3D Printed
~$5K

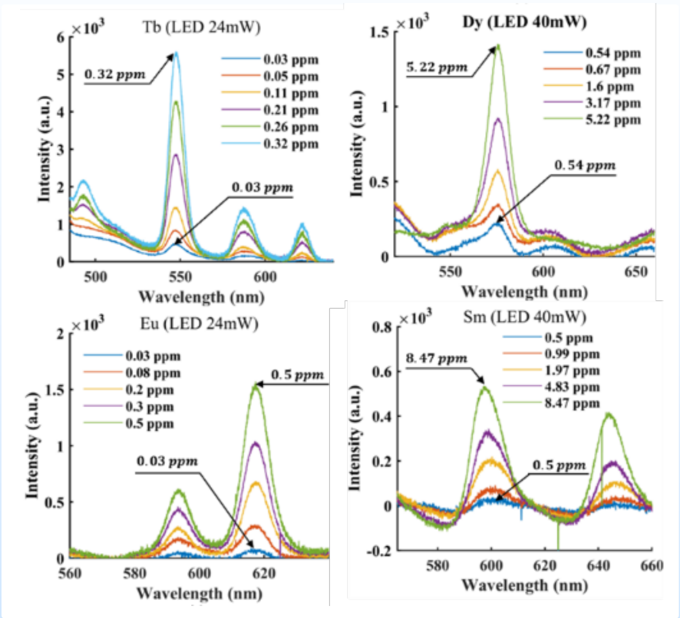
Blue Technology Test Strip Analyzer
~$400





Integration with UPitt Platform



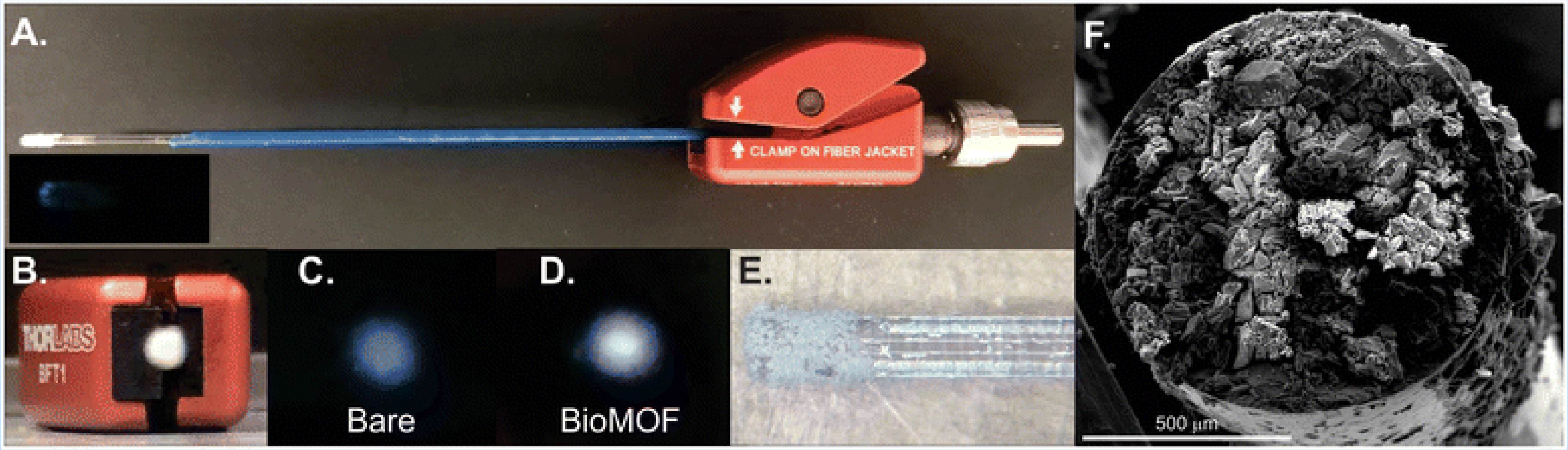


Sample	LOD (ppb)		LOQ (ppb)		Source power (Watt)	
	Our Sensor	Fluorolog 3	Our Sensor	Fluorolog 3	Our Sensor	Fluorolog 3
Tb	21 ± 3	**8 ± 1**	71 ± 10	**27 ± 4**	0.024	450
Eu	**43 ± 2**	70 ± 10	**143 ± 8**	220 ± 40	0.024	450
Dy	324 ± 26	**170 ± 10**	1081 ± 88	**550 ± 30**	0.04	450
Sm	**575 ± 42**	600 ± 90	**1917 ± 141**	2000 ± 300	0.04	450

Wu, Z., Crawford, S., Buric, M., Splain, Z., Chen, K; *IEEE Sens. J.* ***2023,*** *23*(11), 11574-11581

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**



Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int.* **2024**, *Advanced Article* (DOI: 10.1039/D4LF00001C)

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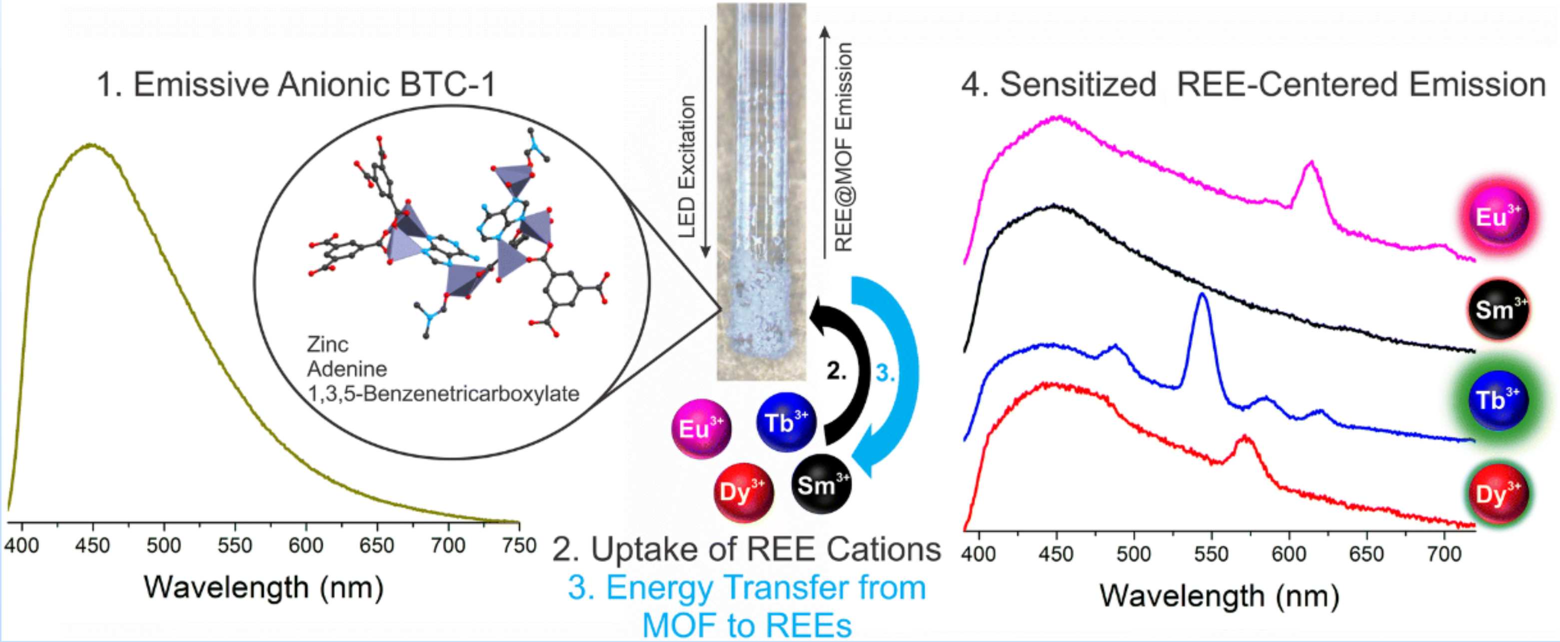


Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int.* **2024**, *Advanced Article* (DOI: 10.1039/D4LF00001C)

Enhanced Emission Signal

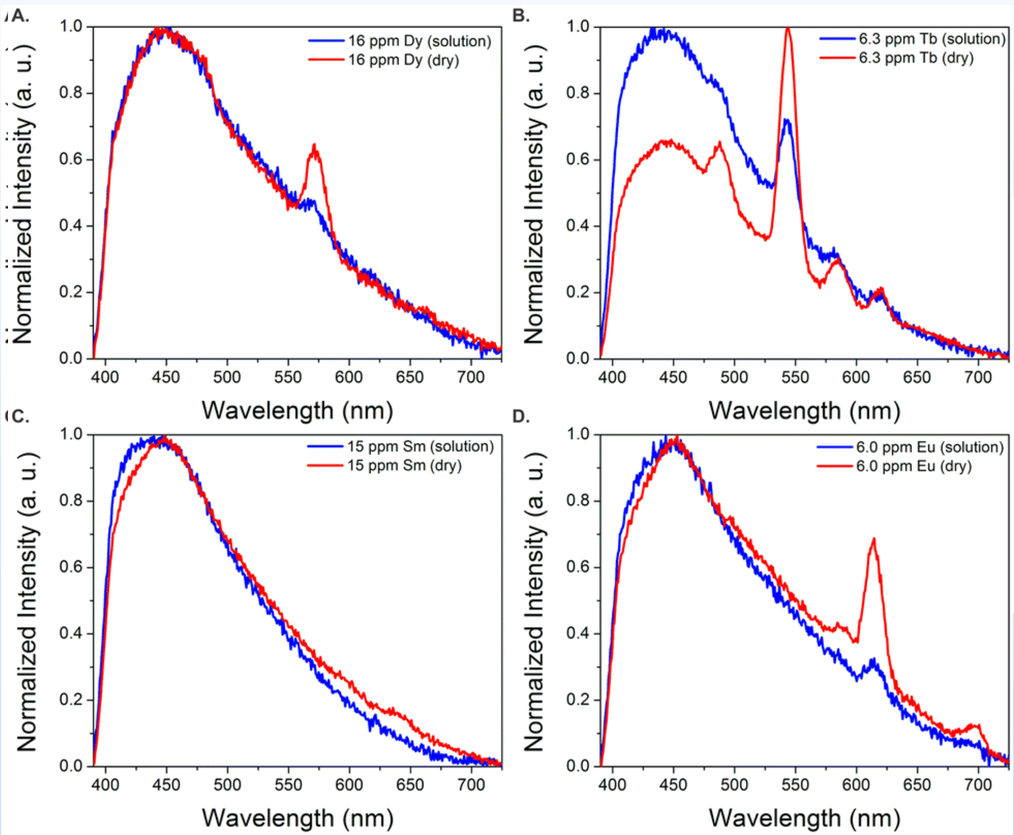
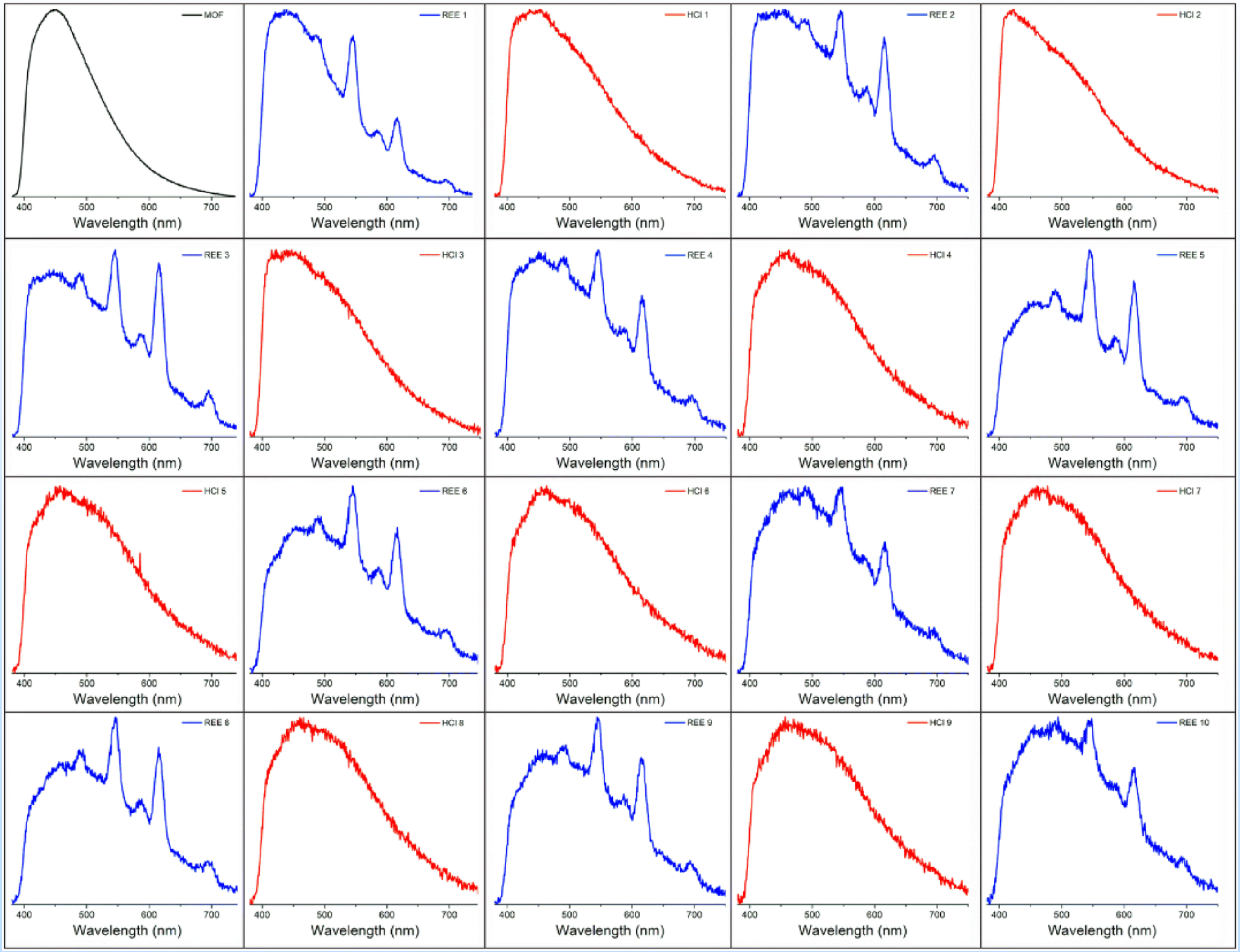


Table 1 Limits of detection and quantification for visible-emitting REEs in water and after drying using immobilized BTC-1 MOF as a sensitizer

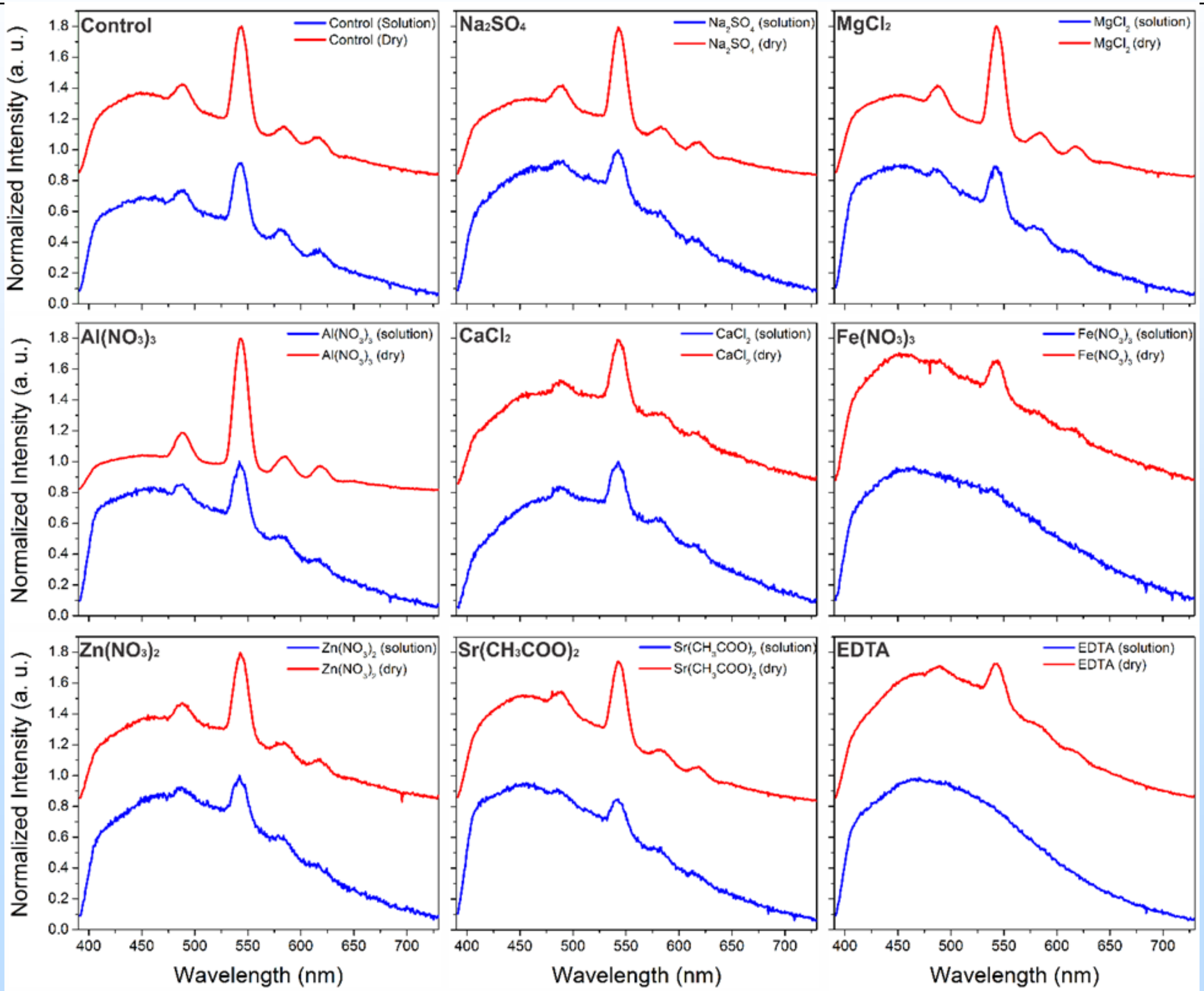
REE		Solution	Dry
Tb	LOD (ppb)	140 ± 20	60 ± 10
	LOQ (ppb)	450 ± 80	210 ± 40
Dy	LOD (ppb)	600 ± 80	440 ± 20
	LOQ (ppb)	2000 ± 200	1460 ± 60
Sm	LOD (ppb)	780 ± 80	620 ± 80
	LOQ (ppb)	2600 ± 300	2100 ± 300
Eu	LOD (ppb)	110 ± 20	90 ± 10
	LOQ (ppb)	380 ± 60	290 ± 30

Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int.* **2024**, *Advanced Article* (DOI: 10.1039/D4LF00001C)

Sensing Material Regeneration

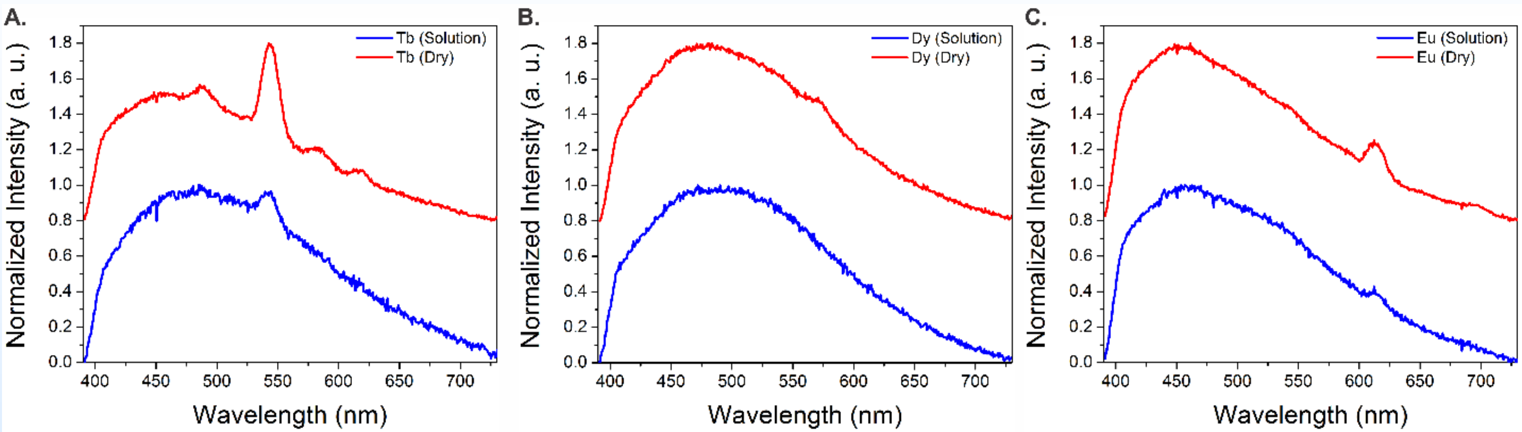


Influence of Other Metals

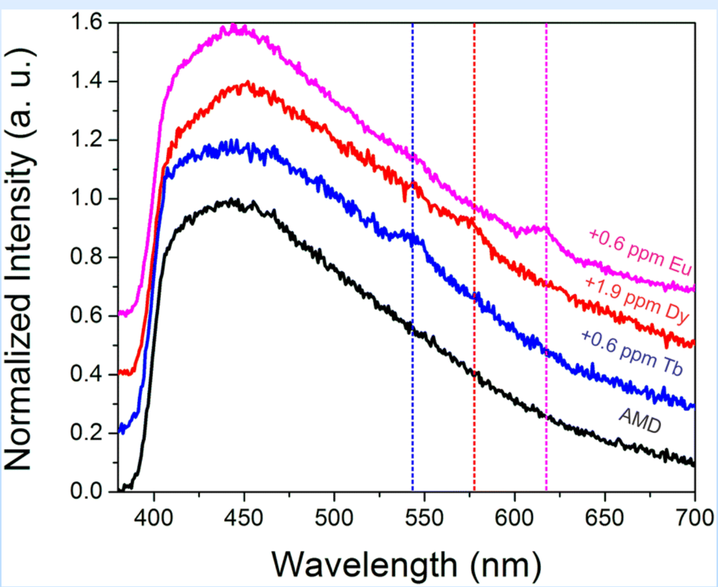


100:1 Metal:Tb

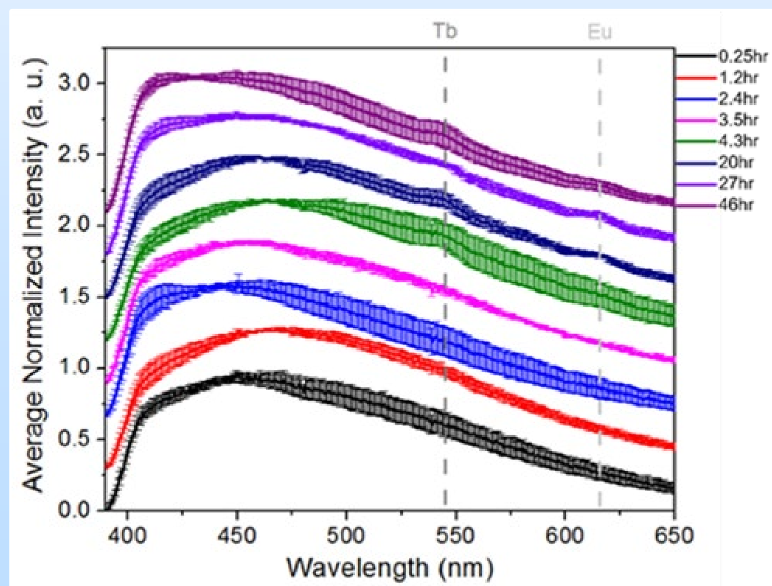
Functionality in Complex Matrices



100:1 <u>each</u> of: K, Al, Fe, Ca, Na, Mg, Zn, Sr:REE



REEs spiked into acid mine drainage

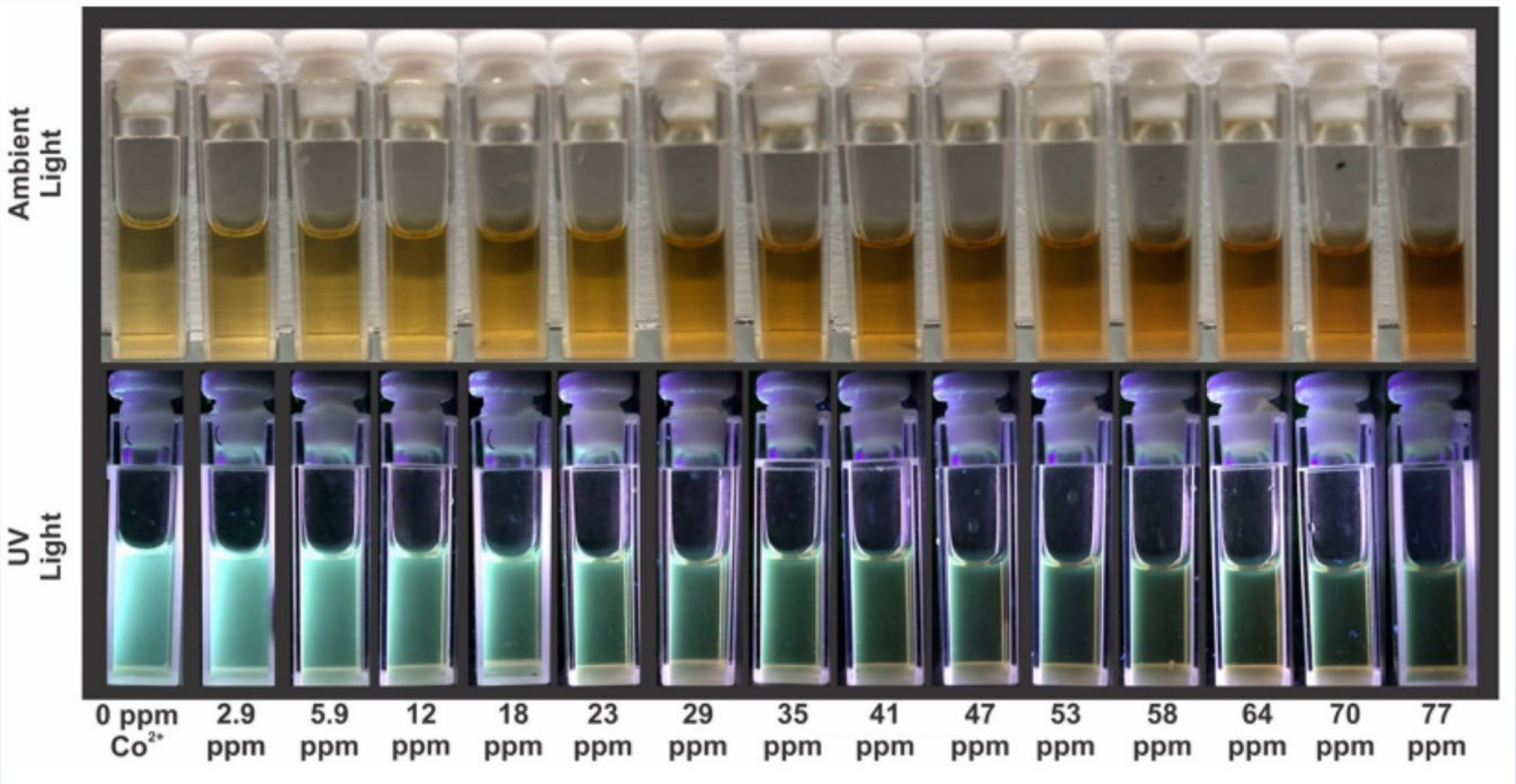


Monitoring simulated extraction process

Other Targets: Cobalt

Crawford, S., Kim, K-J., and Baltrus, J., ***J. Mater. Chem. C***, 2022, *10*, 16506

Other Targets: Cobalt



Material exhibits a selective, sensitive luminescent quenching response to cobalt

Crawford, S., Kim, K-J., and Baltrus, J., ***J. Mater. Chem. C***, 2022, *10*, 16506

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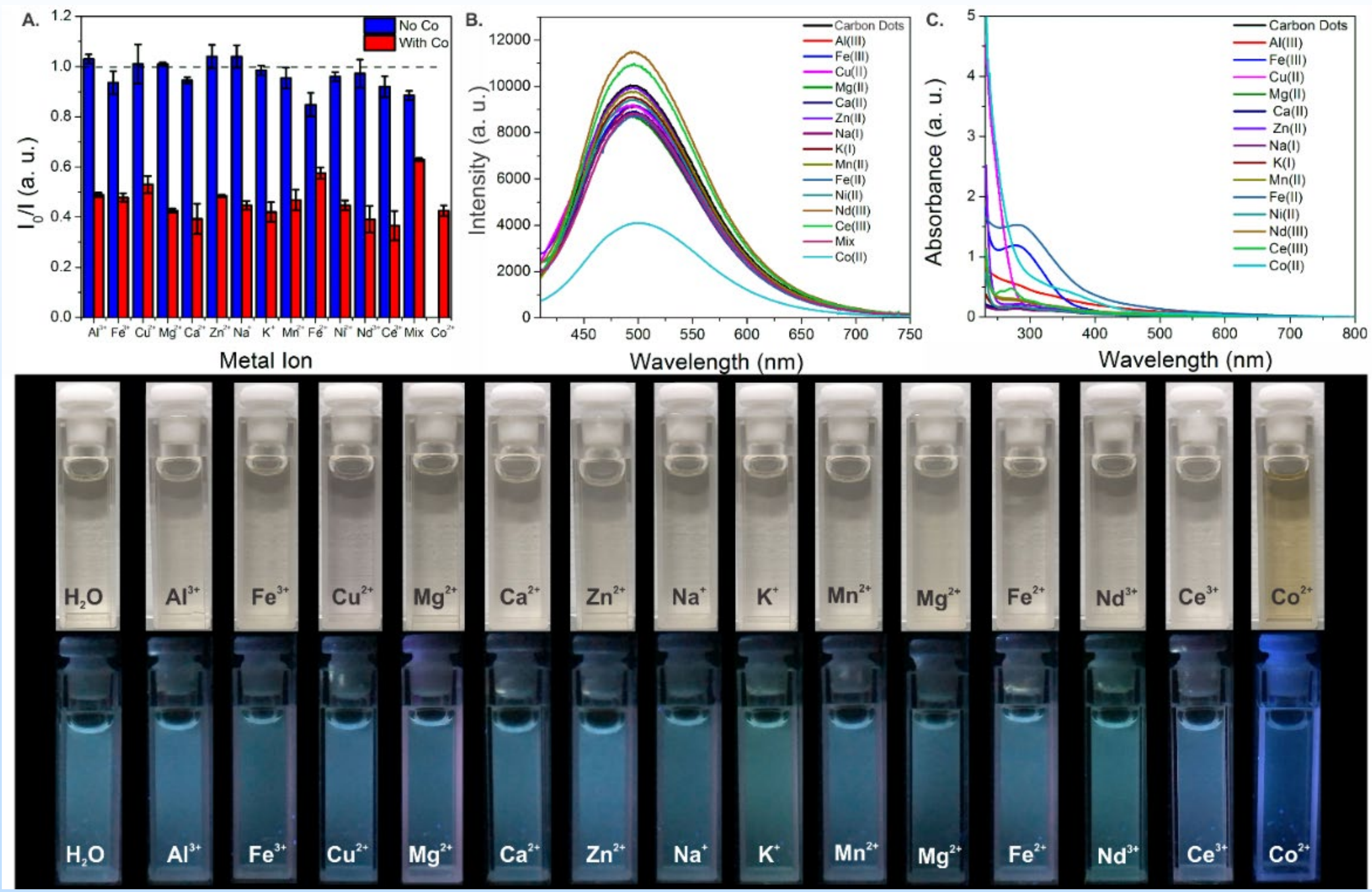
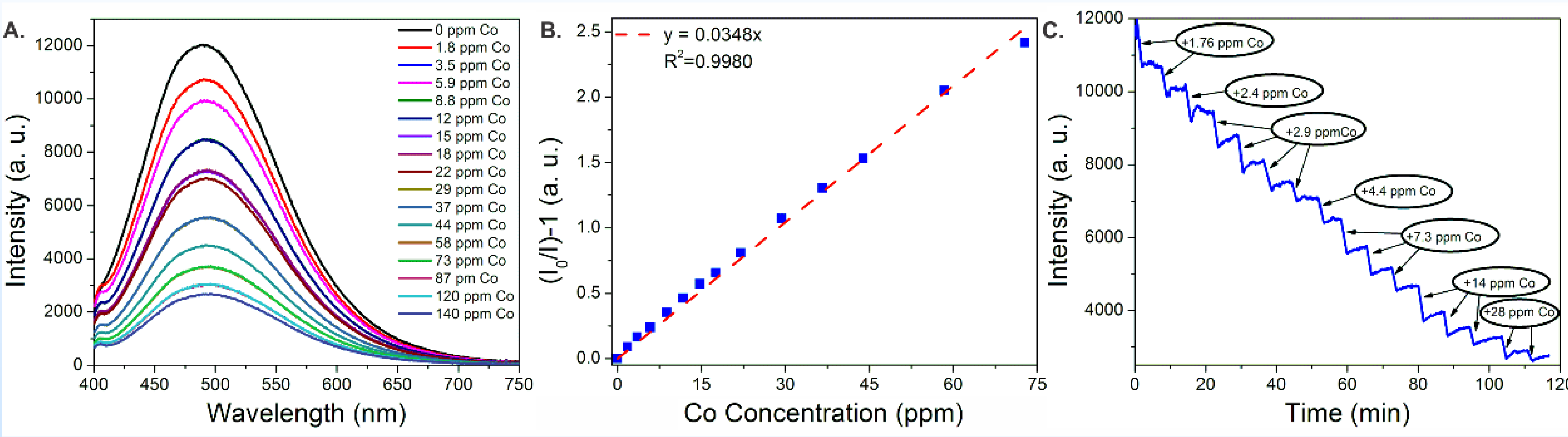


Material exhibits a selective, sensitive luminescent quenching response to cobalt

Crawford, S., Kim, K-J., and Baltrus, J., ***J. Mater. Chem. C***, 2022, *10*, 16506

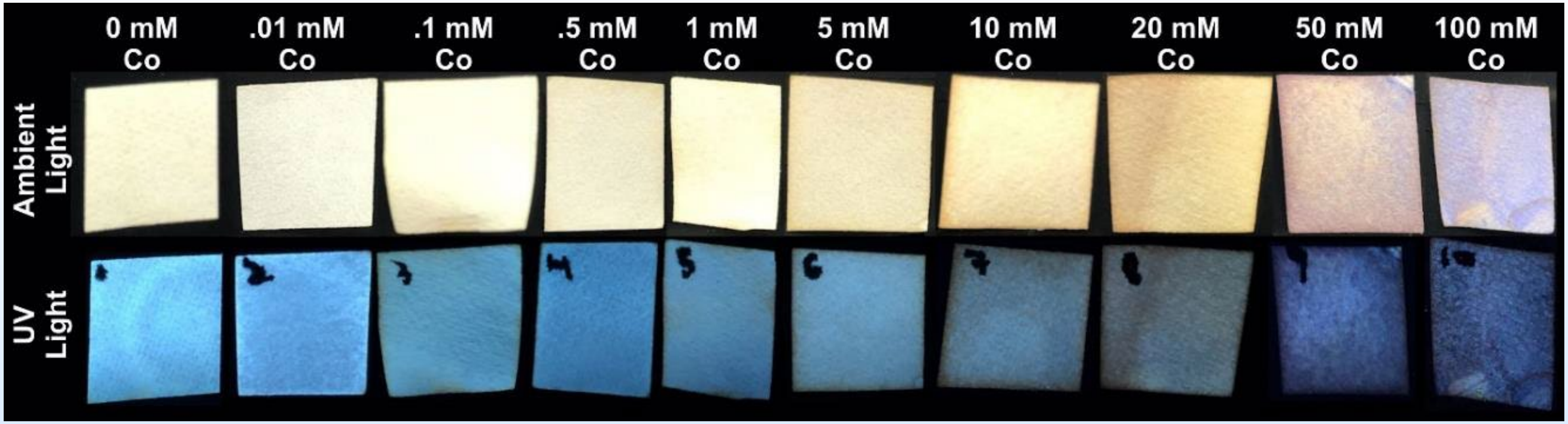
Rapid, Sensitive Co^{2+} Response

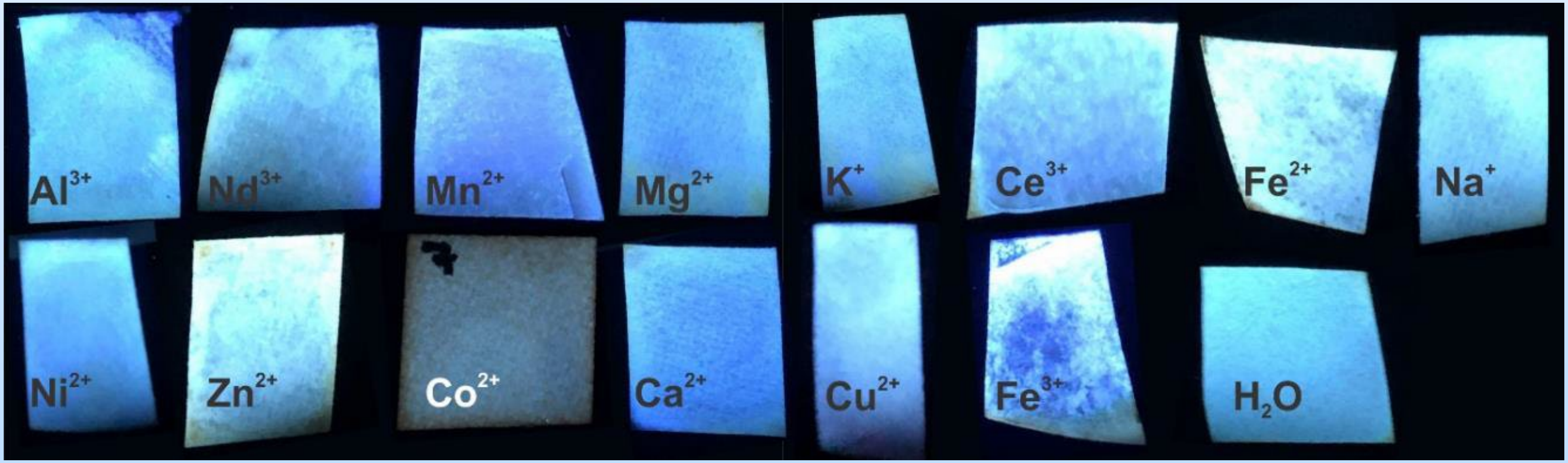


The portable sensor is capable of 0.6 ppm detection limits in water and 3.5 ppm detection limits in pH 1.68 buffer. The response to cobalt addition is nearly instantaneous.

Crawford, S., Kim, K-J., and Baltrus, J., ***J. Mater. Chem. C***, 2022, *10*, 16506

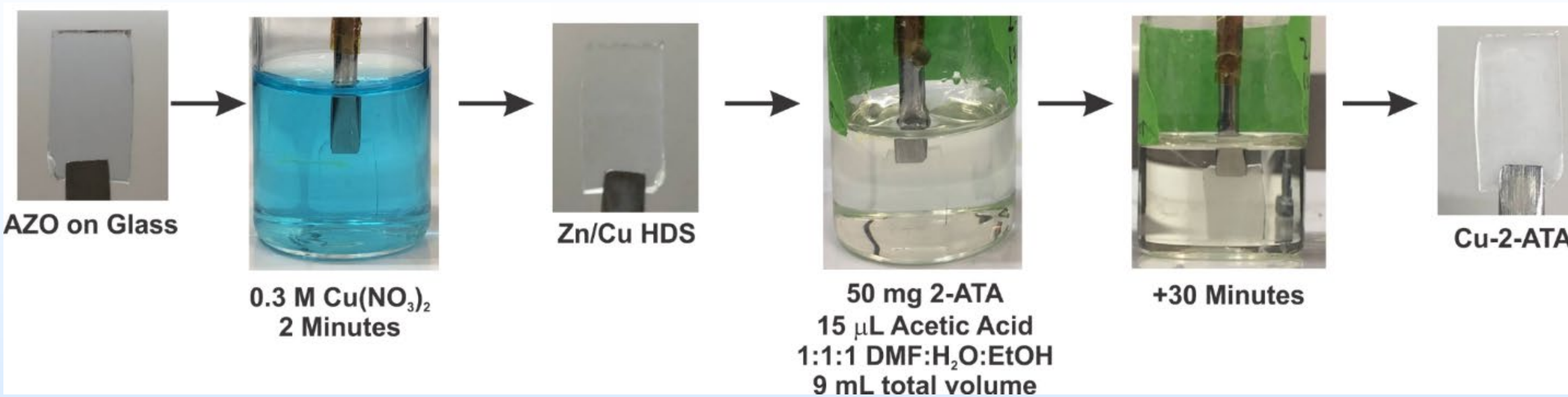
Preparation of Test Strips for Co^{2+}



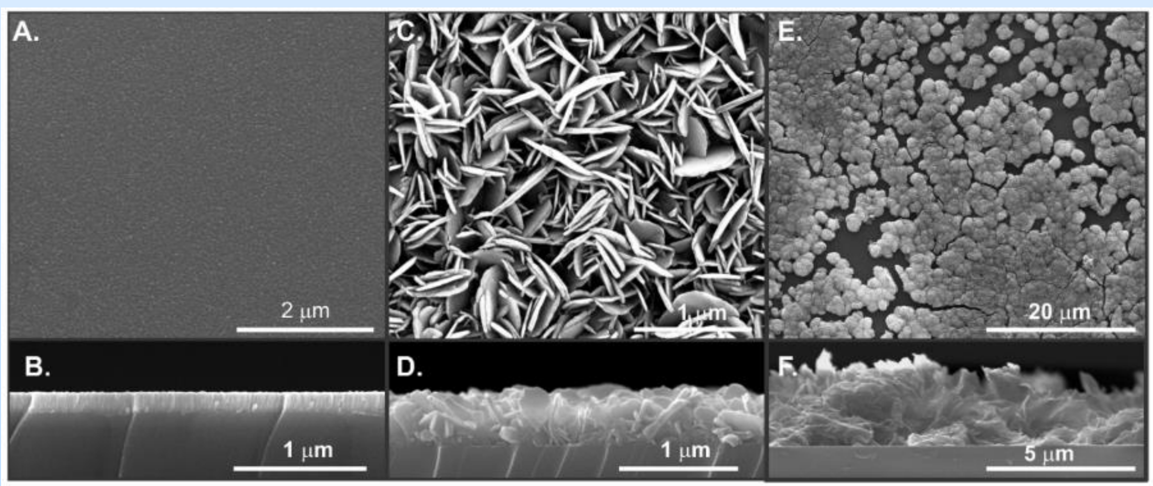


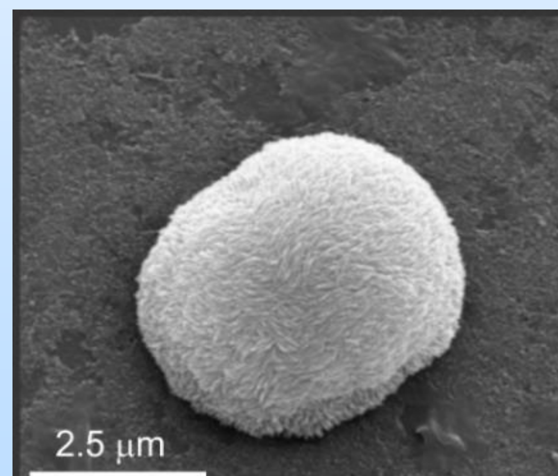
Crawford, S., Kim, K-J., and Baltrus, J., ***J. Mater. Chem. C***, 2022, *10*, 16506

Synthesis of Aluminum Sensor



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



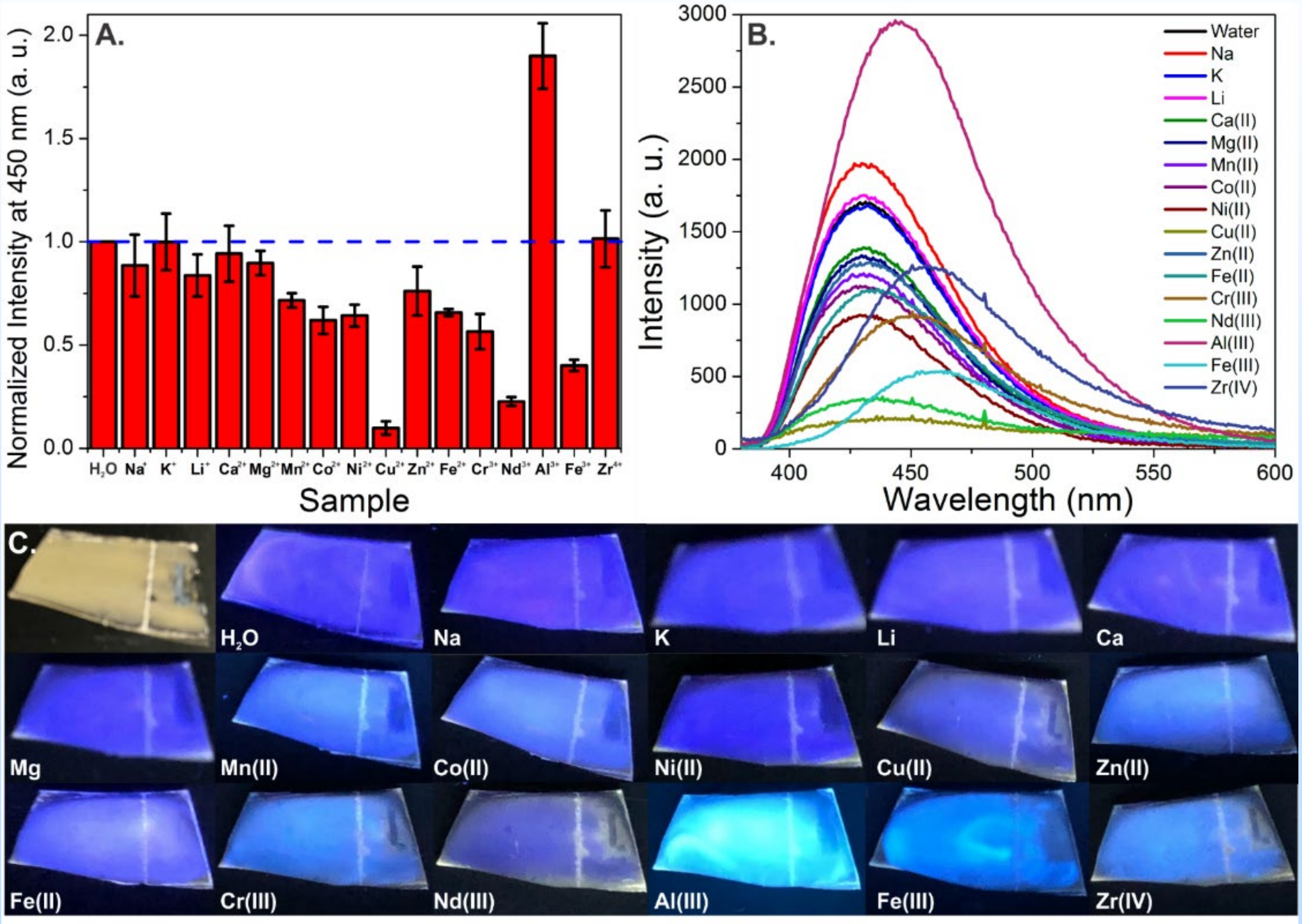


Crawford, S., Kim, K.-J., Diemler, N., Baltrus, J., *ACS Appl. Opt. Mater.* **2023**, *1*, 587

Response to Al(III)

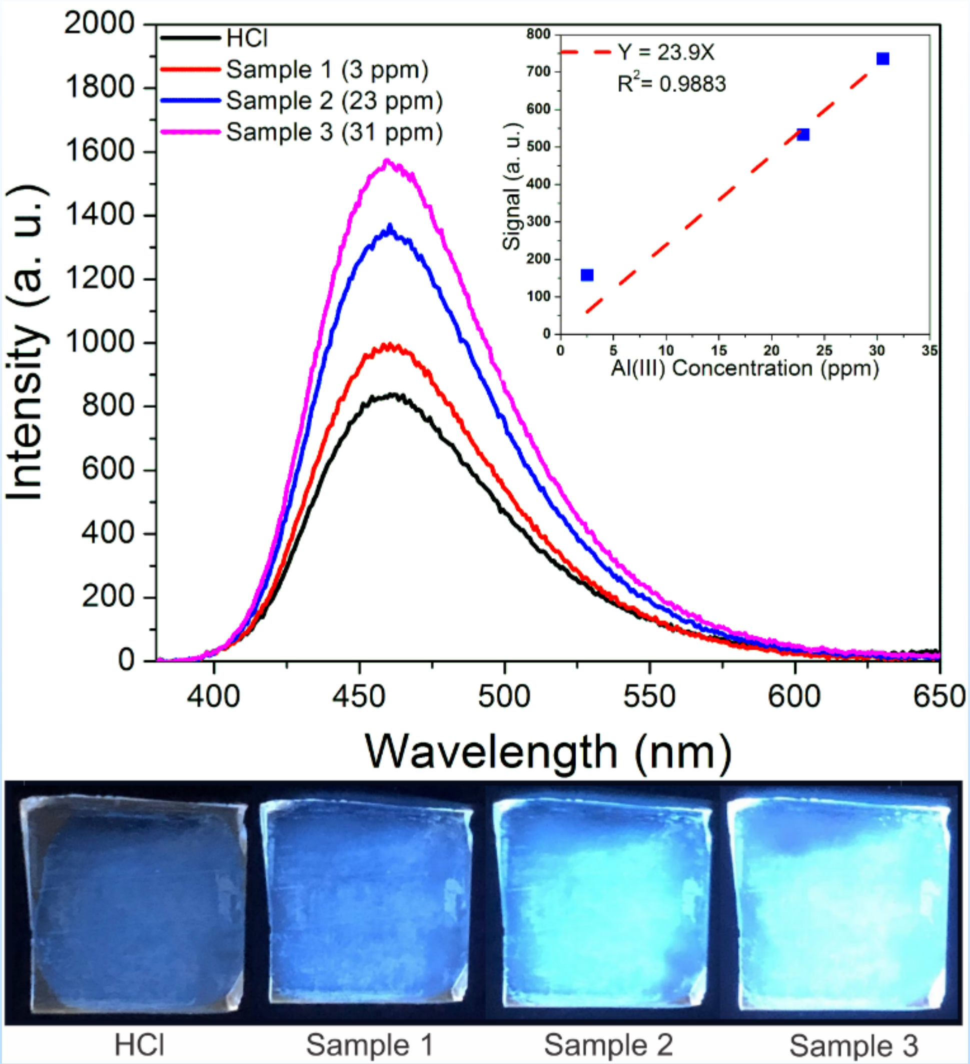
Crawford, S., Kim, K.-J., Diemler, N., Baltrus, J., *ACS Appl. Opt. Mater.* **2023**, *1*, 587

Selective Aluminum Response



Detection limit: 120 ppb in water for Al

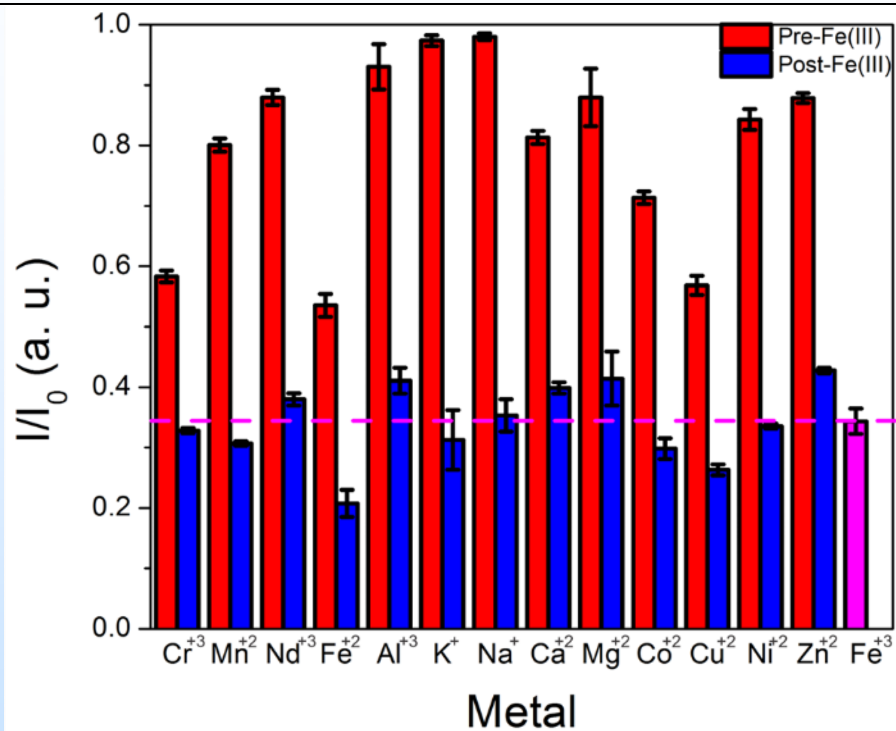
Fly Ash Analysis

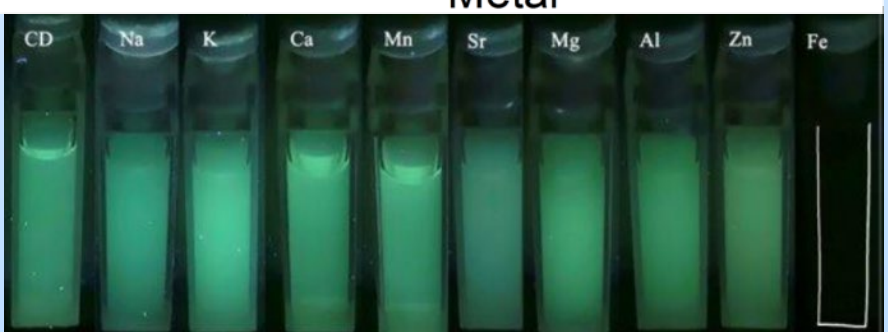


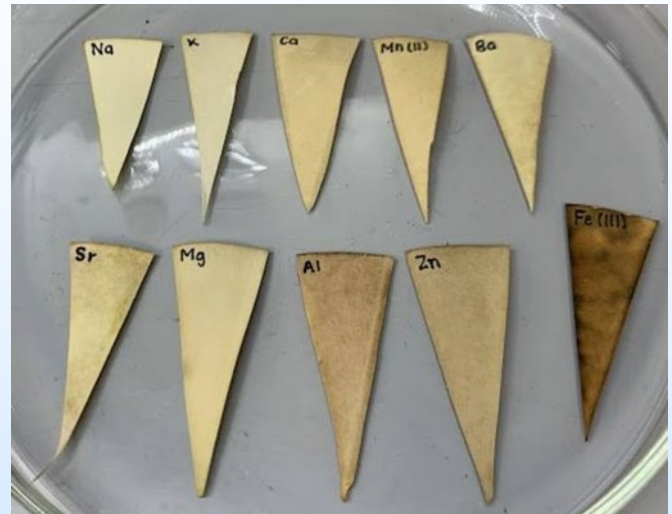
- Diluted fly ash leachates with a final pH of **3.8**, and at least **40 other metal elements** in solution.
- Good correlation with inductively-coupled plasma mass spectrometry.

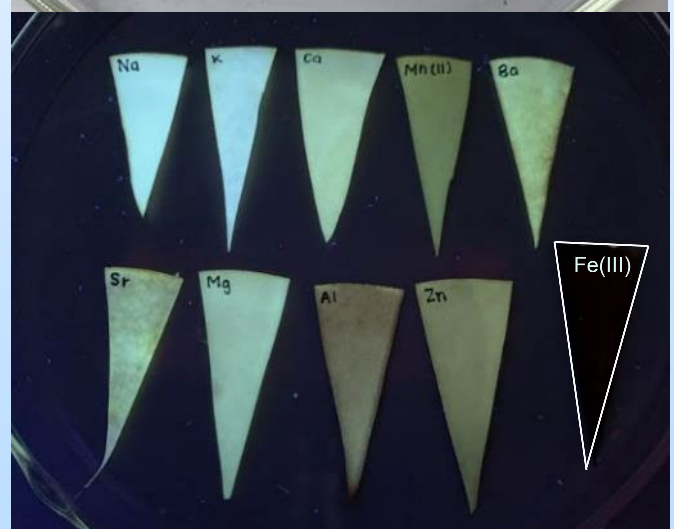
Crawford, S., Kim, K.-J., Diemler, N., Baltrus, J., *ACS Appl. Opt. Mater.* **2023**, *1*, 587

Detection of Fe(III) Interferants



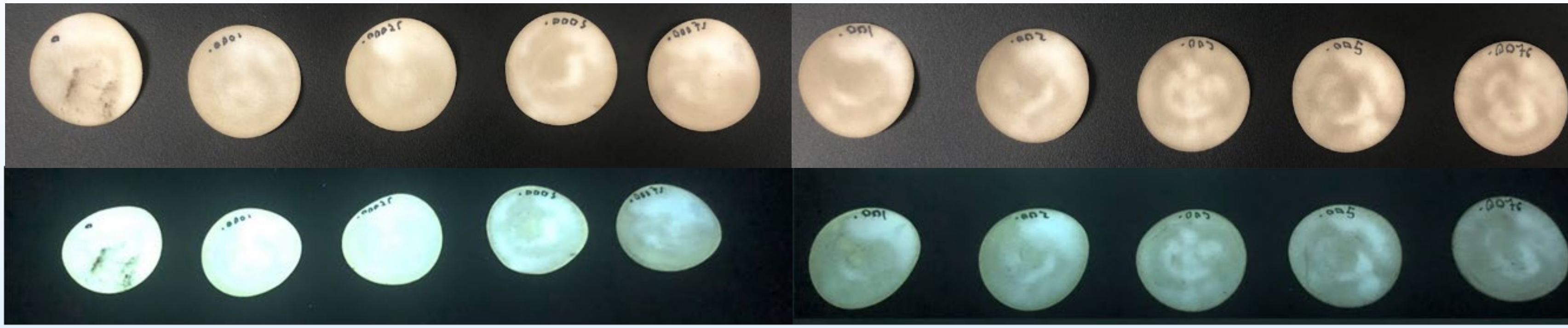




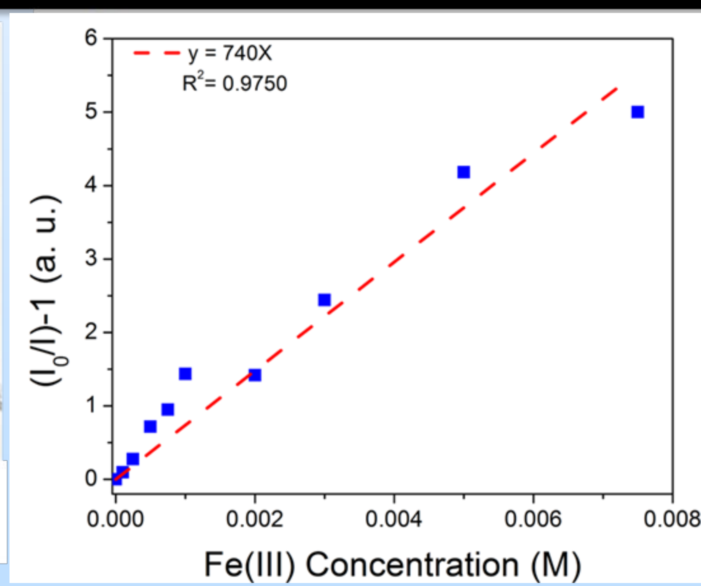


Adkisson, A., Crawford, S., “A synthetic pathway for luminescent N,P co-doped carbon quantum dots for the detection of Fe(III) using a portable spectrometer” *In Preparation*

Detection of Fe(III) Interferants



Increasing Analyte Concentration



Adkisson, A., Crawford, S., "A synthetic pathway for luminescent N,P co-doped carbon quantum dots for the detection of Fe(III) using a portable spectrometer" *In Preparation*

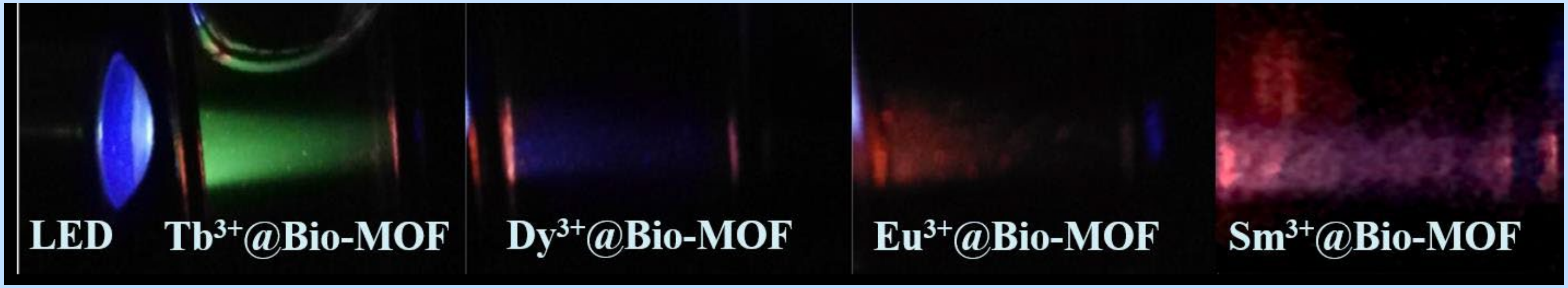
Future Directions

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, et.

Collaboration is ongoing to further lower cost/size of spectrometers



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. *Journal of Materials Chemistry C, 10*(43), 16506-16516.
7. Crawford, S. E., Kim, K. J., Diemler, N. A., & Baltrus, J. P. (2023). Efficient and Rapid Synthesis of a Luminescent, Solvent and Ion-Responsive Copper 2-aminoterephthalate Thin Film. *ACS Applied Optical Materials*, *1*(2), 587-597
8. Wu, Z., Crawford, S.E., Buric, M.P., Splain, Z., & Chen, K. P., Development of a Low-Cost, Sensitivity-Optimized Fluorescence Sensor for Visible Spectrum Analysis (2023). *IEEE Sensors Journal*, *23*(11), 11574-11581
9. Crawford, S.E., Burgess, W.A., Kim, K.-J., Baltrus, J.P, & Diemler, N.A. (2024). Zinc adeninate metal–organic framework-coated optical fibers for enhanced luminescence-based detection of rare earth elements. *RSC Applied Interfaces*, Advance Article, DOI: 10.1039/D4LF00001C

Outreach: Selected Presentations

1. March 2024, “Materials for the Photoluminescence-Based Detection of Economically Critical Metals,” **#RSCPoster 2024**, Virtual
2. June 2023, “Portable Luminescent Sensing Technologies for Economically Critical Metal Ions,” **TechConnect World Innovation Conference & Exposition 2023**, Washington, DC
3. March 2023, “Fiber Optic Luminescent Sensing of Economically Critical Metals” **Pittcon 2023**, Philadelphia, PA (Invited)
4. October 2022, “Portable Fiber Optic Sensors for Critical Metal Ions” **2022 NETL Resource Sustainability Project Review Meeting**, Pittsburgh, PA (Invited)
5. August 2022, “Metal-organic Framework Thin Films: From Synthetic Strategies To Critical Metal Ion Sensing,” **International Materials Research Congress 2022**, Cancun, Mexico (Invited, virtual)
6. June 2022, “Development of a Portable Fiber Optic Luminescence Sensor for Rare Earth Elements,” **TechConnect World Innovation Conference & Exposition 2022**, Washington, DC
7. 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)
8. March 2021, “Metal-Organic Framework-based Luminescent Sensors for Rare Earth Elements,” **Pittcon 2021**, Virtual Conference
9. November 2020, “Luminescent Metal-Organic Framework-Based Sensors for Rare Earth Elements in Aqueous Streams,” **Materials Science & Technology 2020**, Virtual Conference
10. December 2019, “Metal-Organic Framework - Based Luminescent Detection of Rare Earth Elements,” **Materials Research Society Fall Meeting and Exhibit**, Boston, MA

Outreach: Workforce Development

- 2 summer students through Mickey Leland Energy Fellowship
- Participants learn about DOE goals related to critical minerals, research and communication skills
- Paper on iron(III) sensor currently under development based on summer project
- Another project planned for summer 2024
- Outreach research presentations at high school (Reynoldsburg High School) and college level (University of Pittsburgh 3x, Washington & Jefferson College)

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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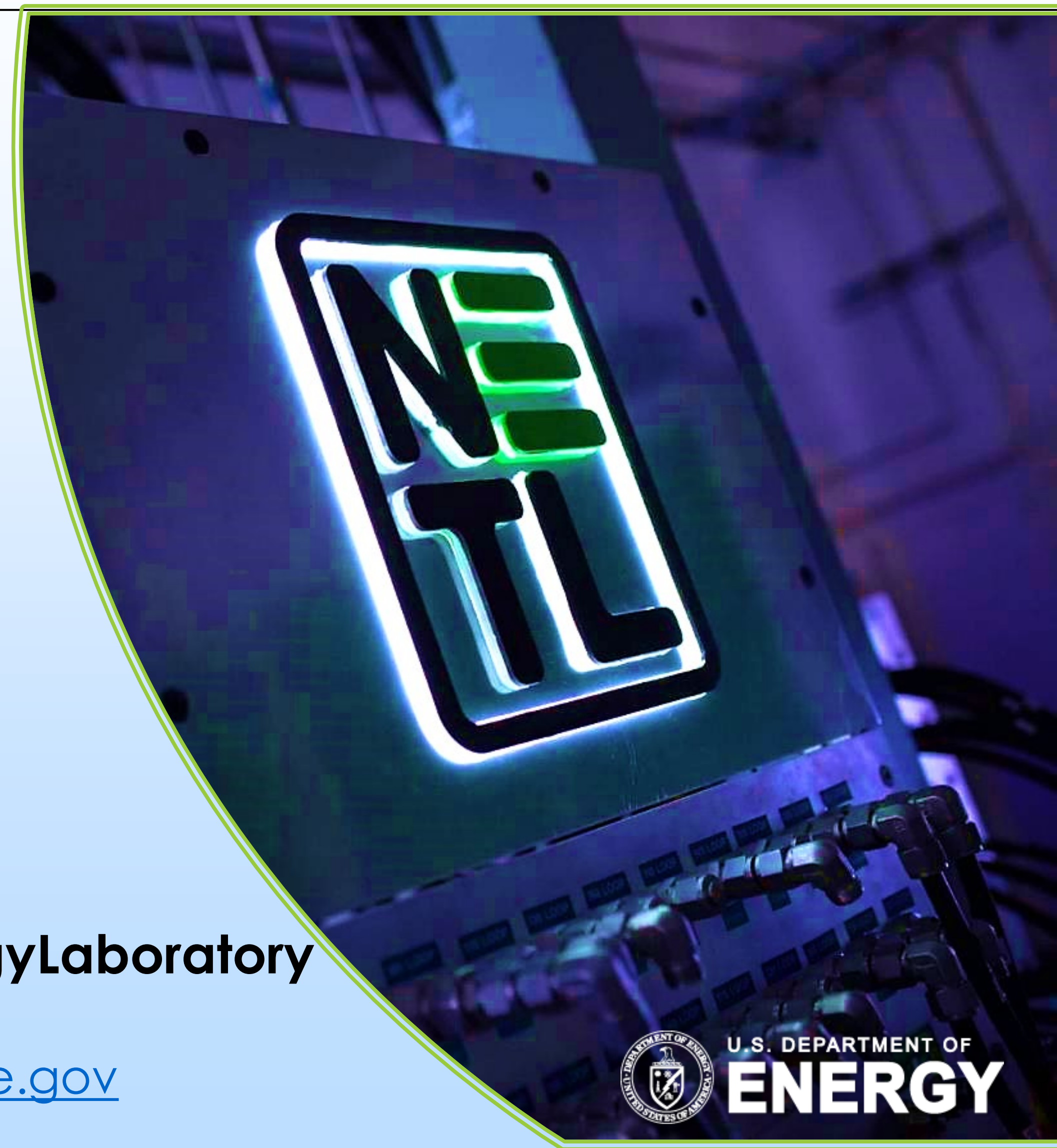
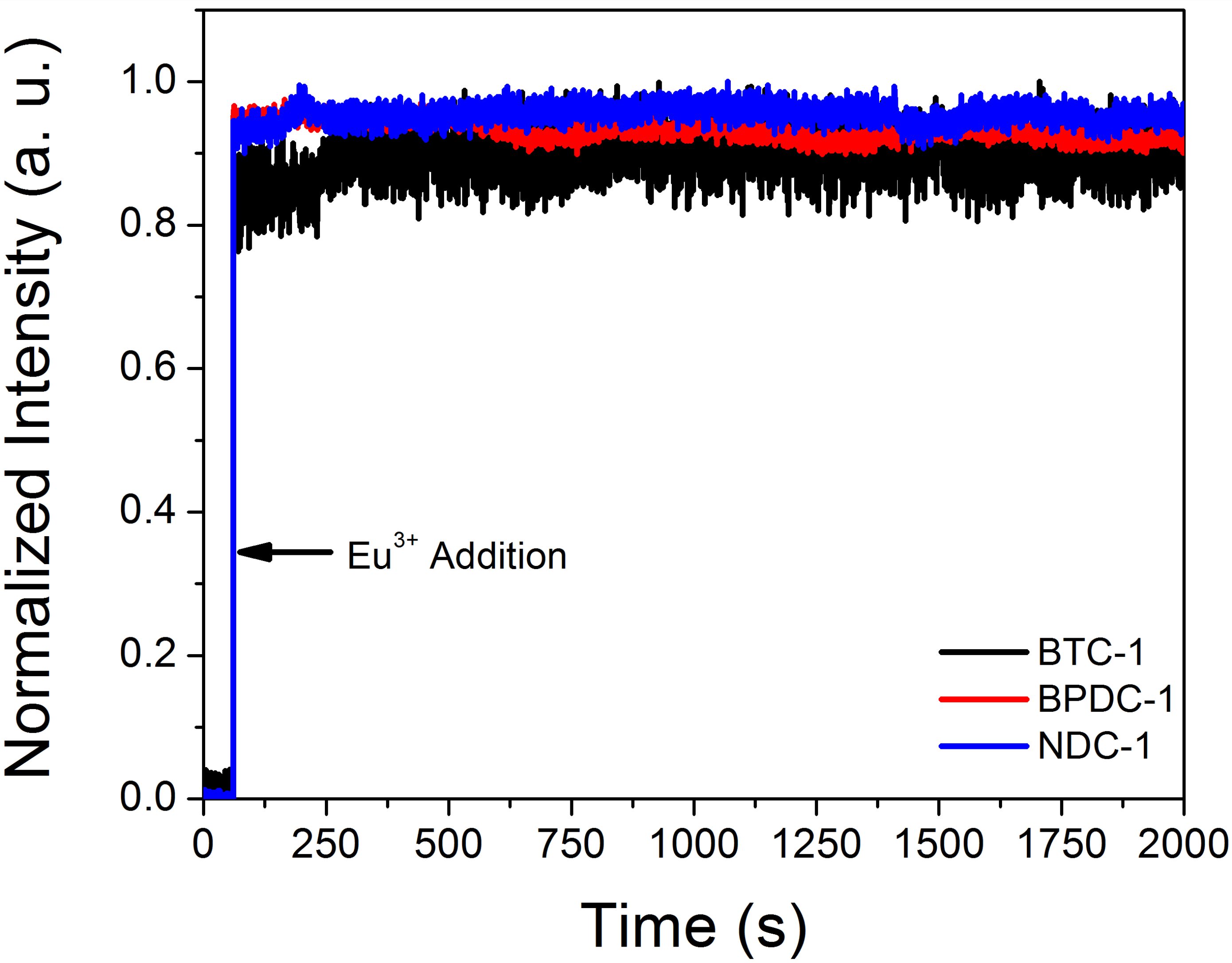
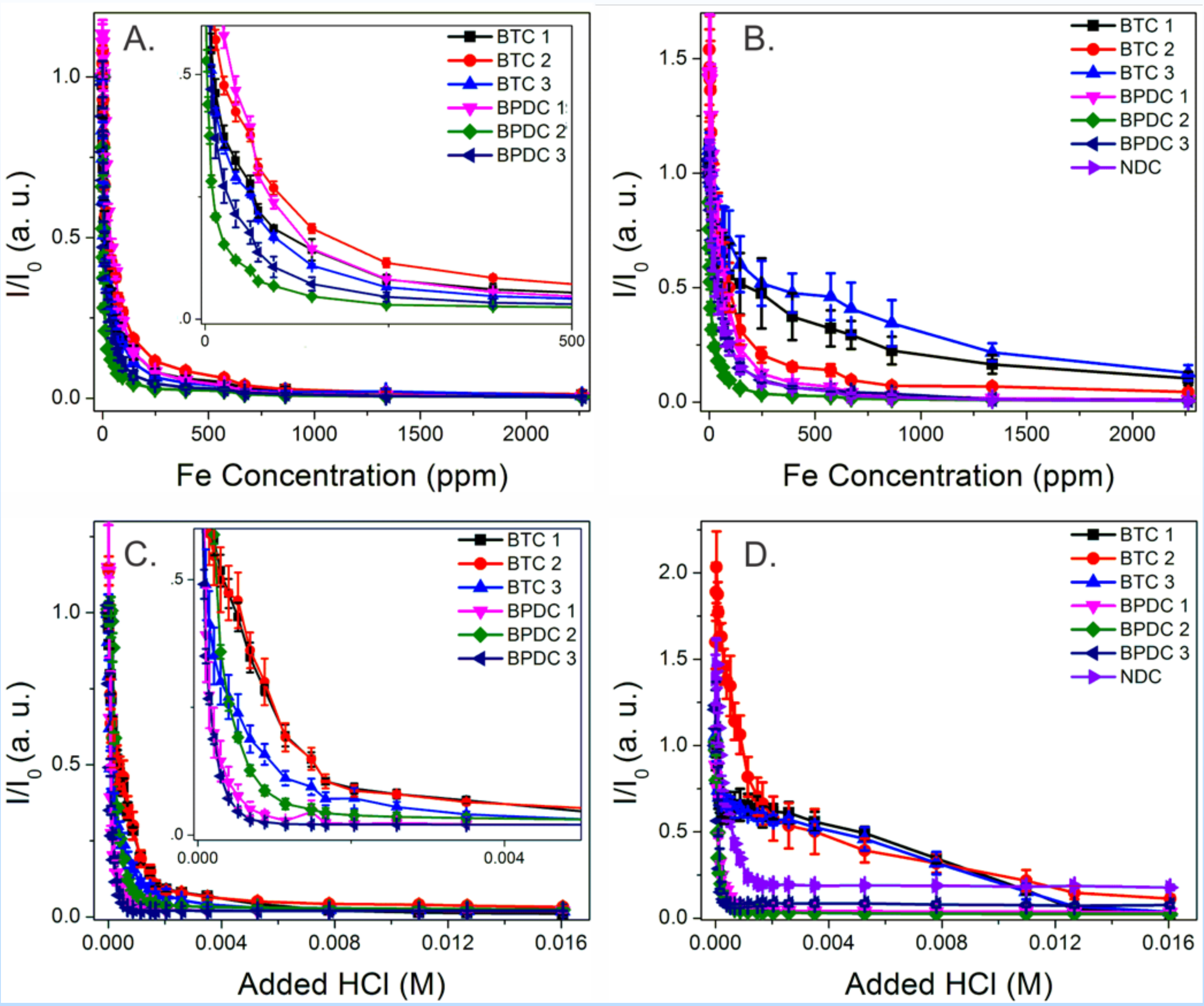
Contact: Scott.Crawford@netl.doe.gov



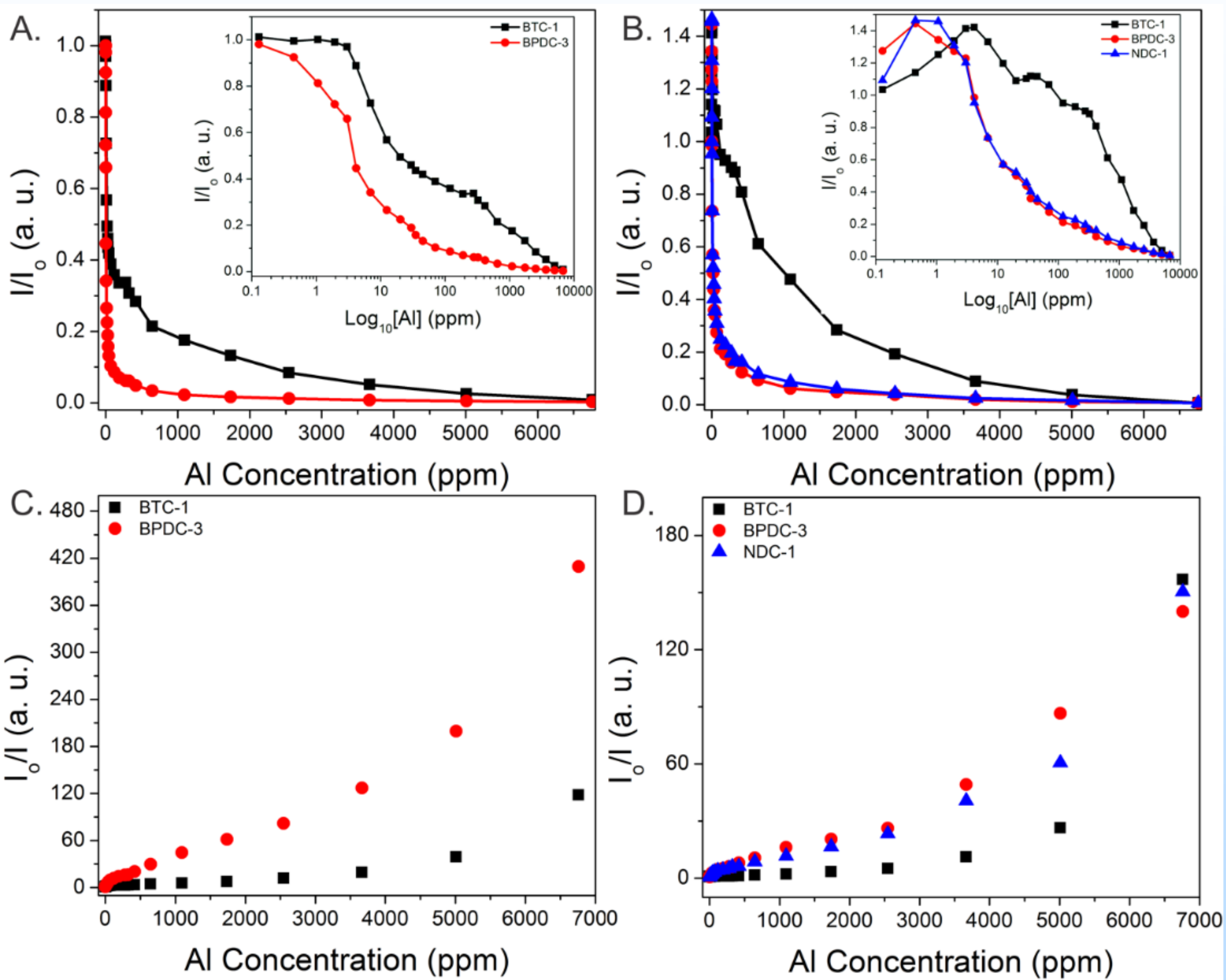
Appendix: Response Time



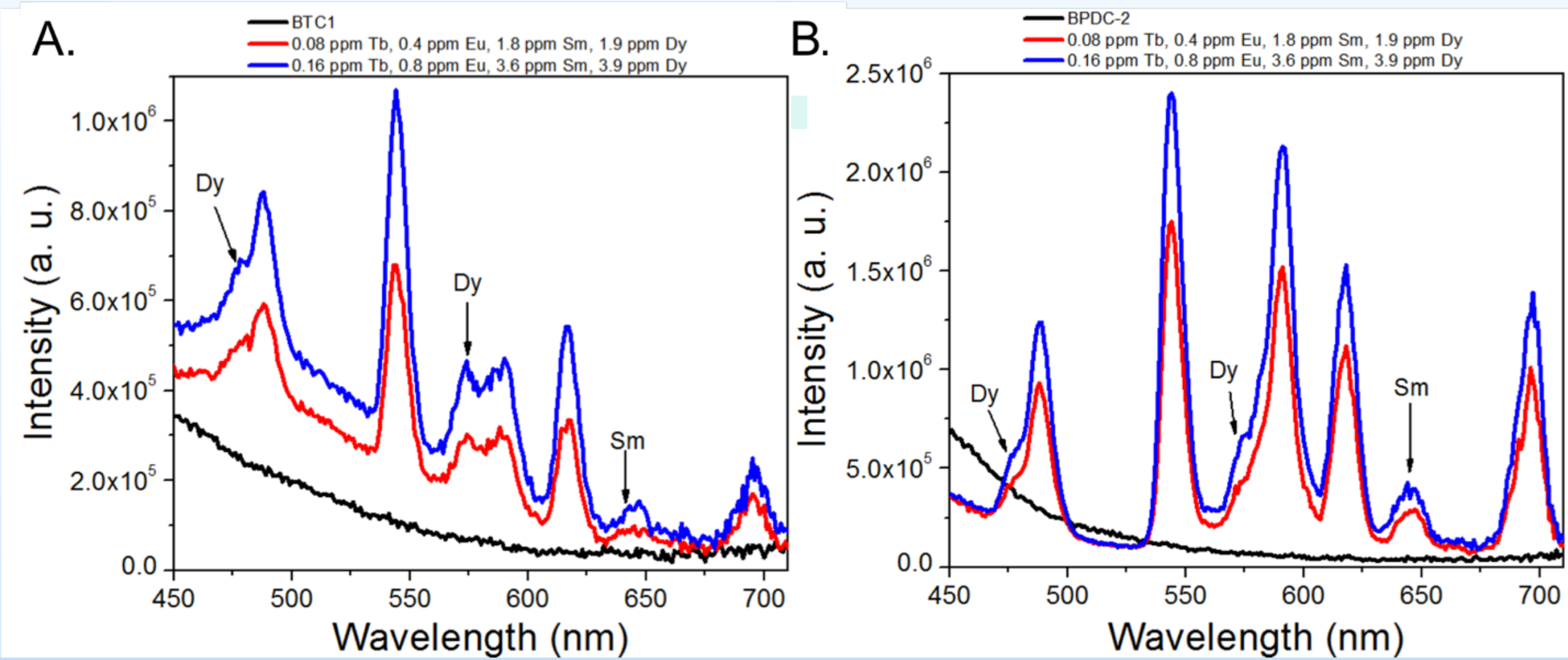
Appendix: Structural Influence



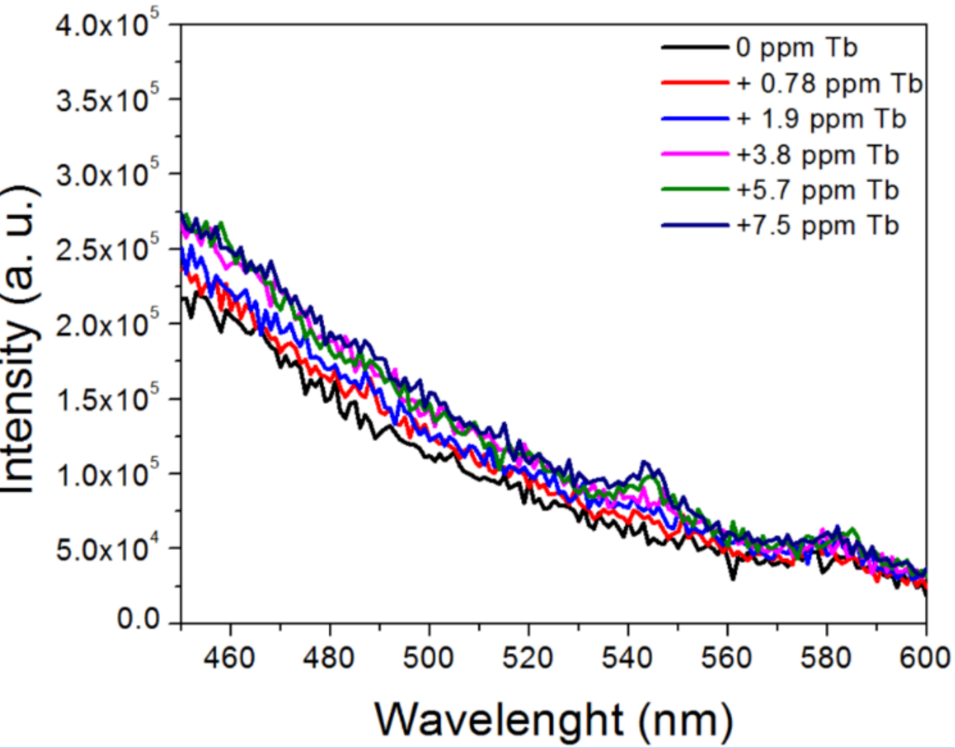
Appendix: Al(III) Interference

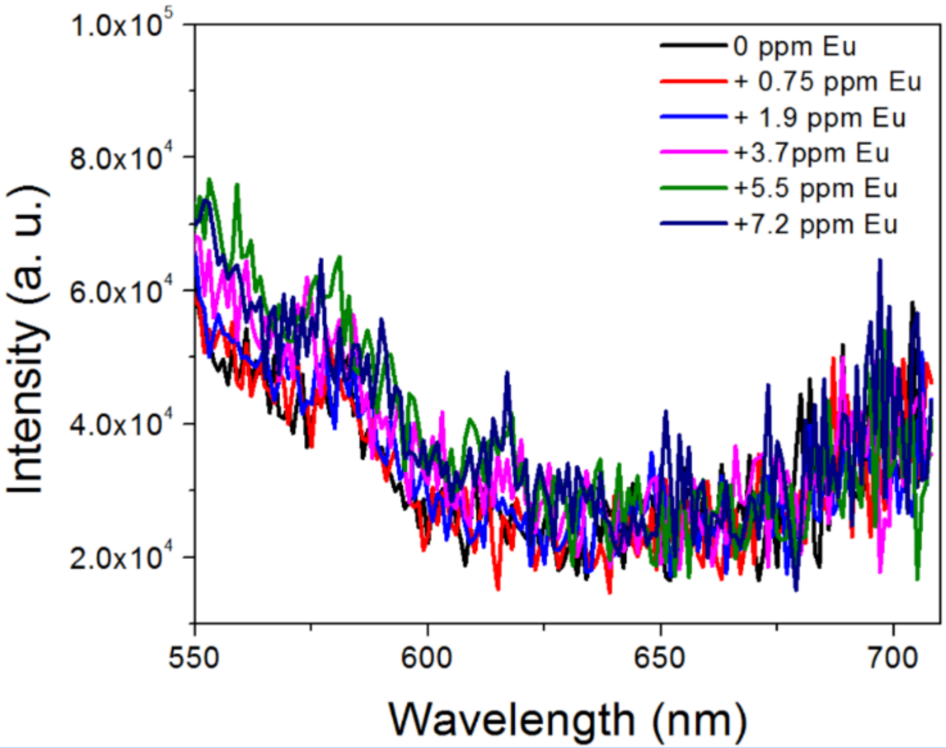


Appendix: Multiple REEs

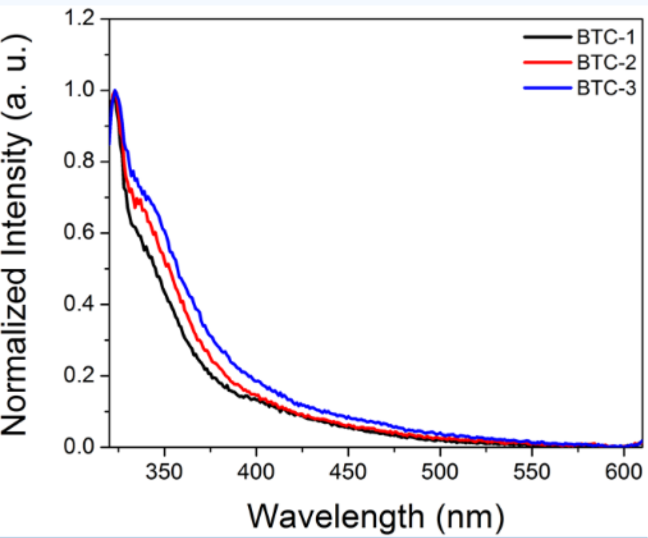


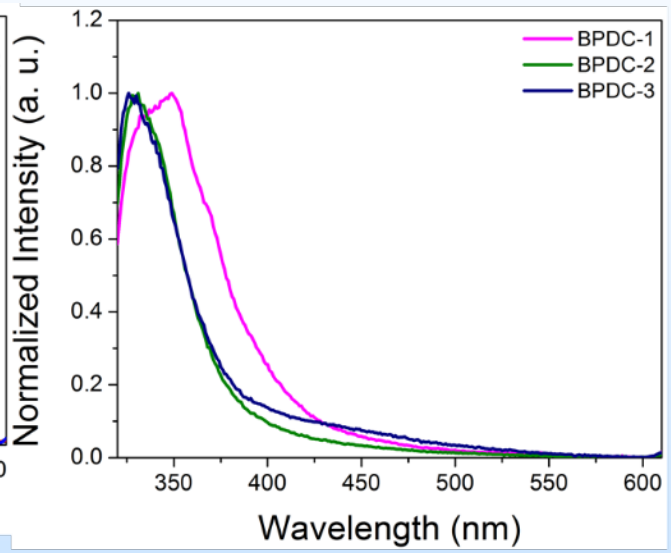
Appendix: No Sensitizer

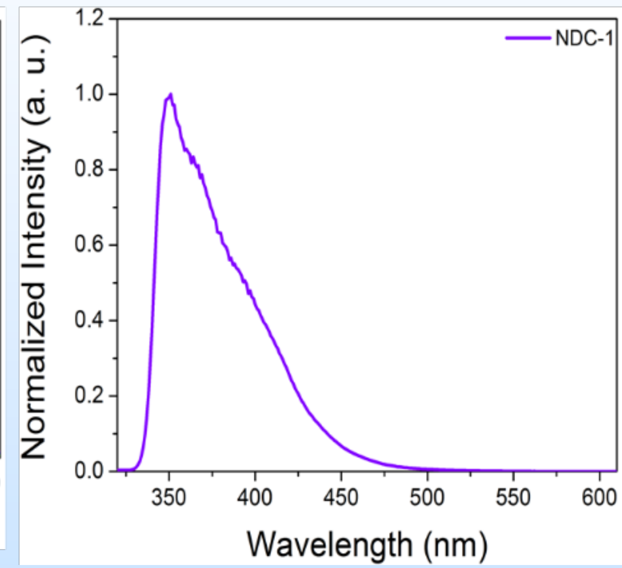




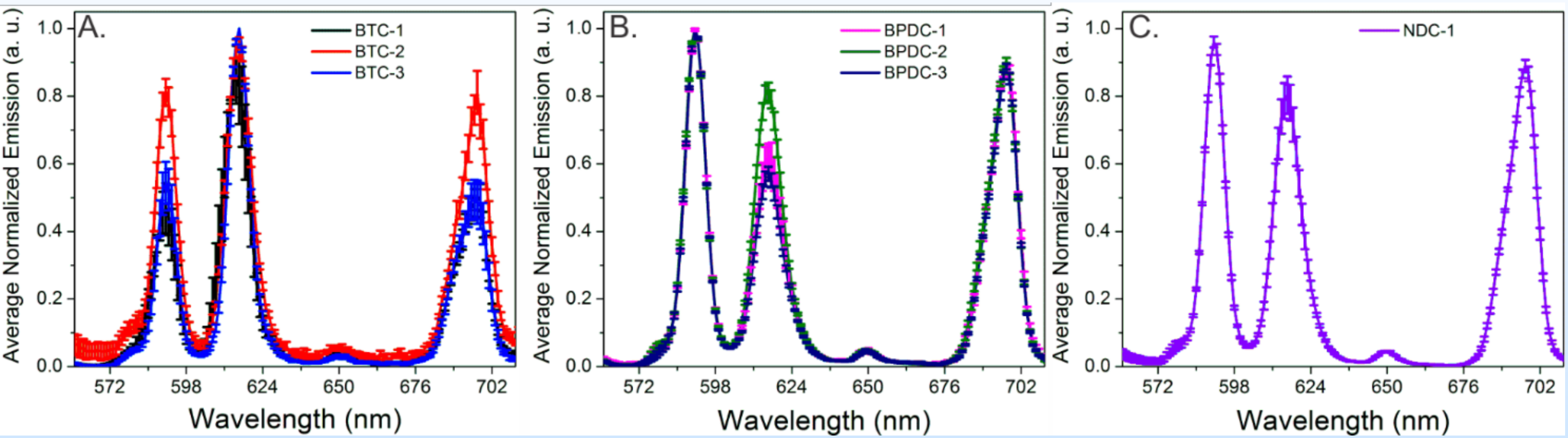
Appendix: Emission of MOF only





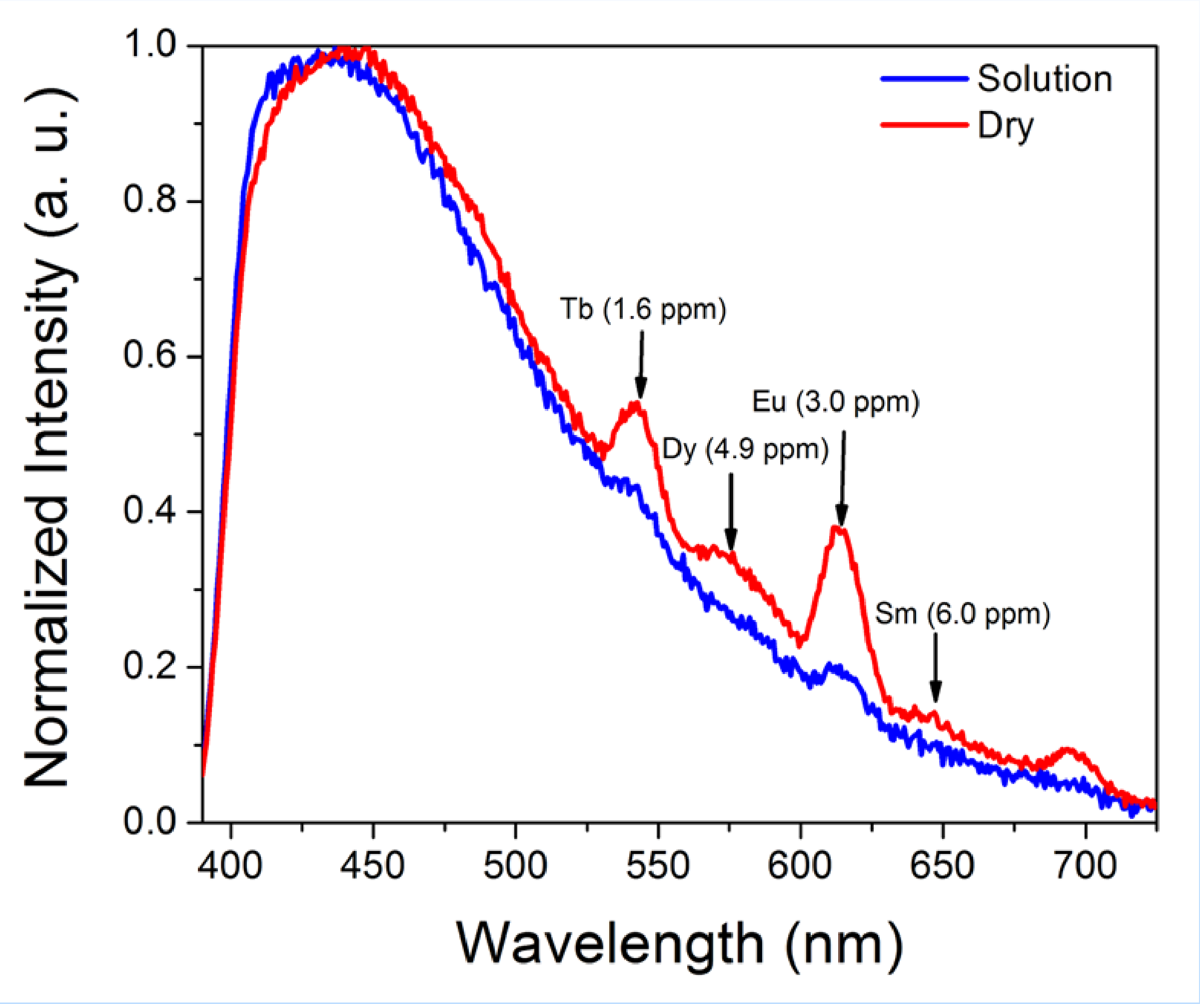


Appendix: Eu Differences

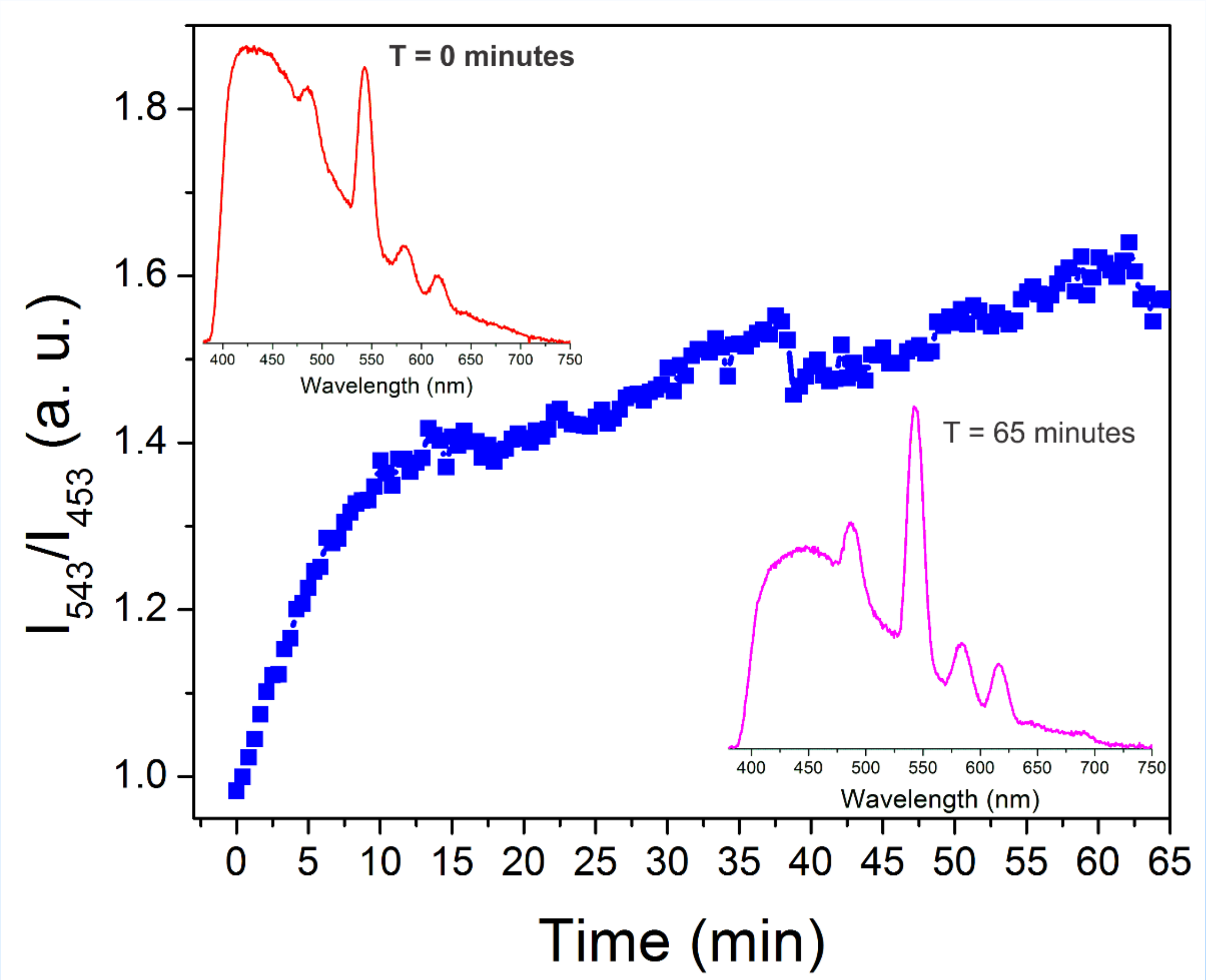


BTC MOFs exhibit enhanced Eu hypersensitive transition peak at 617 nm relative to the BPDC and NDC MOFs, indicating linker-dependent REE coordination.

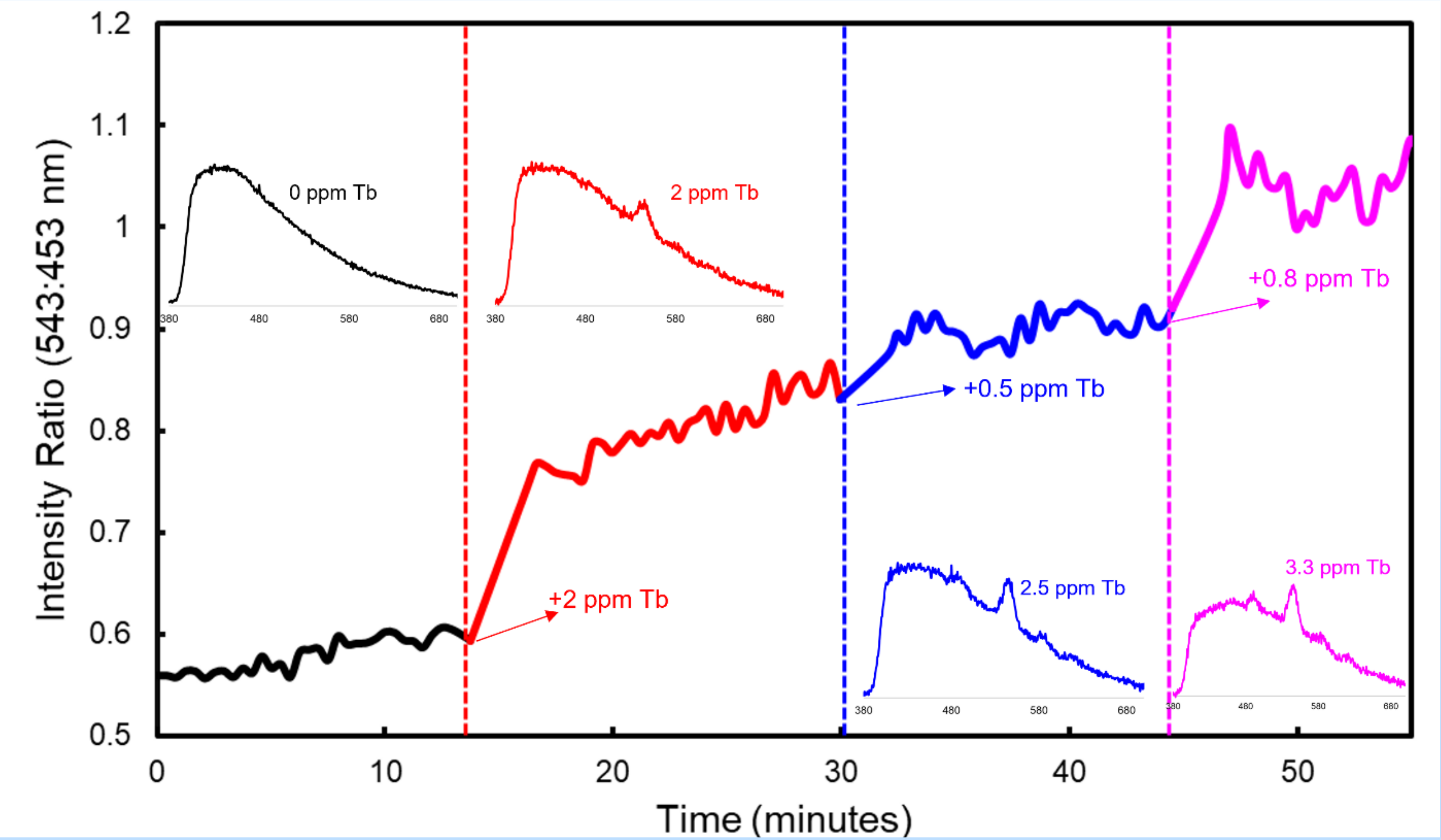
Appendix: Multiple REEs



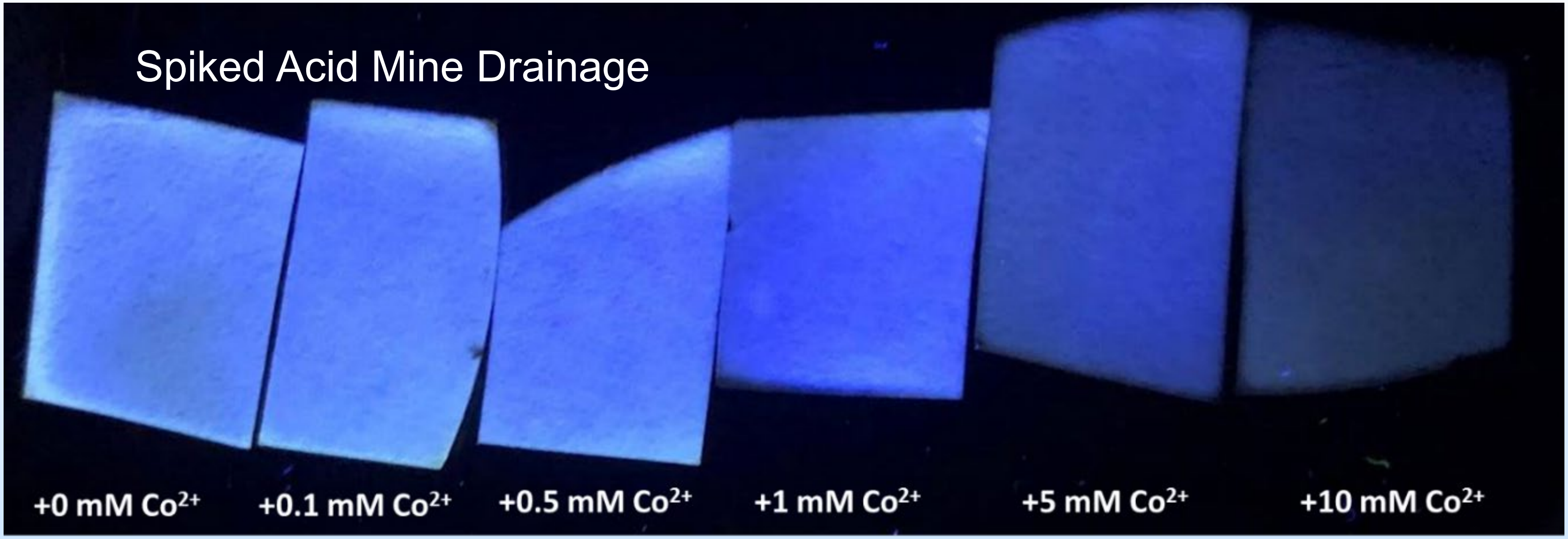
Appendix: MOF Stability to Flow

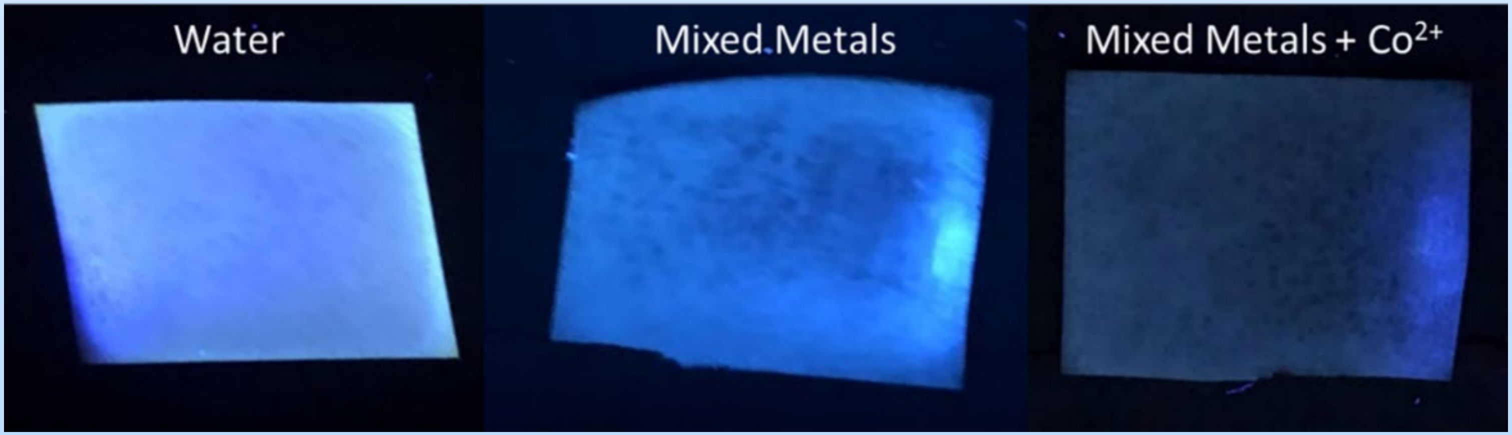


Appendix: Real-Time Monitoring



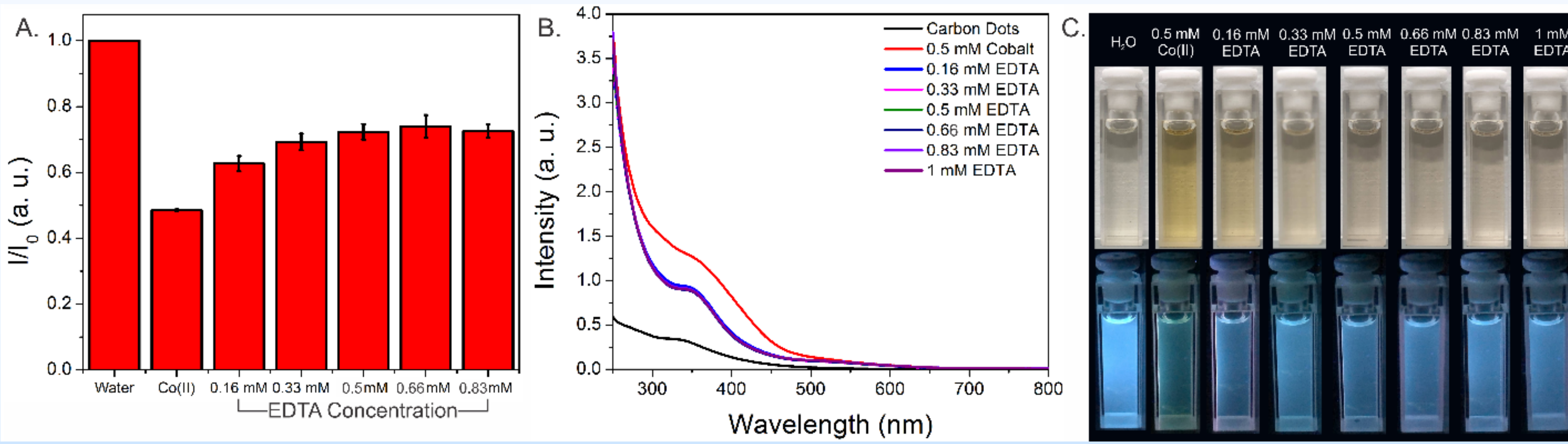
Appendix: Co Performance



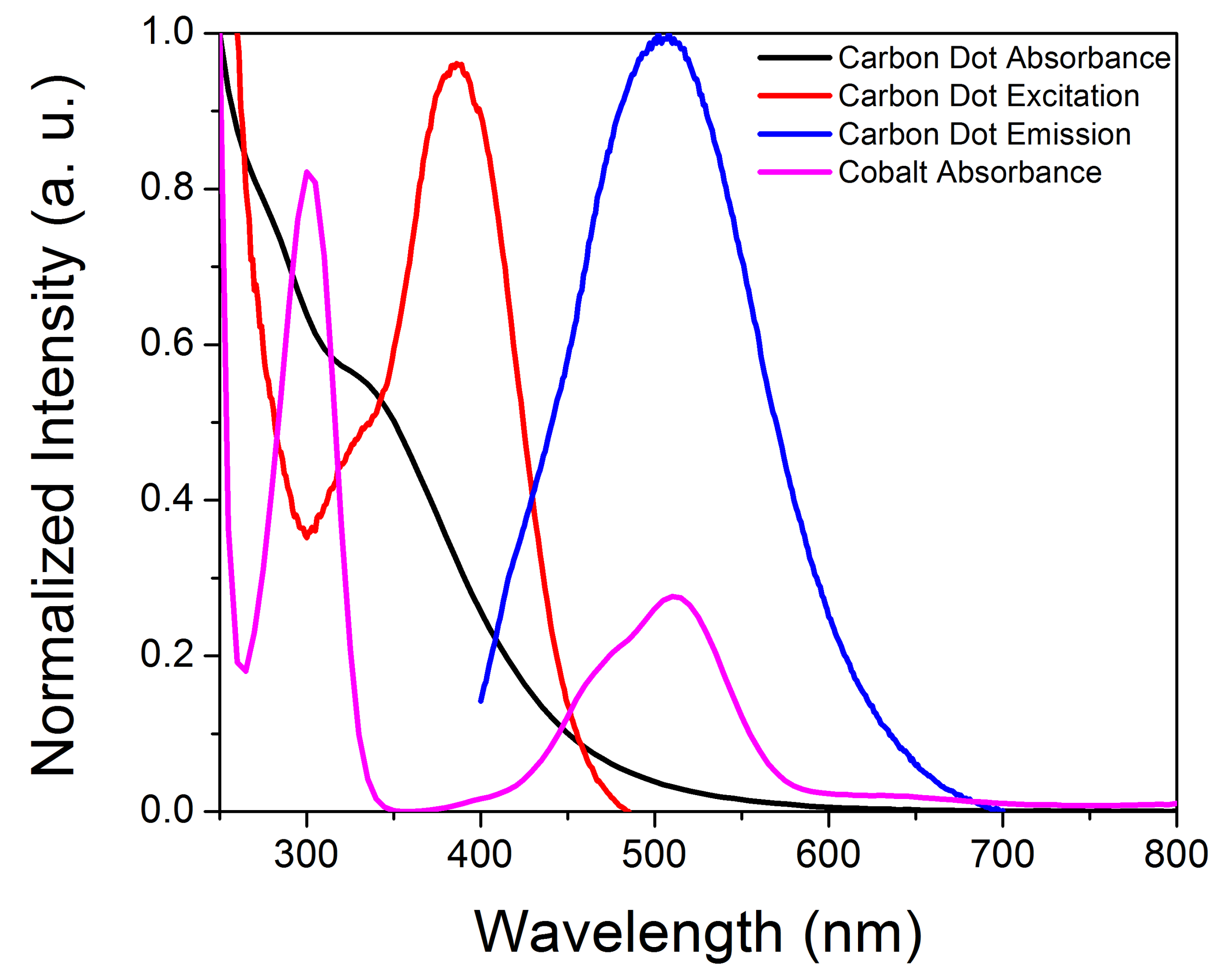


Appendix: Co Reversibility

Spiked Acid Mine Drainage

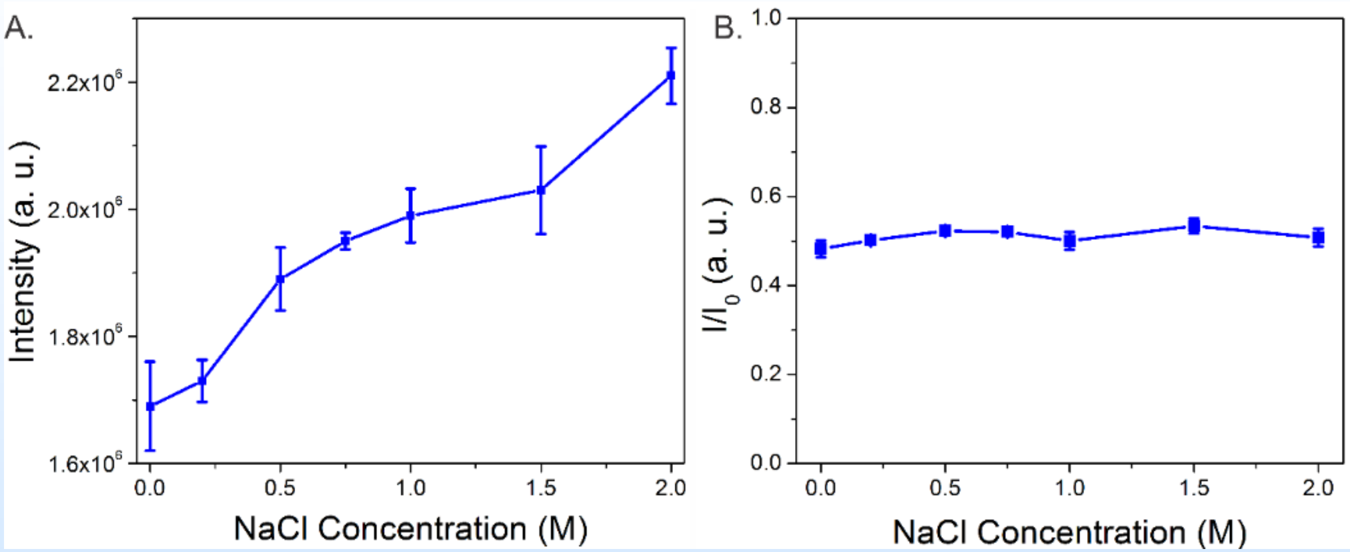


Appendix: Co Mechanism

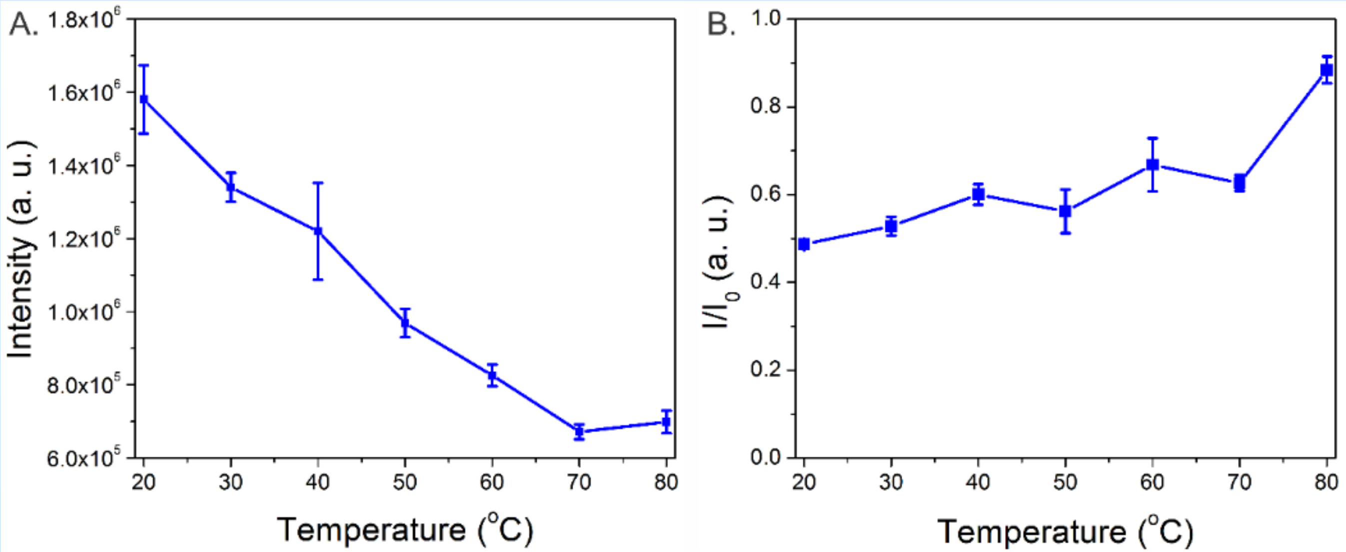


Appendix: Co Controls

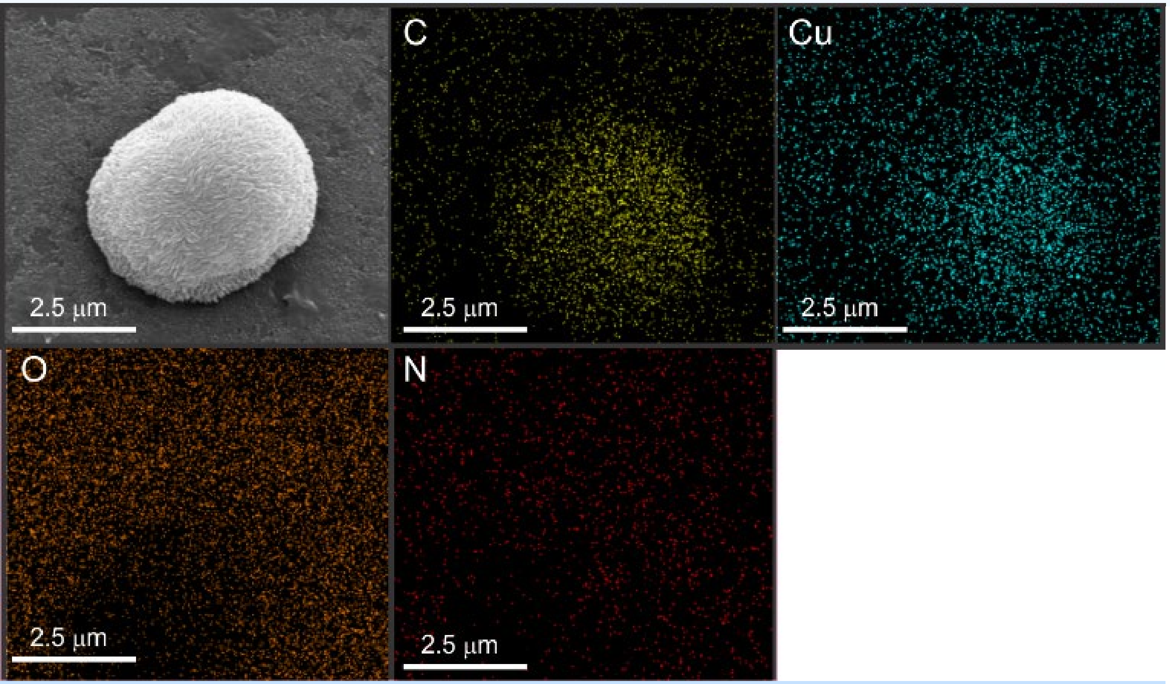
Salinity:

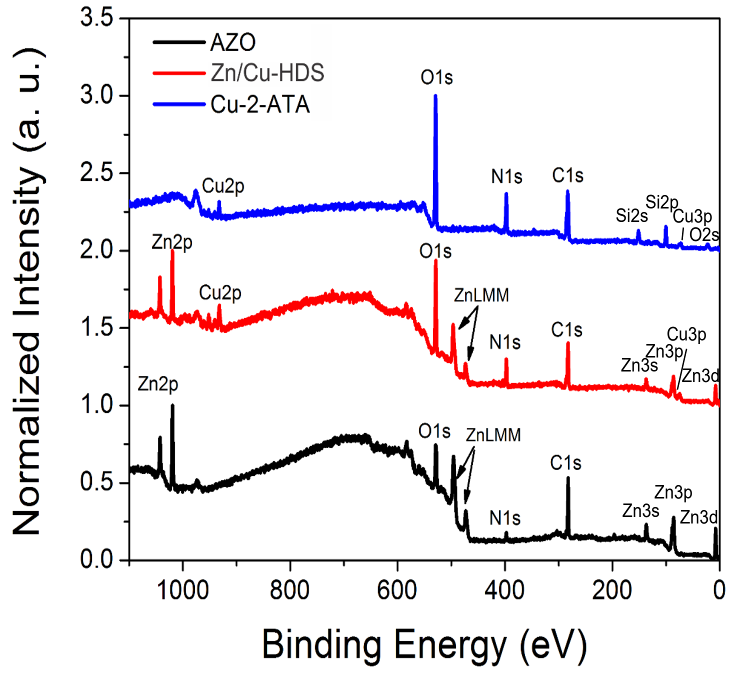


Temperature:

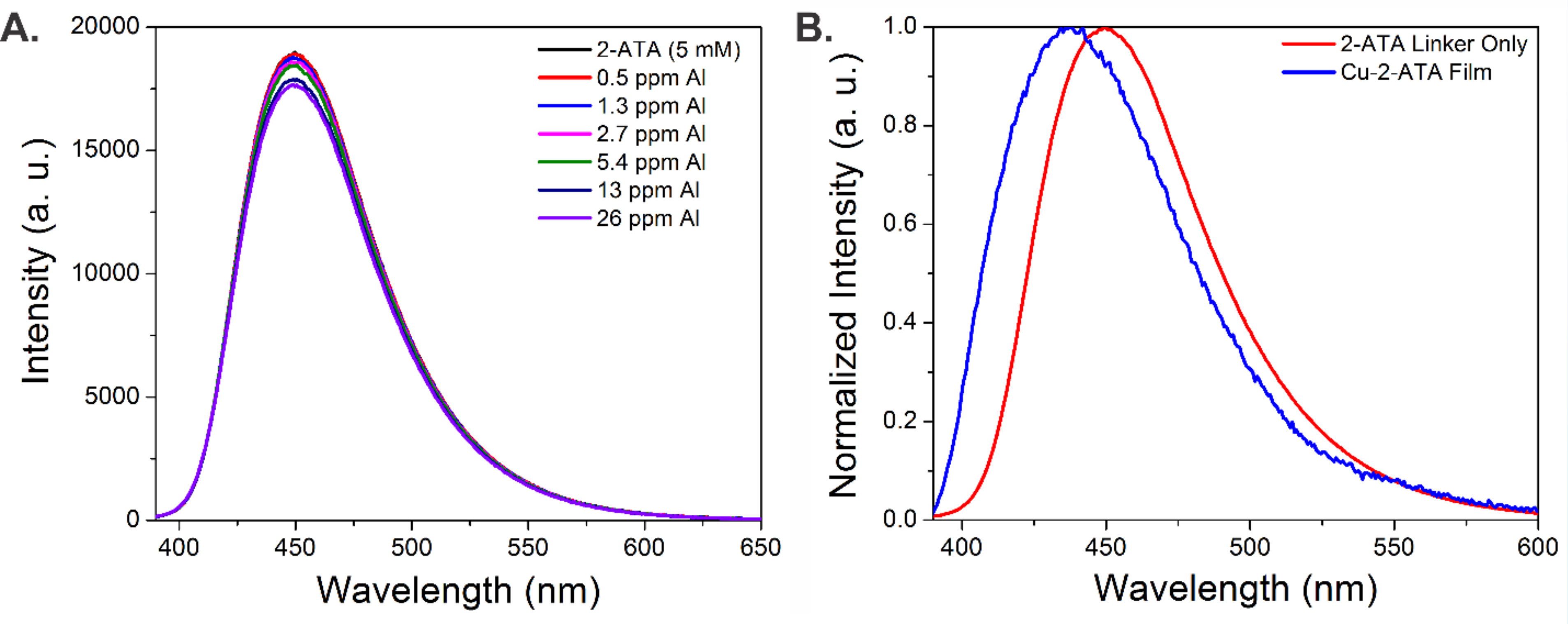


Appendix: Film Characterization

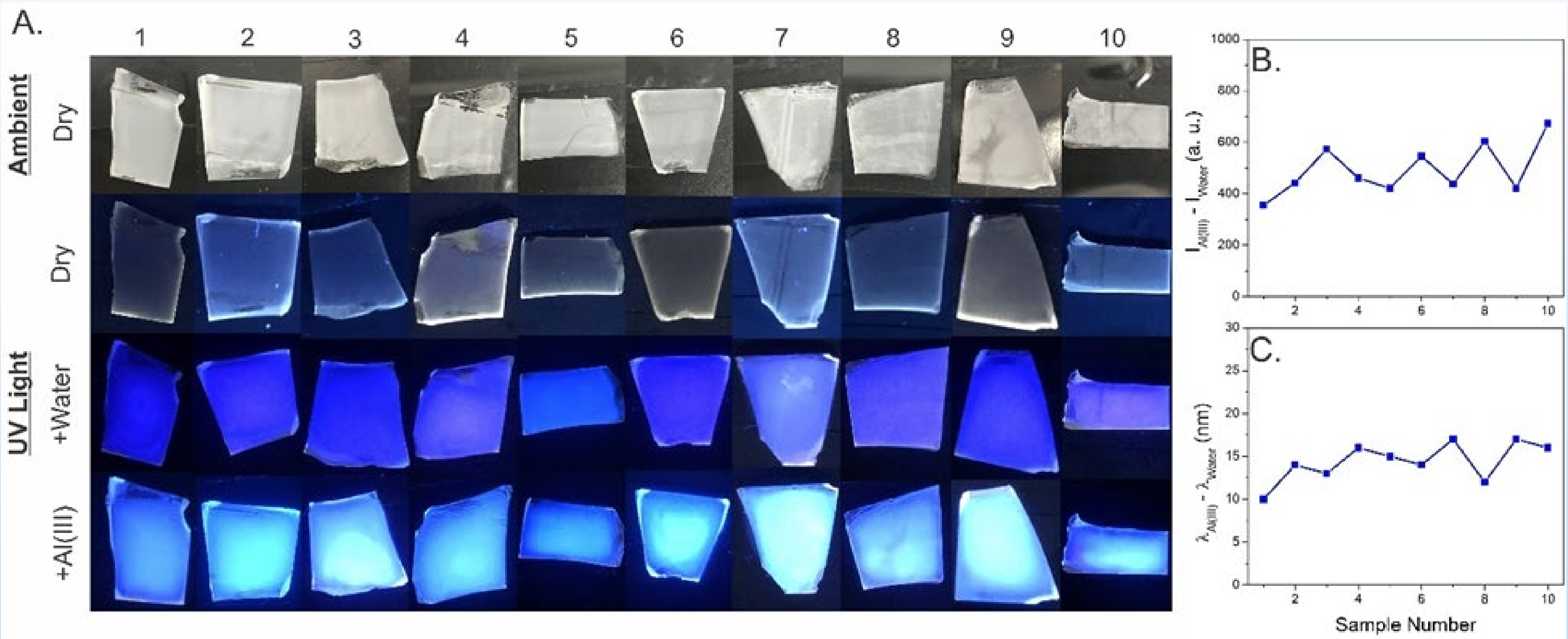




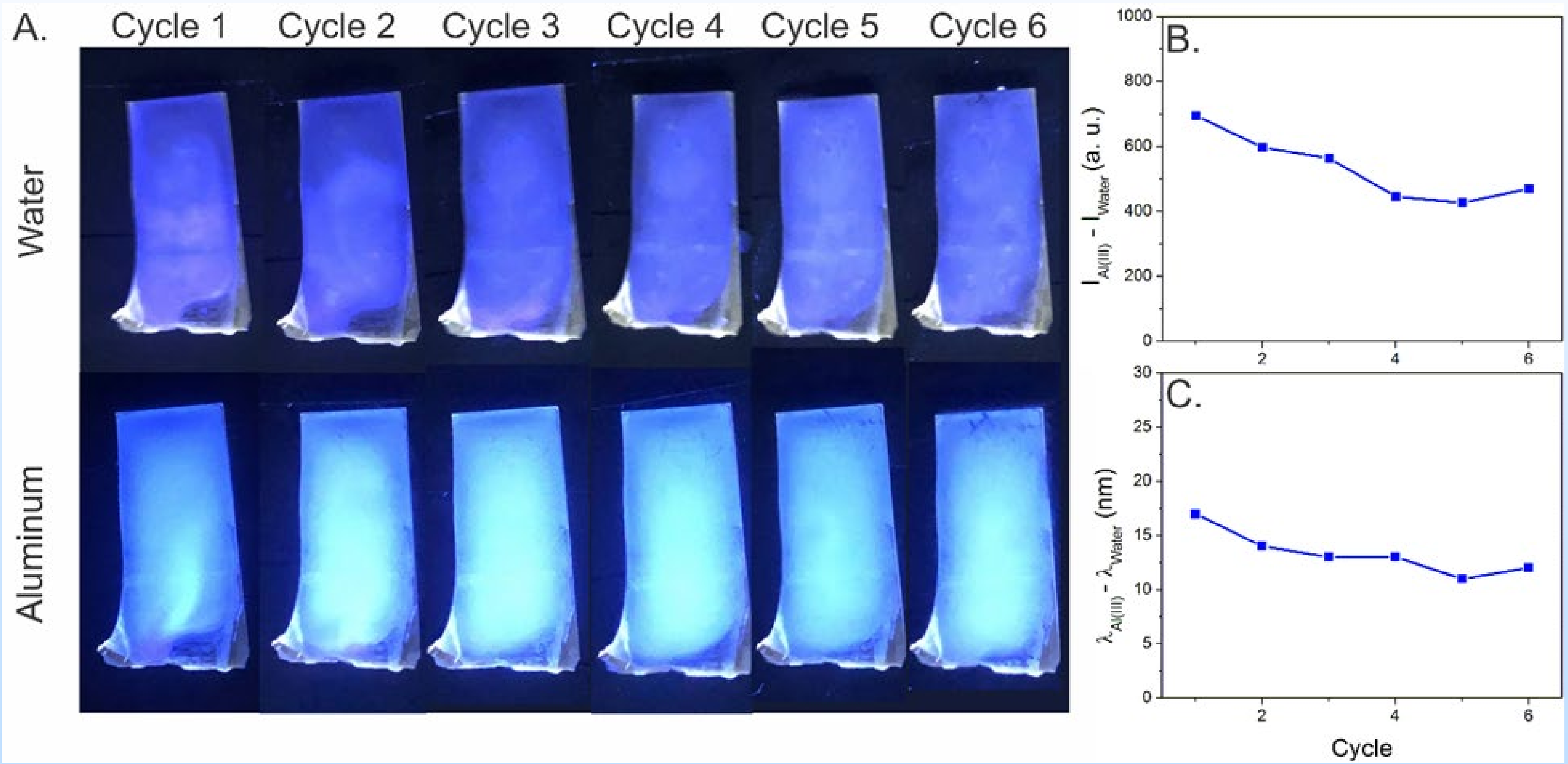
Appendix: Linker Control for Al(III)



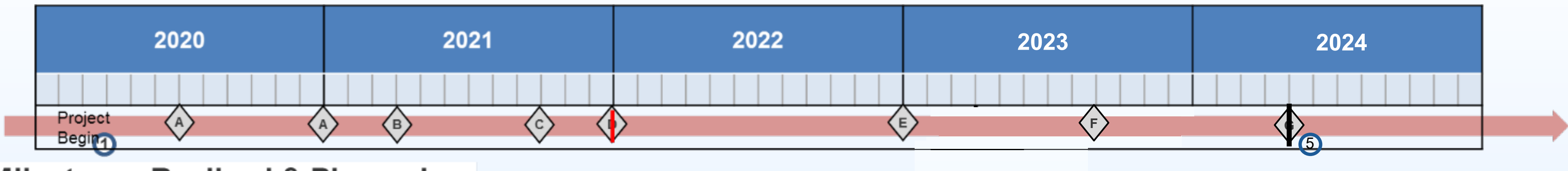
Appendix: Al(III) Sensor Variability



Appendix: Al(III) Sensor Reuse



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
F. Submit patent application on the immobilization of MOF material on fiber for REE detection
G. Report on possible ways for meeting optimal conditions for luminescent probe deployment in process streams and in a field deployable device.

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)

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

Chart Key