Portable fiber optic sensor for rare earth elements and other critical metals using photoluminescence methods

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Disclaimer

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What Drives Emerging Energy Technologies?

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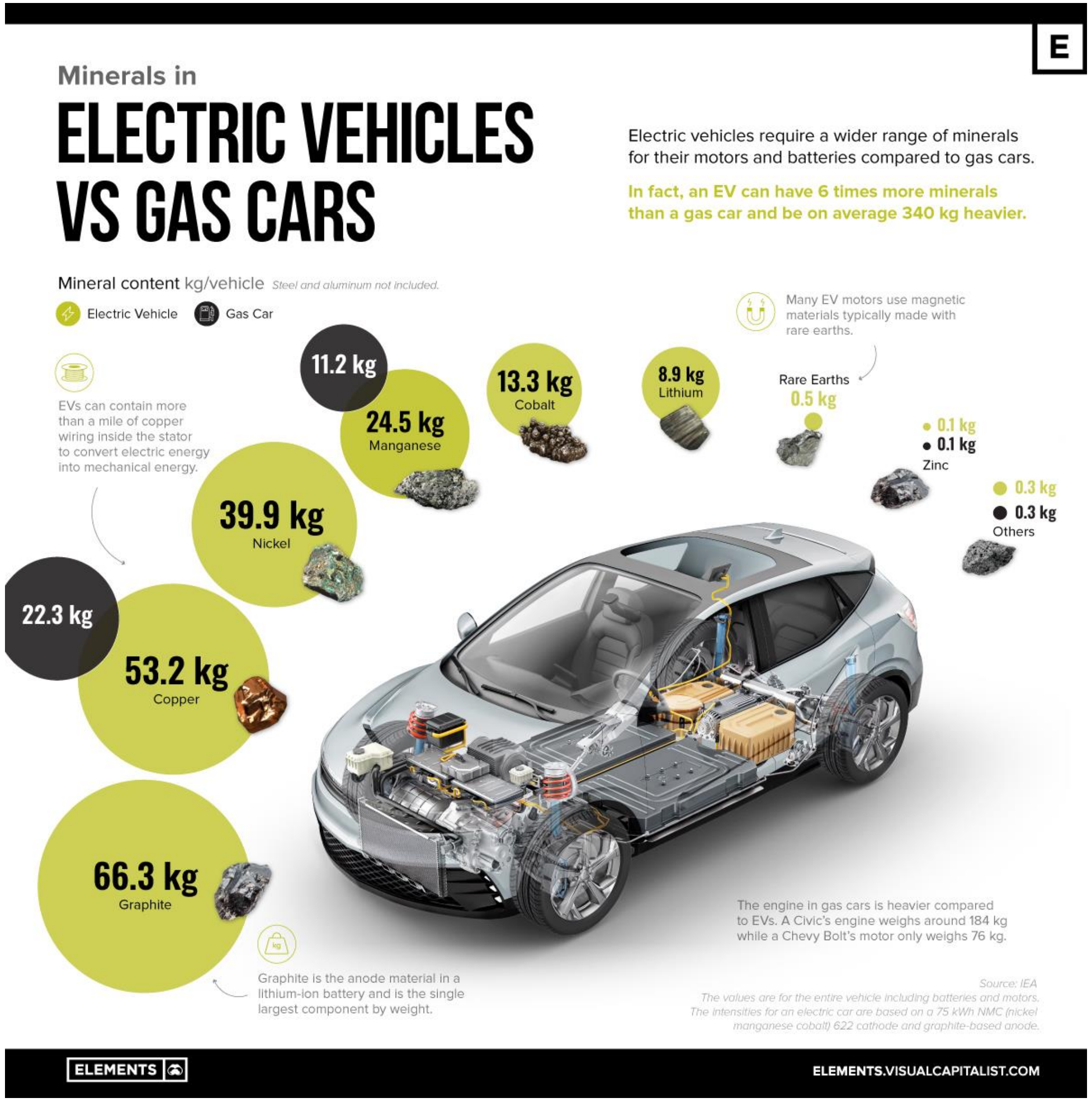
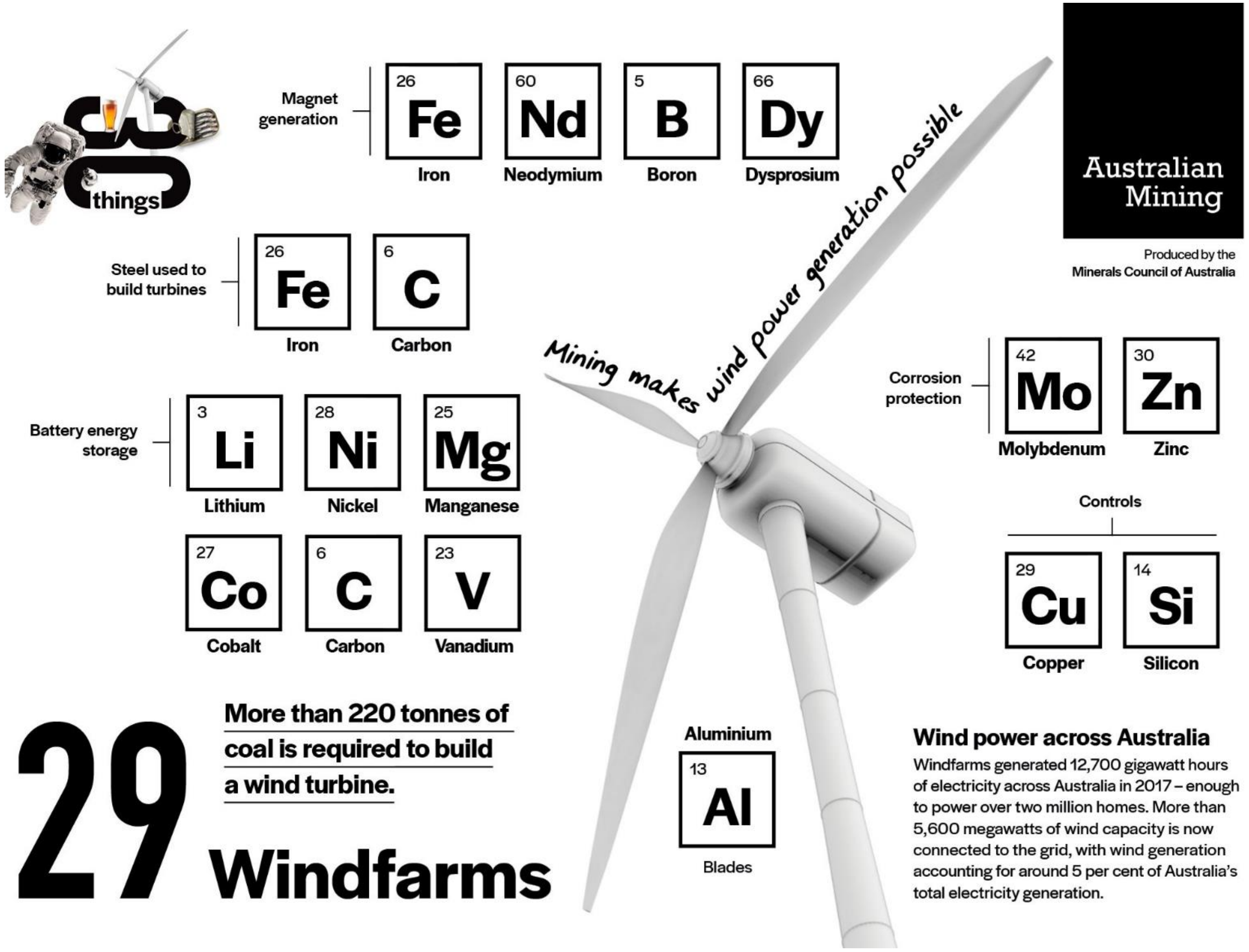
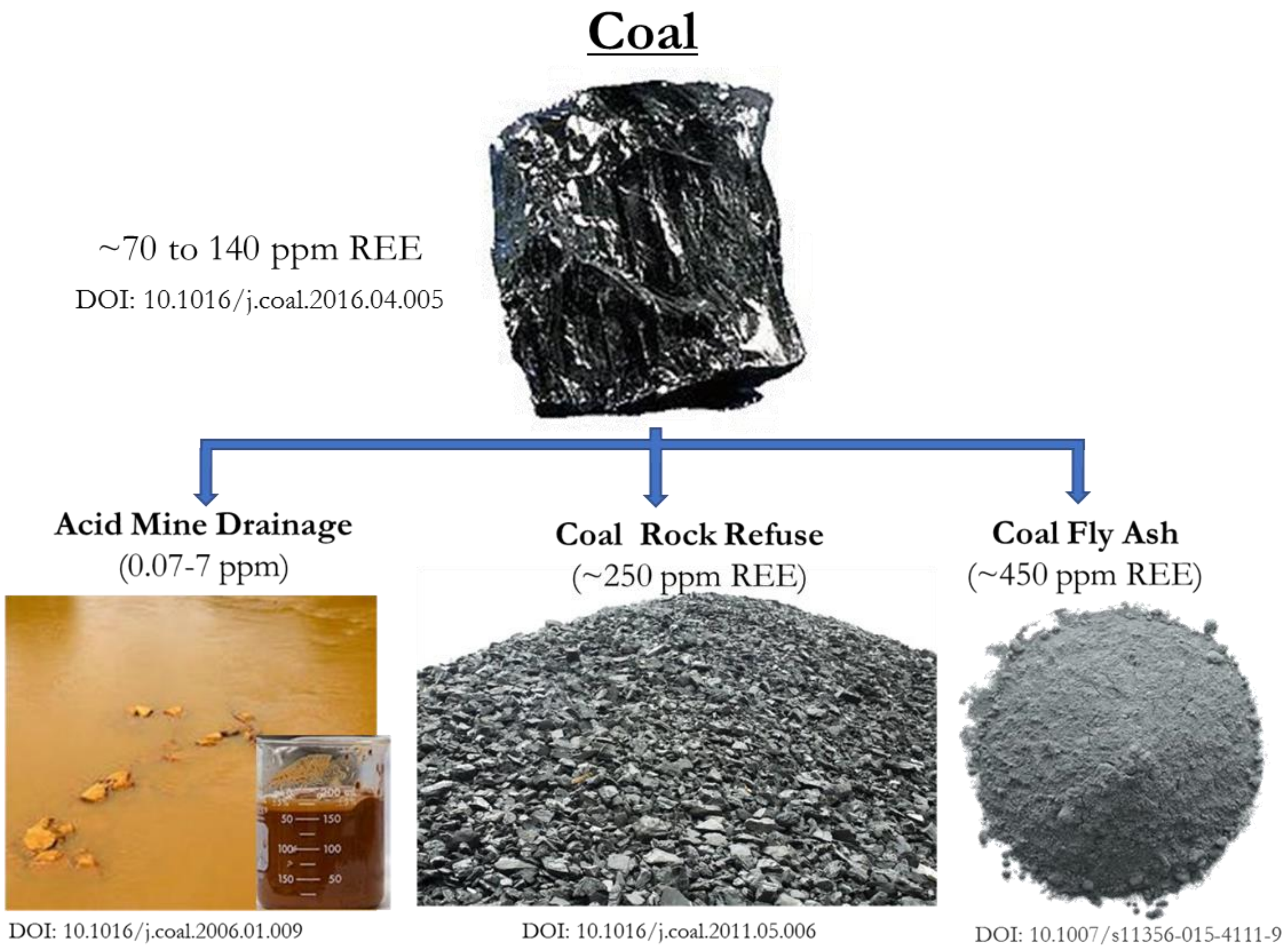




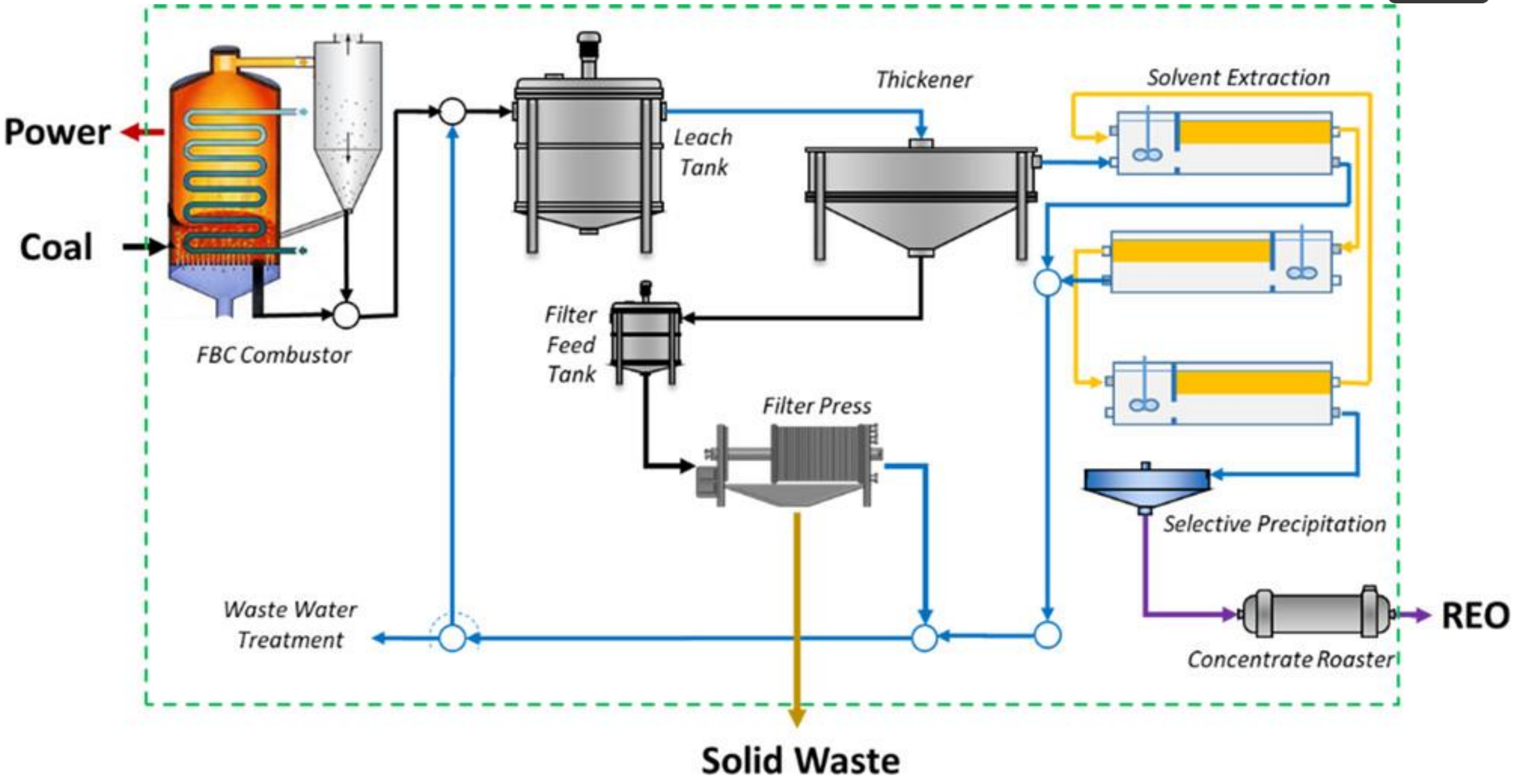
Sensors for Metals Prospecting

- Various alternative sources of critical metals are being explored:
    - Lithium-rich brines
    - Acid mine drainage
    - Mine tailings
    - Industrial waste
    - Electronic waste, etc.
- Critical metals content **may vary significantly** from source to source
- Transporting samples from the field to lab for characterization **increases cost** and delays feedback
- Rapid, sensitive, and portable characterization **saves time and transportation/processing costs**



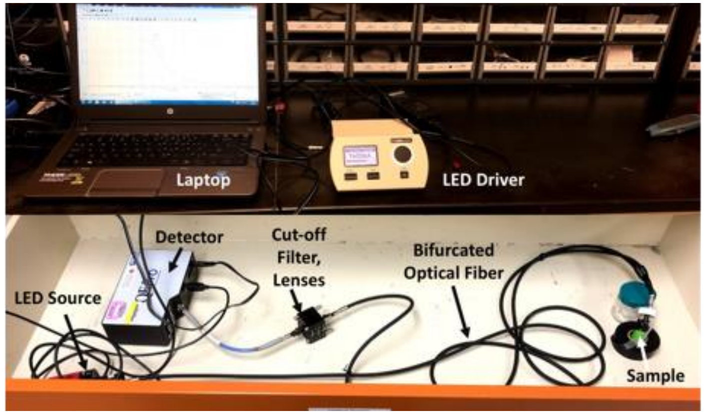
*REE: Rare Earth Element

Sensors for Process Monitoring



DOI: 10.1021/acs.energyfuels.9b00295

Rapid Characterization Methods Needed

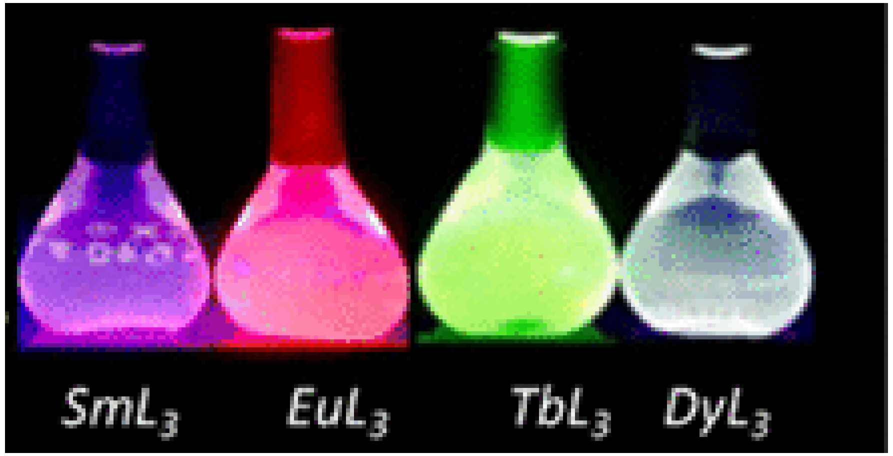


Technique	Instrument Cost	Detection Limit	Portable?
Inductively-Coupled Plasma Mass-Spectrometry	~$180k	Part-per-trillion	No
X-Ray Fluorescence Spectroscopy	~$13-17k	10s of part-per-million	Yes
Laser-Induced Breakdown Spectroscopy	~$30-50k	10s of part-per-million	Yes
Luminescence Spectroscopy	~$18-35k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

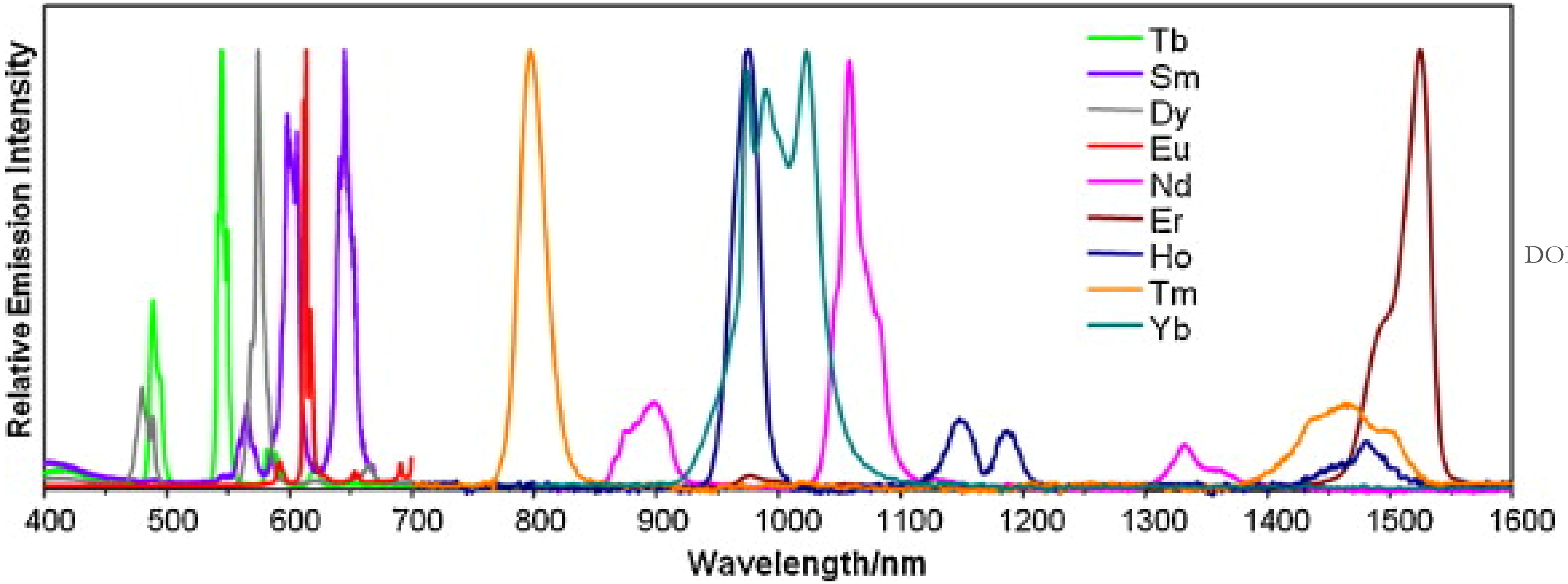
Luminescent sensors can provide significantly higher sensitivity than portable XRF or LIBs techniques at a comparable cost, while providing significant cost and time savings over ICP-MS

Element-Specific REE Emission Enables Sensing

Raymond Lab, Cal Berkley

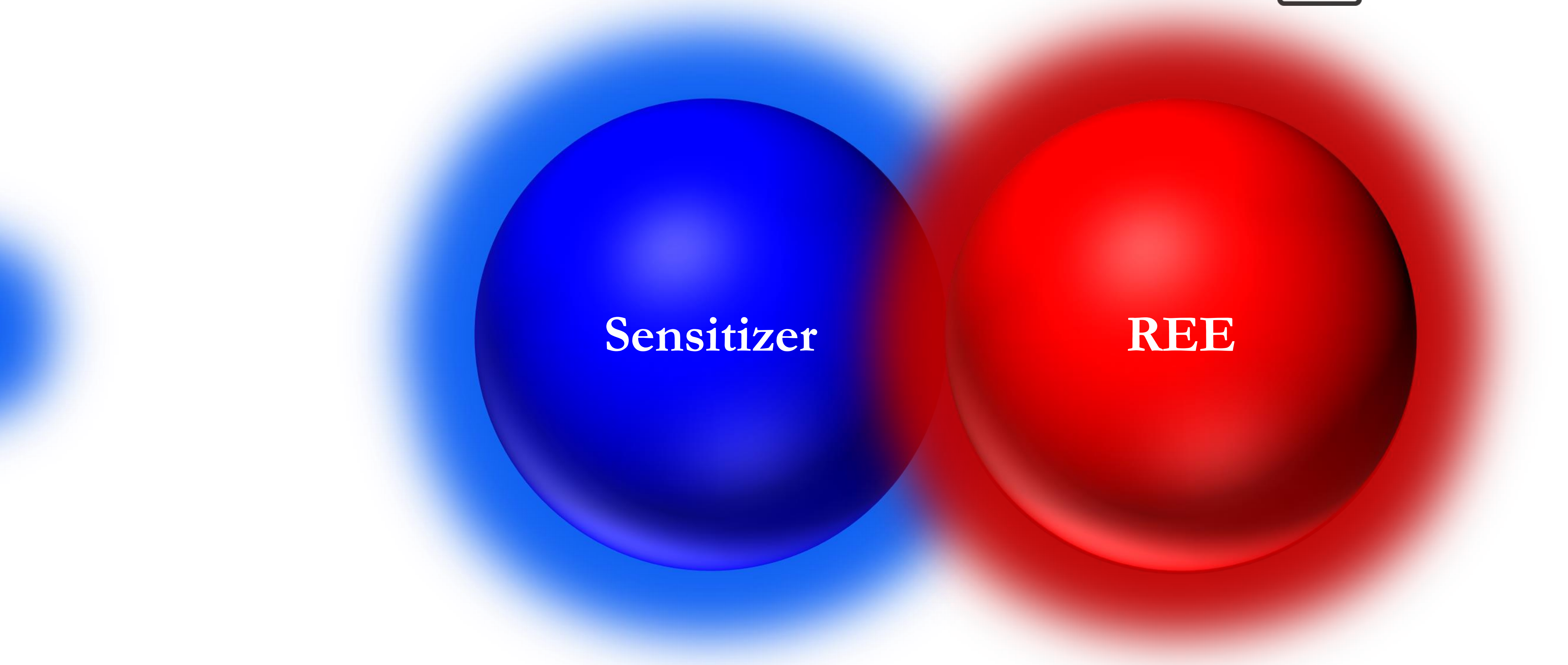


DOI: 10.1021/acs.inorgchem.7b02861



DOI: 10.1016/j.crci.2010.05.007

Sensitizer Material is Needed to Induce Emission



For Further Reading…


Journal of Materials Chemistry C

ROYAL SOCIETY OF CHEMISTRY

REVIEW

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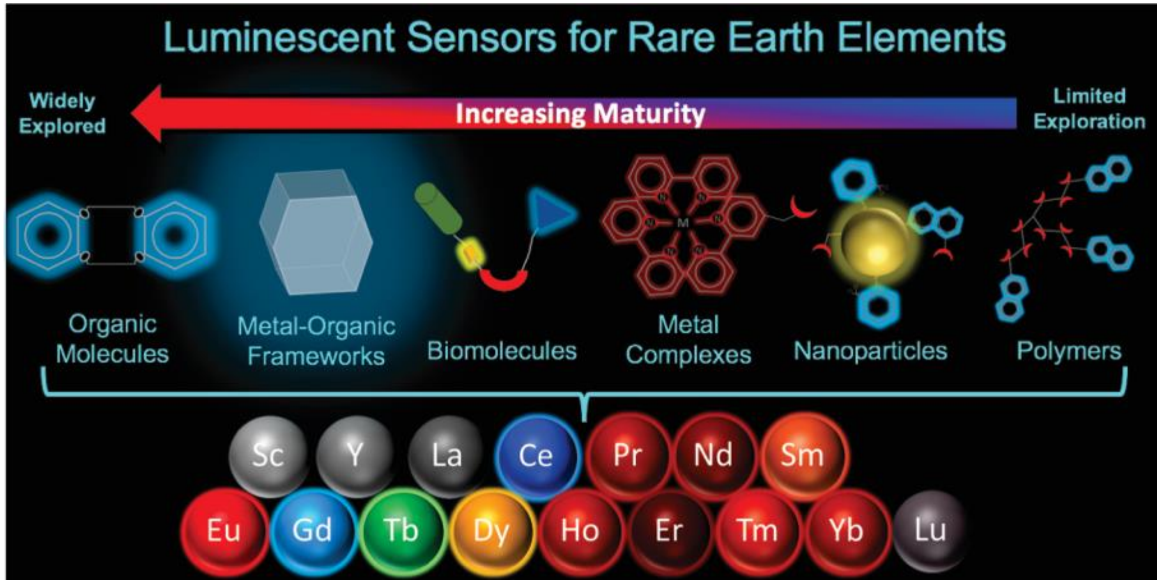
Cite this: DOI: 10.1039/d0tc01939a

Materials for the photoluminescent sensing of rare earth elements: challenges and opportunities†

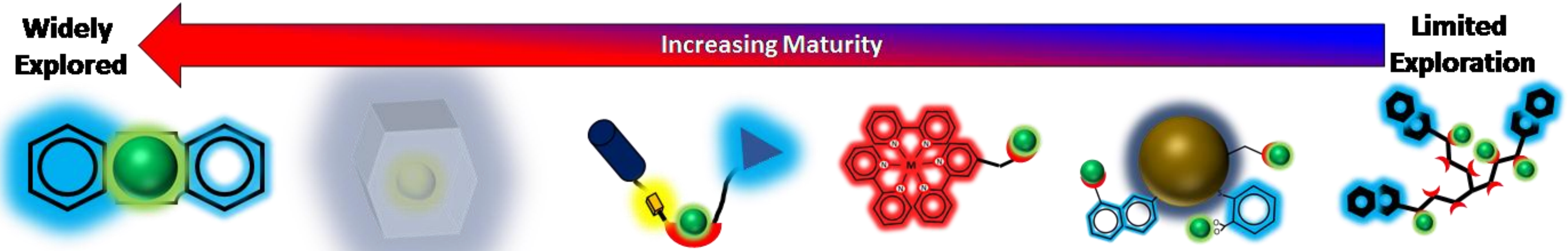
Scott E. Crawford,* Paul R. Ohodnicki Jr and John P. Baltrus



Comprehensive analysis (as of 2020) of materials, techniques, and outlook for luminescence-based sensors of REEs

Opportunity for Material Science Solution

NATIONAL ENERGY TECHNOLOGY LABORATORY

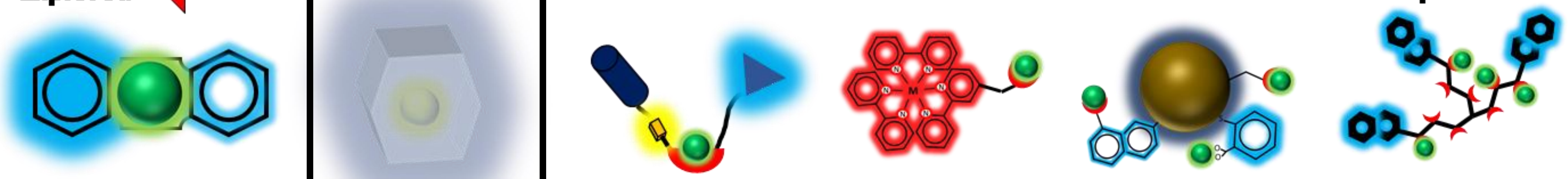


	Organic Compounds	MOFs	Biomolecules	Metal Complexes	Nanoparticles	Polymers
Sensitive?	√	√	√	√	?	?
Selective?	√	X	√	X	?	?
Water Compatible?	X	√	√	X	X	X
Easy to Synthesize?	X	√	X	X	√	X
Incorporated into Portable Sensors?	√	√	?	?	√	√

For additional details, see our recent review article: “Materials for the Luminescent Sensing of Rare Earth Elements: Challenges and Opportunities” in Journal of Materials Chemistry C

Opportunity for Material Science Solution

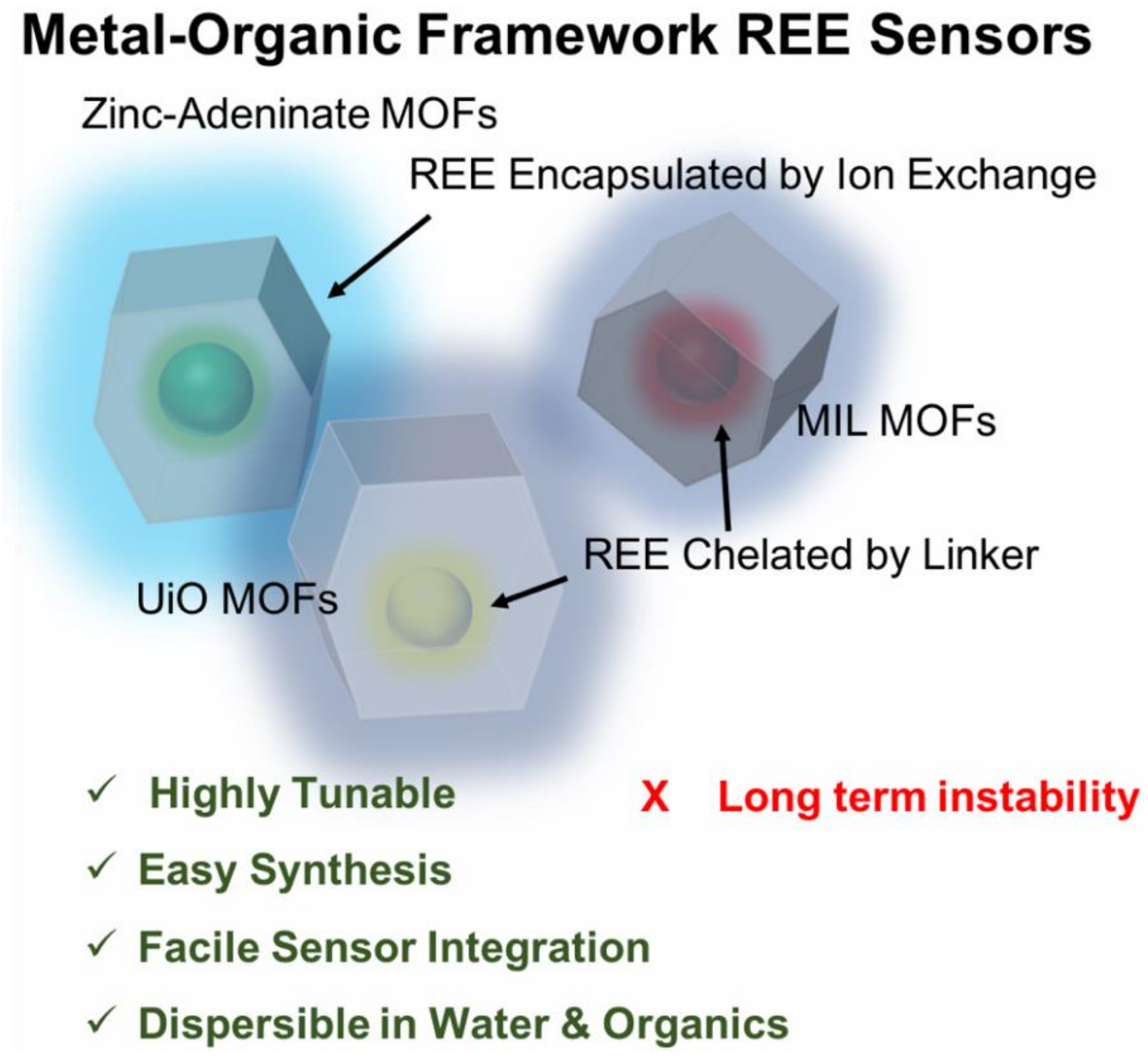
Widely Explored ← Increasing Maturity — Limited Exploration

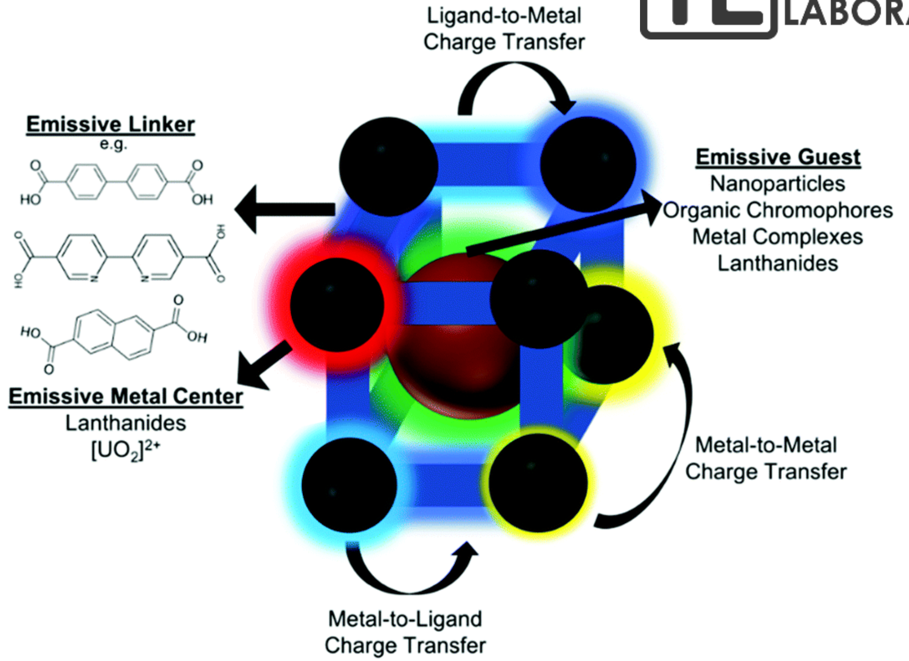


	Organic Compounds	MOFs	Biomolecules	Metal Complexes	Nanoparticles	Polymers
Sensitive?	√	√	√	√	?	?
Selective?	√	X	√	X	?	?
Water Compatible?	X	√	√	X	X	X
Easy to Synthesize?	X	√	X	X	√	X
Incorporated into Portable Sensors?	√	√	?	?	√	√

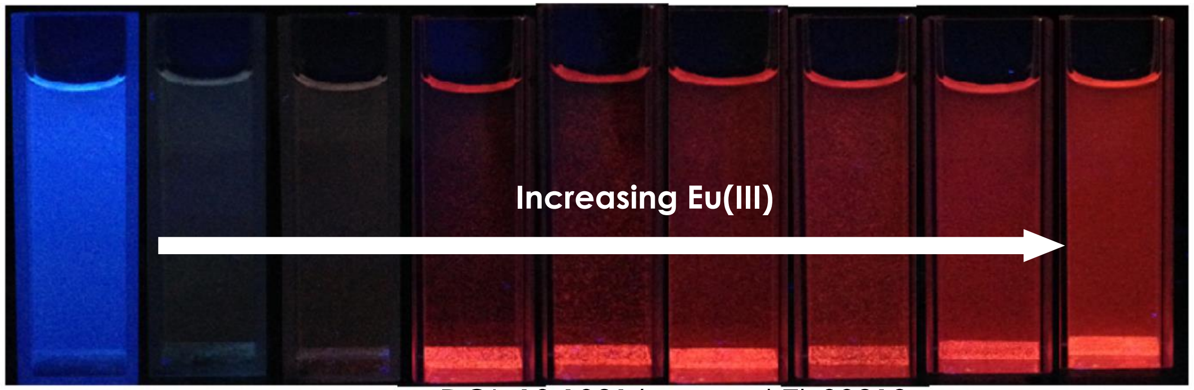
Crawford*, Ohodnicki, Baltrus, *Journal of Materials Chemistry C* **2020**, *8, 7975*

MOFs: A Flexible Sensing Material for REEs



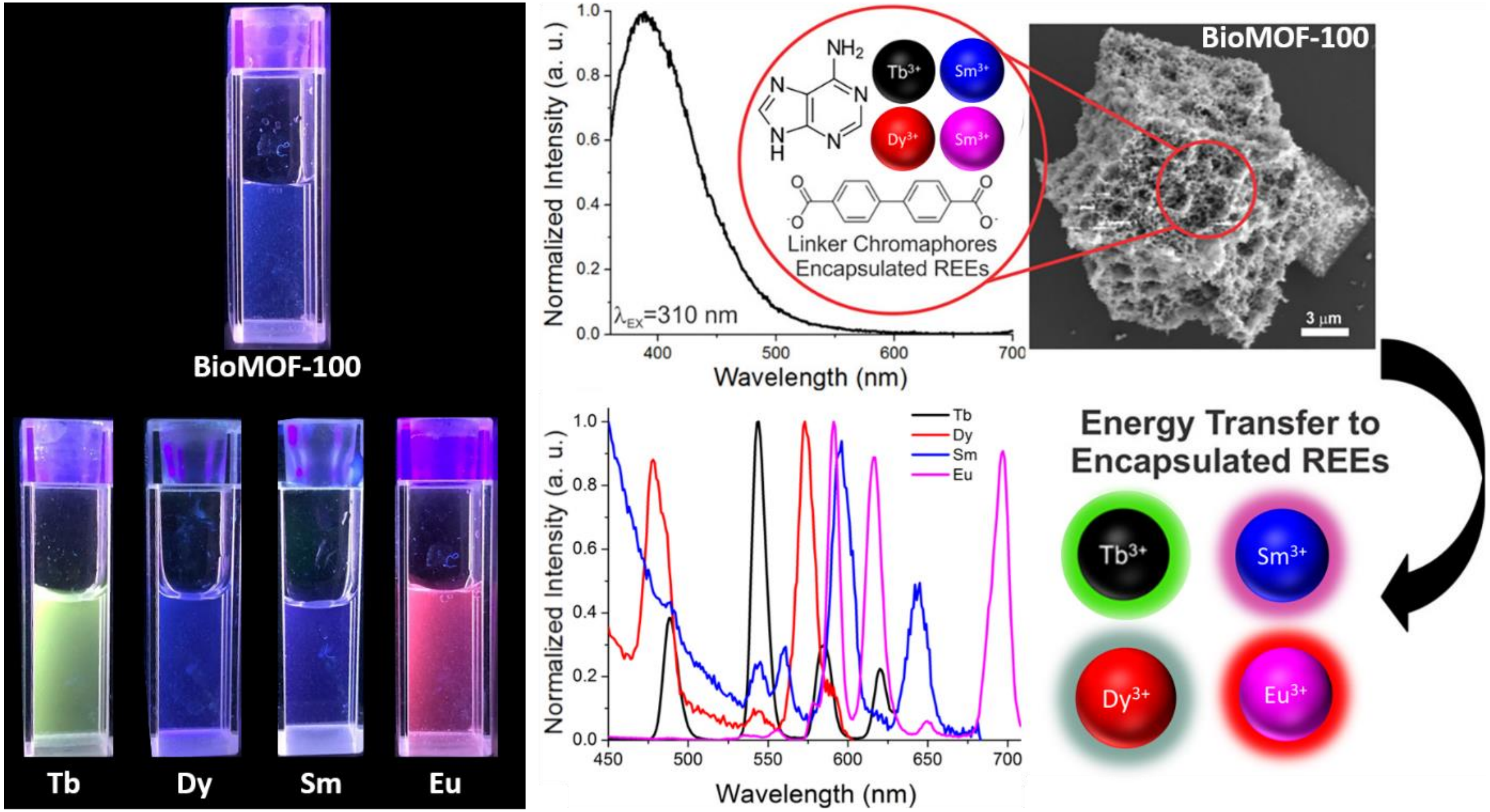


Ellis, Crawford, and Kim, *Mater. Adv.* 2020, **2**, 6169-6196



DOI: 10.1021/acs.cgd.7b00219

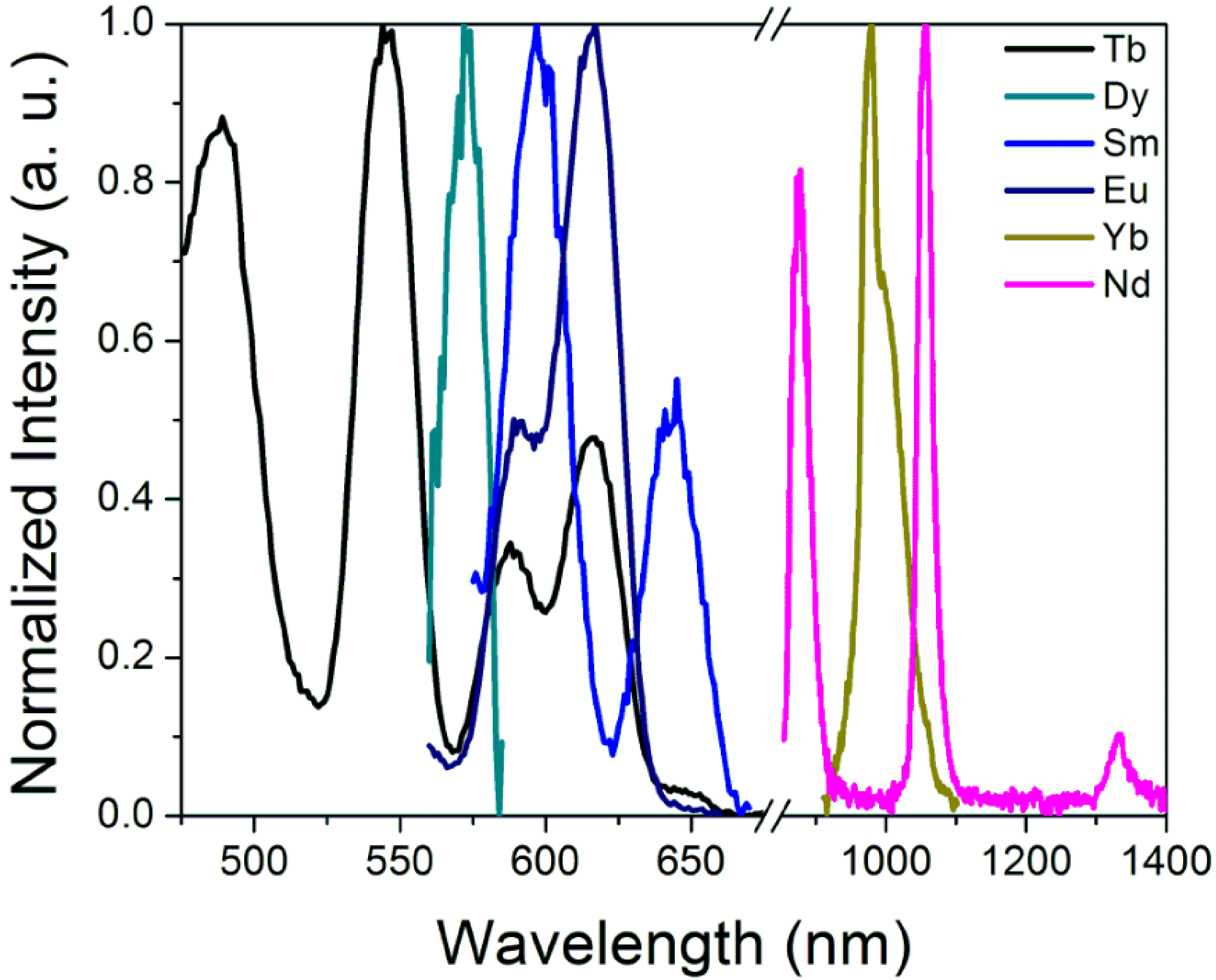
BioMOF-Based REE Sensitizers

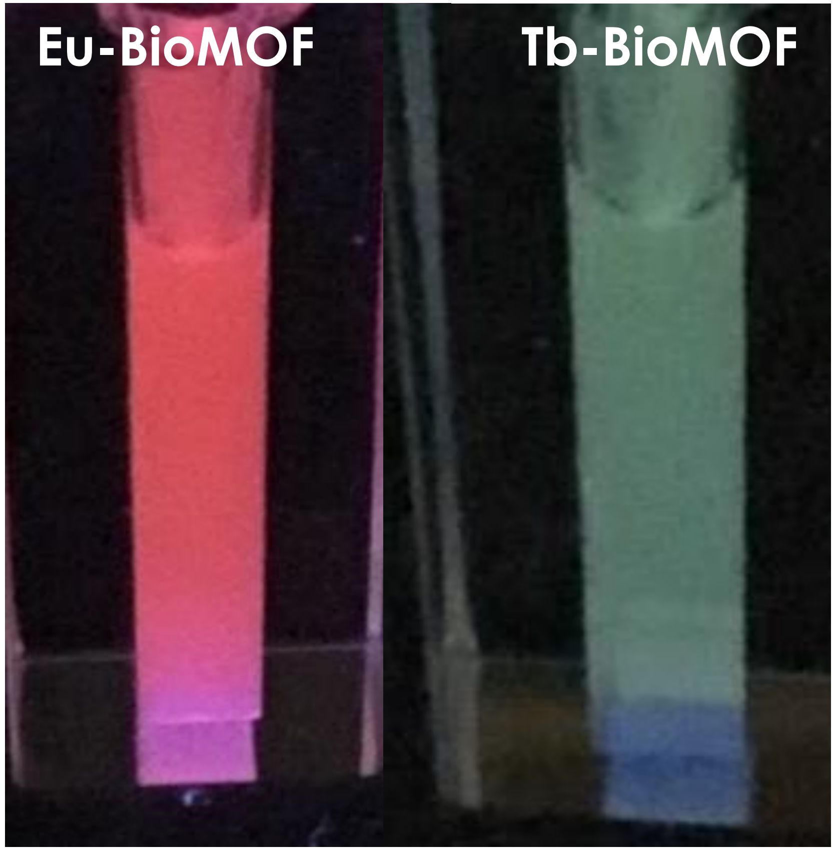


1. REE encapsulated via cation exchange
2. Organic chormophoric linkers are excited by UV light
3. Energy is transferred from chromophore to REEs
4. REE centered emission is observed

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

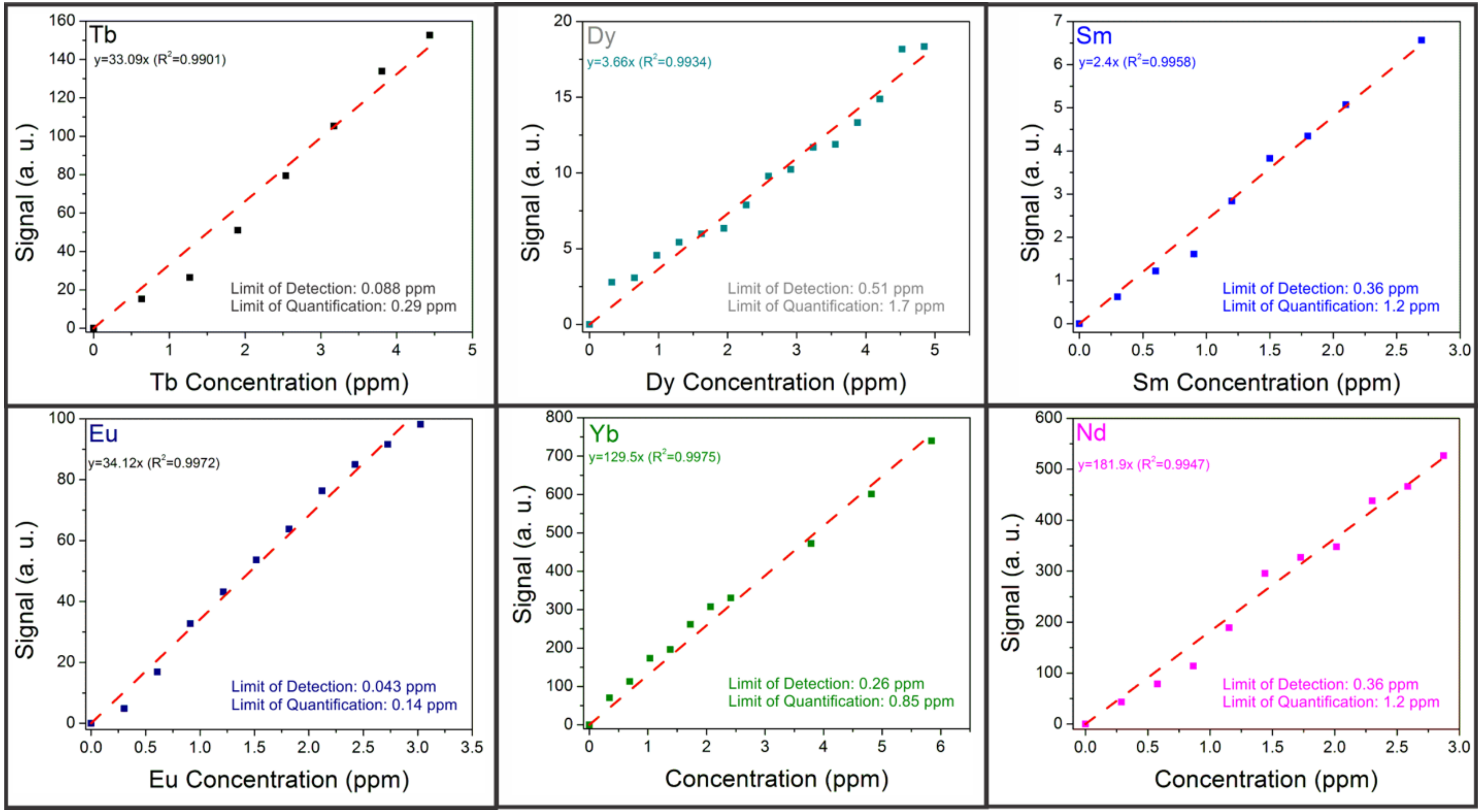
Sensitization of Six REEs with One Material!





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

Sub-ppm Limits of Detection for Six REEs!



Sub-ppm Limits of Detection for Six REEs!

NATIONAL ENERGY TECHNOLOGY LABORATORY

REE	LOD (ppb)	LOQ (ppb)	λ_{EM} (nm)[a]	fwhm (nm)[b]
Tb	5.6	18	545	22
Dy	170	550	572	18
Sm	180	600	597	24
Eu	18	60	617	36
Yb	280	850	980	54
Nd	360	1200	1056	24

Sub-ppm limits of detection (LODs) measured for all REEs analyzed, with low-ppm or ppb-level limits of quantification (LOQs). The best results are obtained for Eu and Tb.

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

Selectivity is a Significant Challenge

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

Competing metal ions have concentrations that can be thousands of times higher than **total** REE content, in addition to highly acidic matrices

MOF Structure Influences Selectivity

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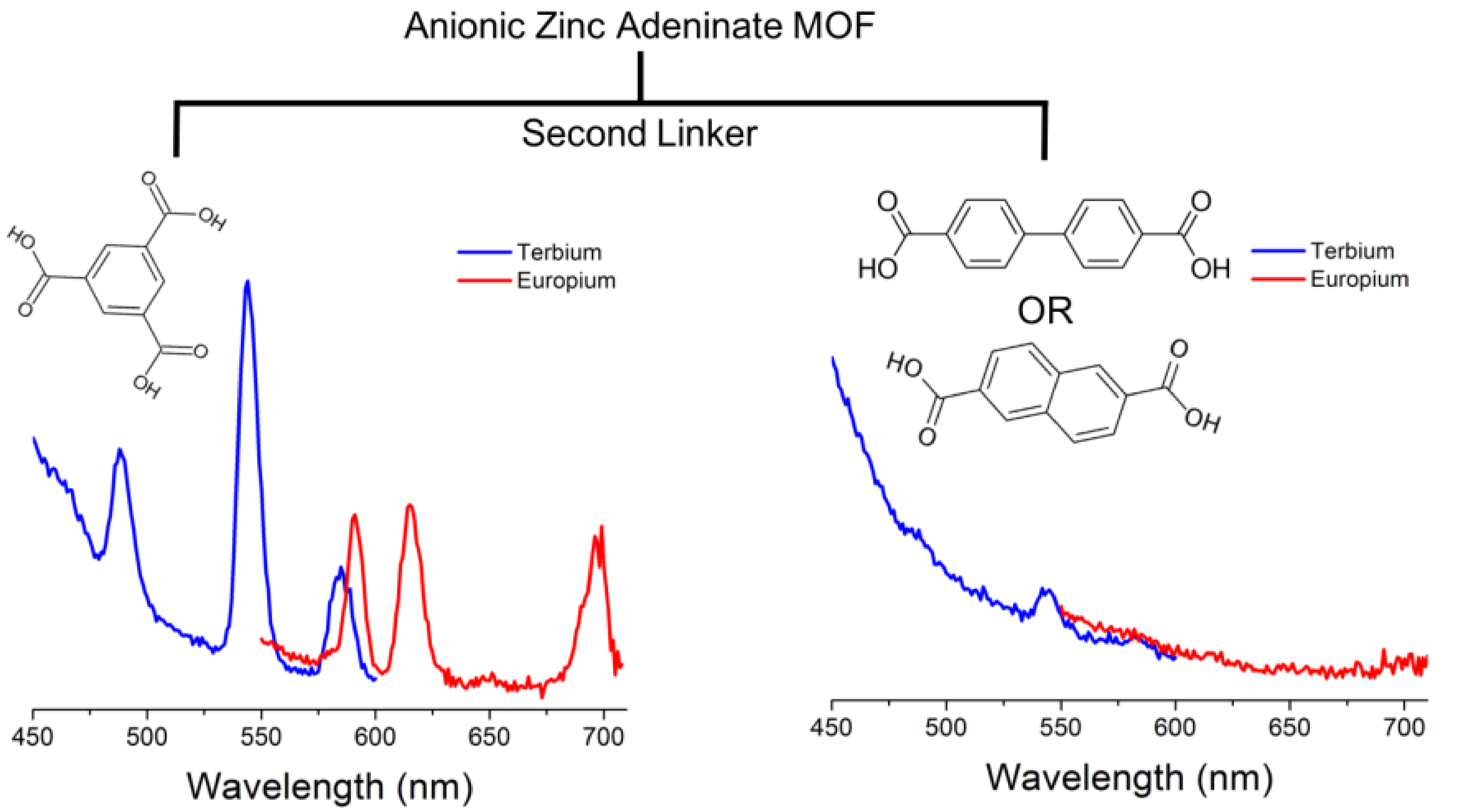
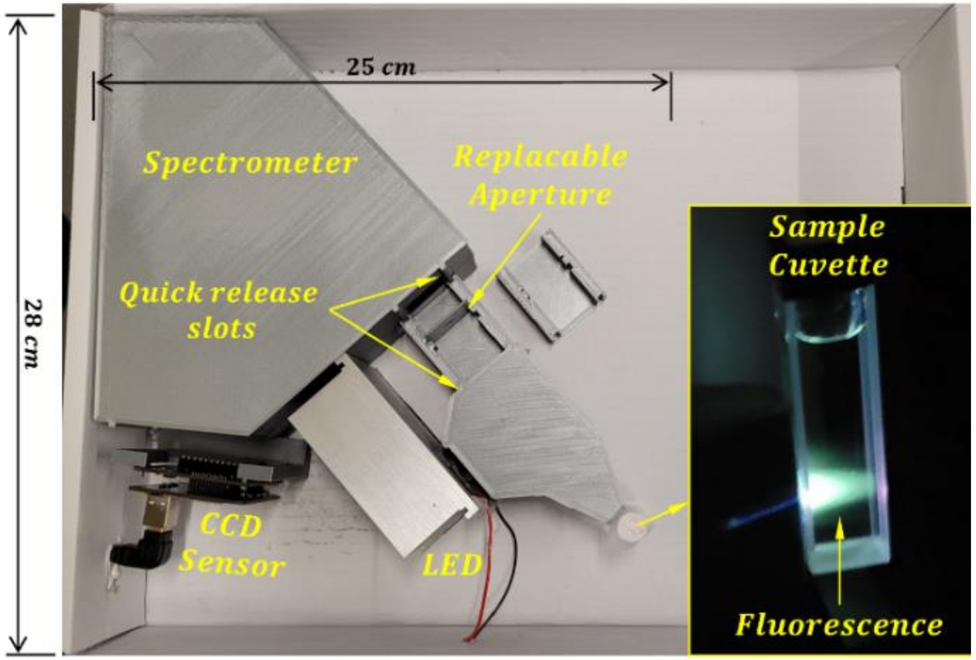


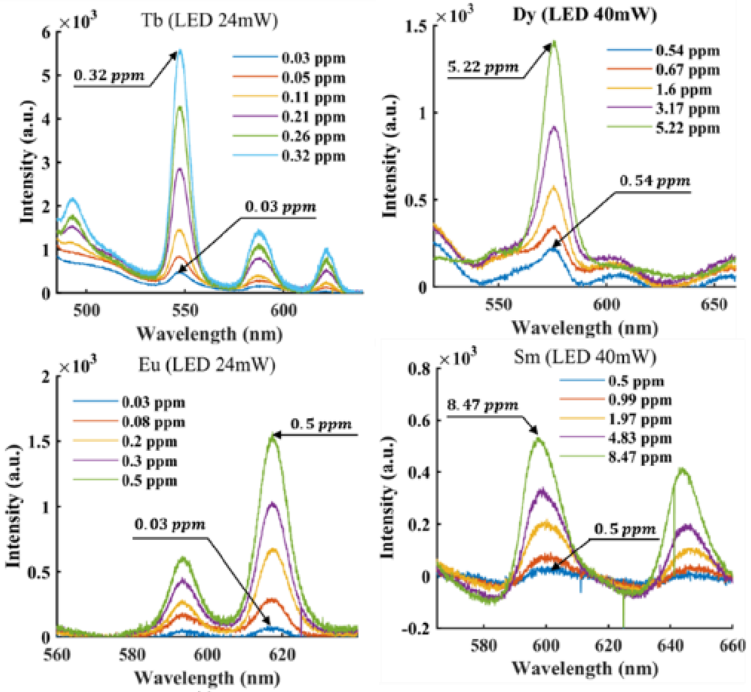
Emission in Acid Mine Drainage Matrix: 3.3 pH, [Ca] = 59 ppm, [Mn] = 29 ppm, [Al] = 10 ppm

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

Development of Low-Cost Systems

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



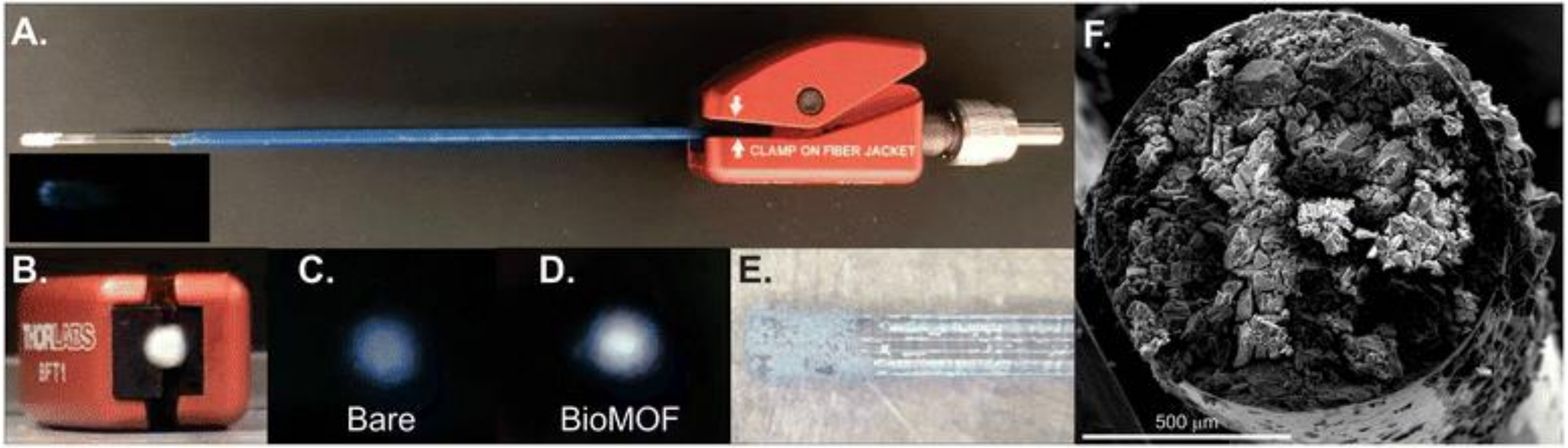


- Collaboration with University of Pittsburgh
- Sensitivity on par or better than a commercial system tested under identical conditions
- Similar performance at a fraction of the cost (~$2,000 vs. $100,000)

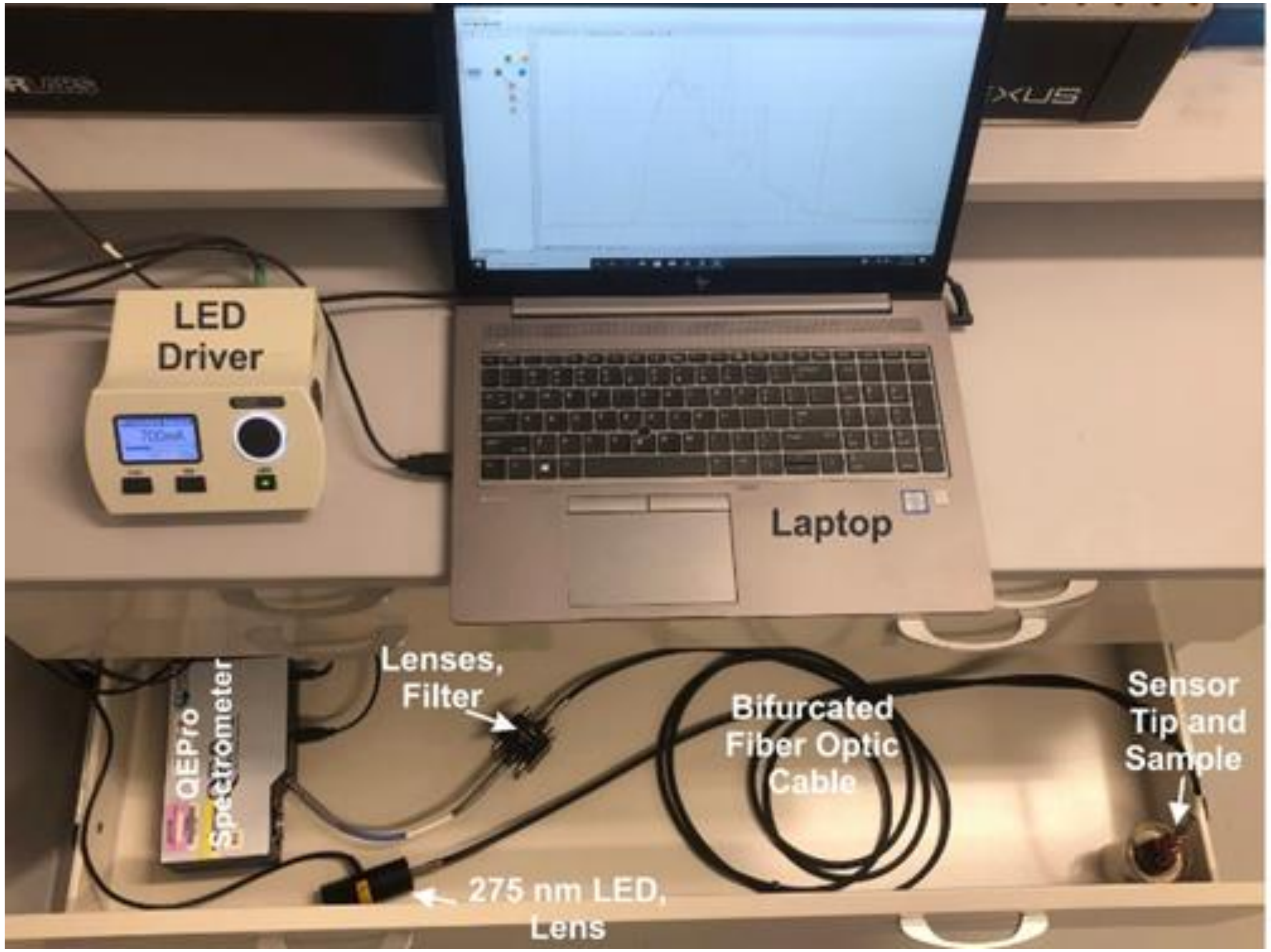
Wu, Z., Crawford, S., Buric, M., Splain, Z., Chen, K; *IEEE Sens. J.* ***2023,*** *23*(11), 11574-11581

Integration onto Portable Fiber Optic Platform

- 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)



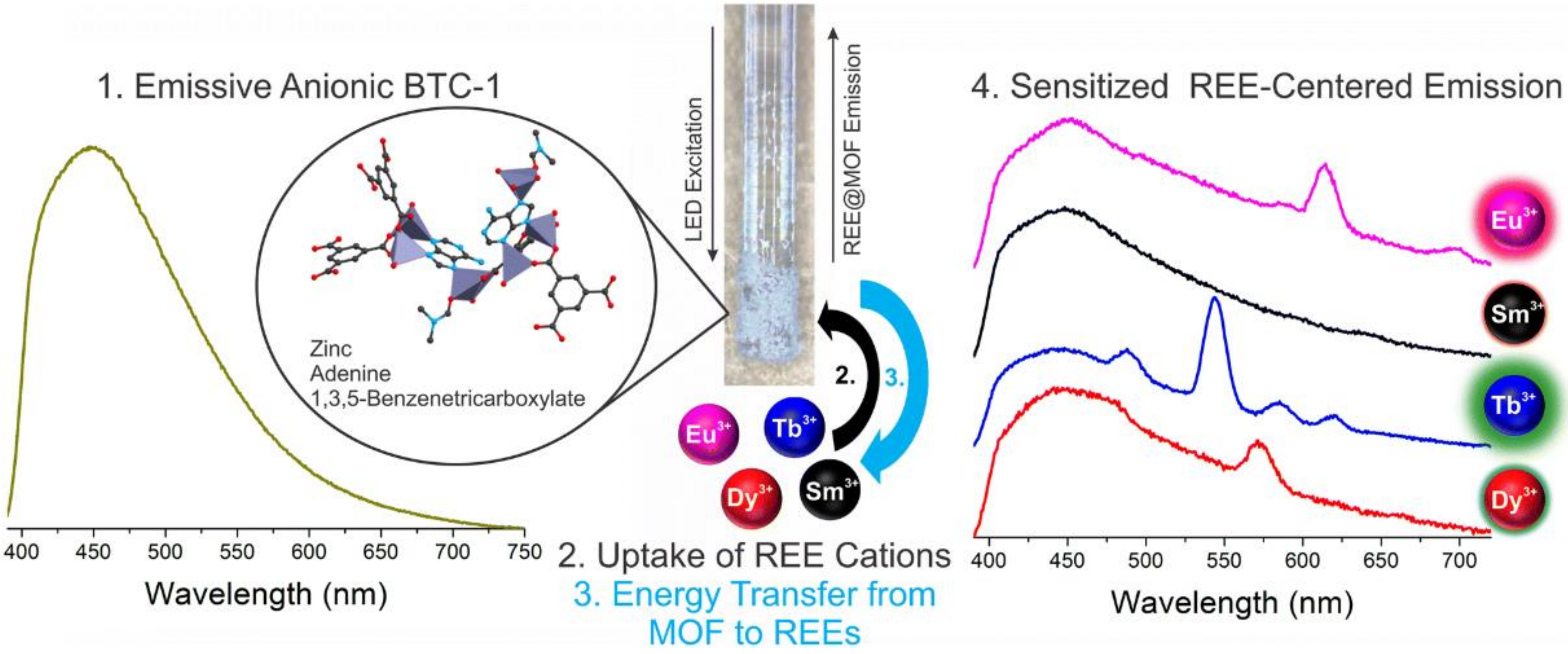
Integration onto Portable Fiber Optic Platform



- Assembled from off-the-shelf, commercially available components
- Total cost is ~$20k, the bulk of which comes from the QEPro spectrometer
- Advantages over commercial systems include lower cost, portability, and low power consumption

Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int.* **2024**, *1*, 689

Integration onto Portable Fiber Optic Platform



Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int*. **2024**, *1*, 689

Solvent Removal Enhances Signal

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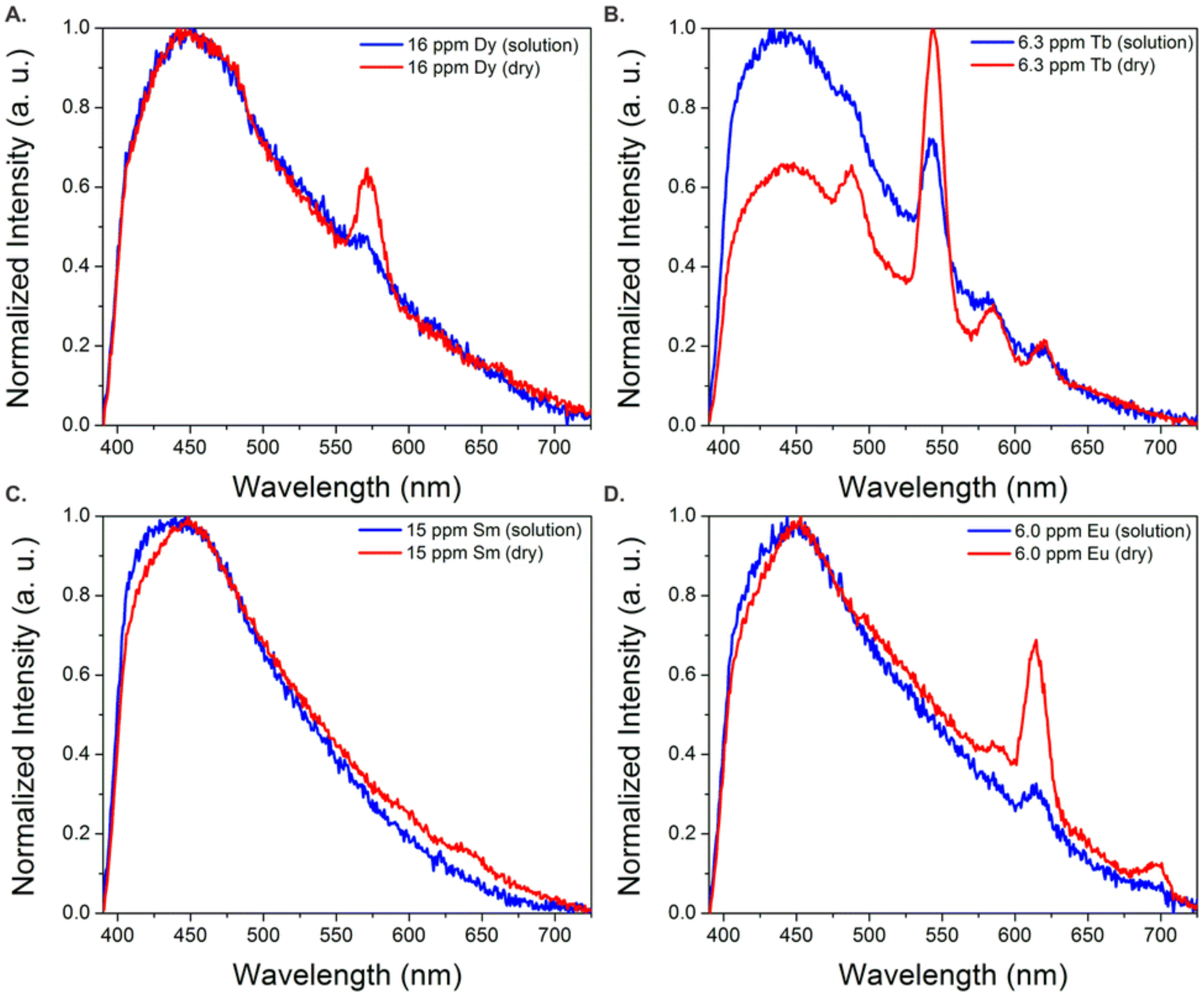


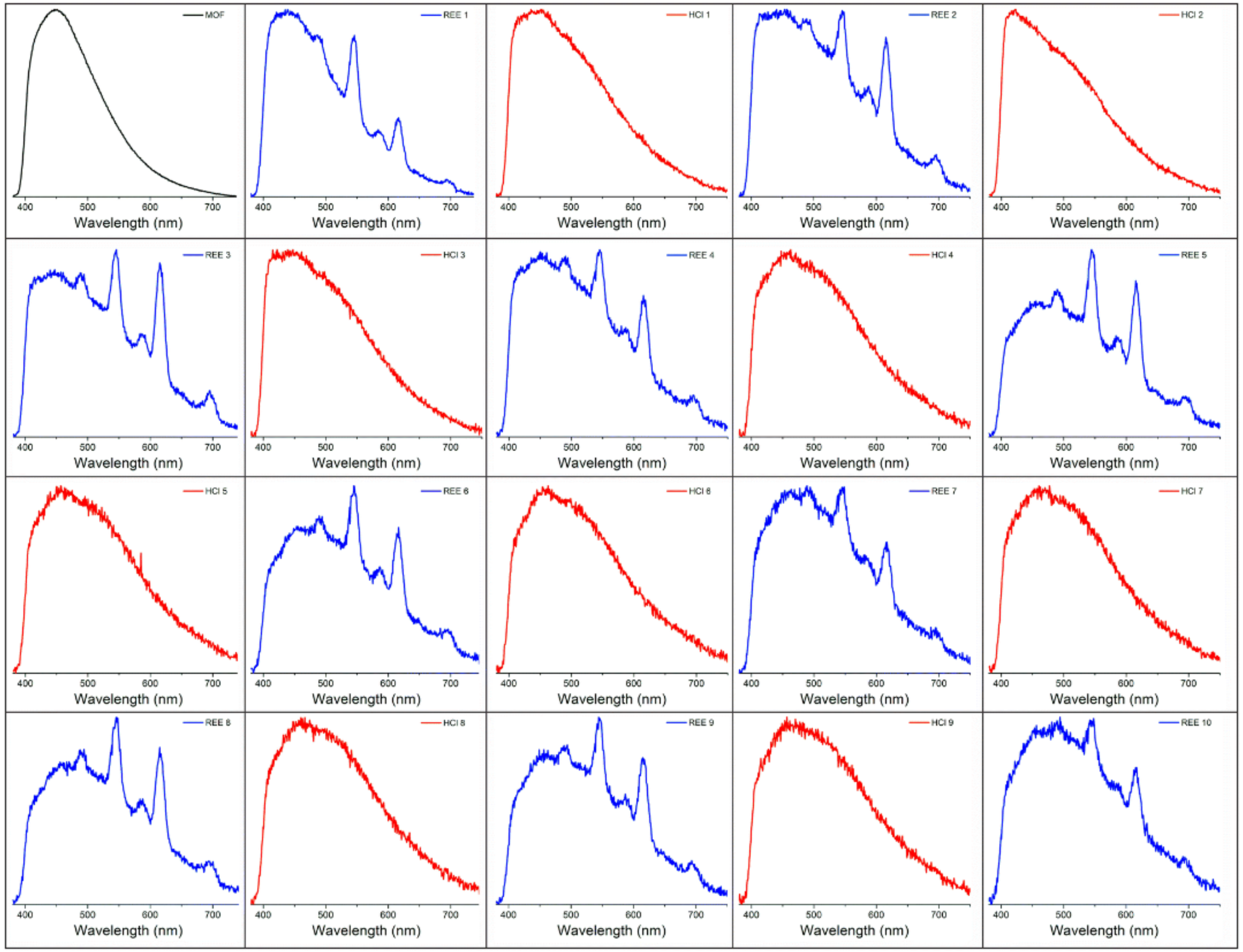
- Drying sensor tip reduced vibronic quenching from solvent, **improving signal**
- Can reduce the detection limit by **~a factor of 2**

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

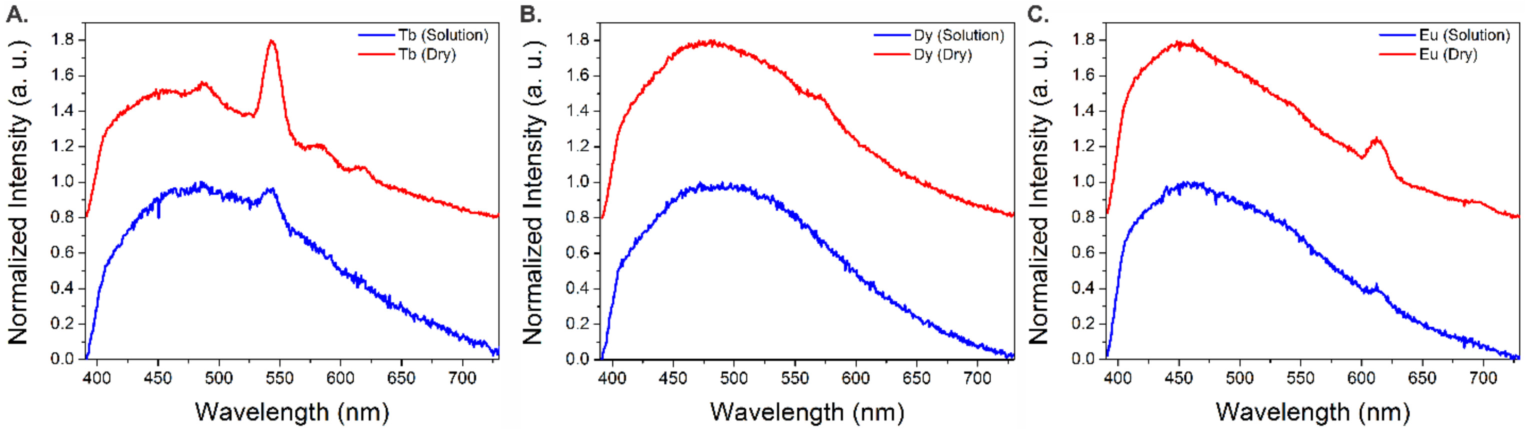
Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int.* **2024**, *1*, 689

Sensitive, Reversible Sensing Response

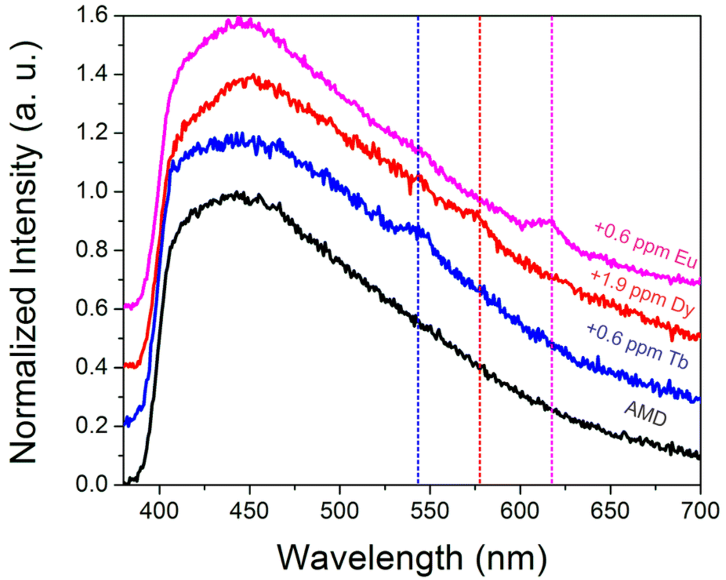


Qualitative regeneration of signal across multiple cycles using dilute acid

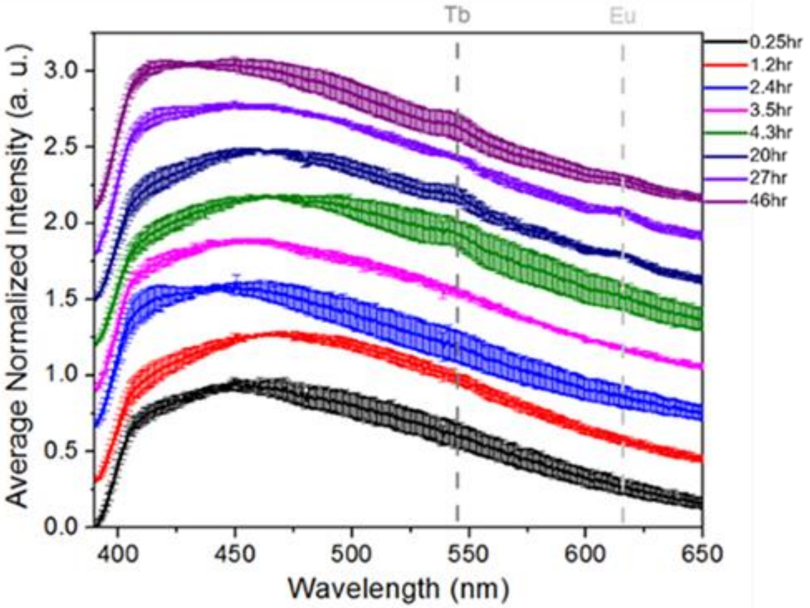
Performance in Simulated Process Stream



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

Ability to detect trace (low ppm) concentrations of REEs even in complex environments such as acid mine drainage, simulated leachate streams, and in the presence of high concentrations of interfering metal ions is an encouraging step towards a commercially viable technology

Importance of Cobalt

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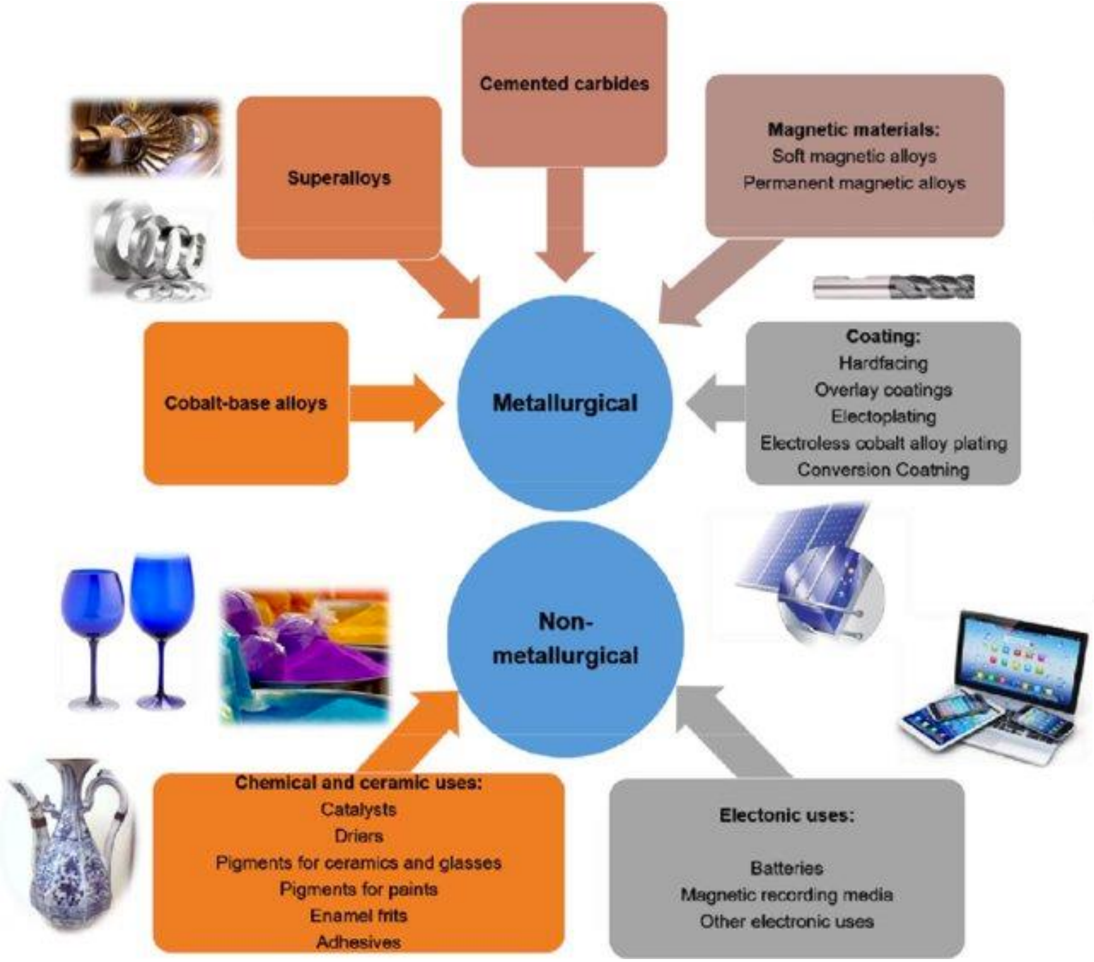
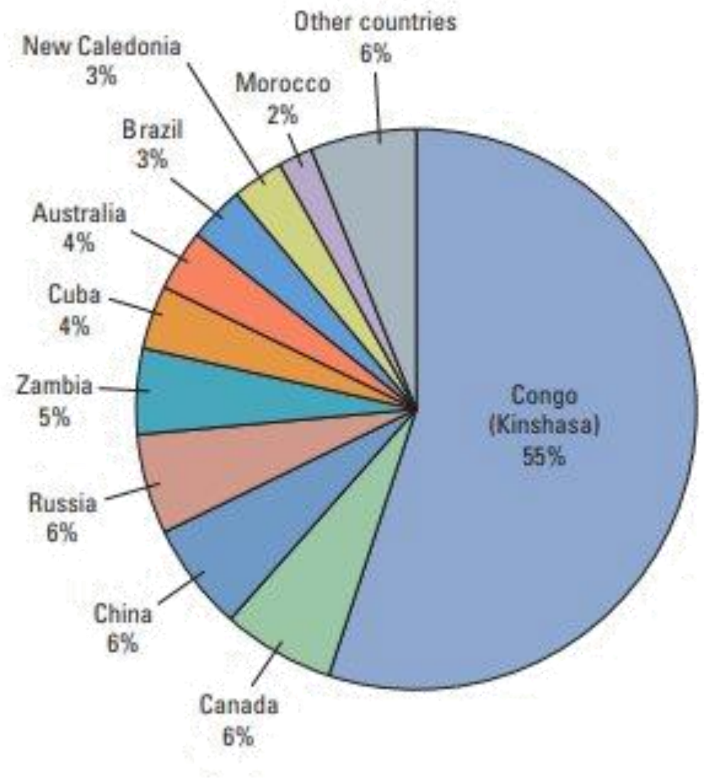


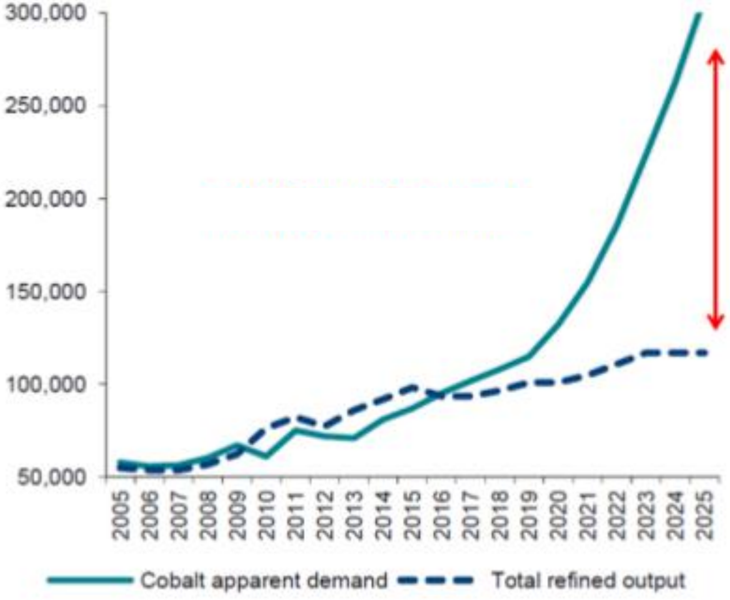
DOI: 10.1080/00986445.2018.1442332

Global Cobalt Supply by Country



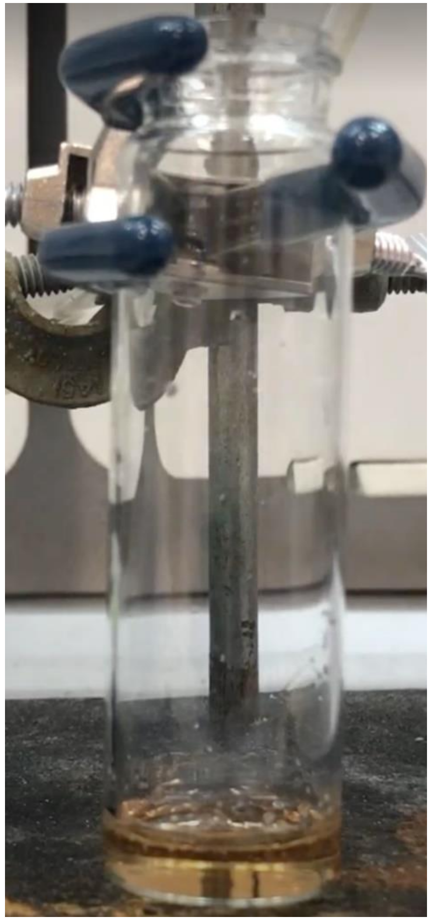
DOI: 10.3133/pp1802F

Supply vs. Demand

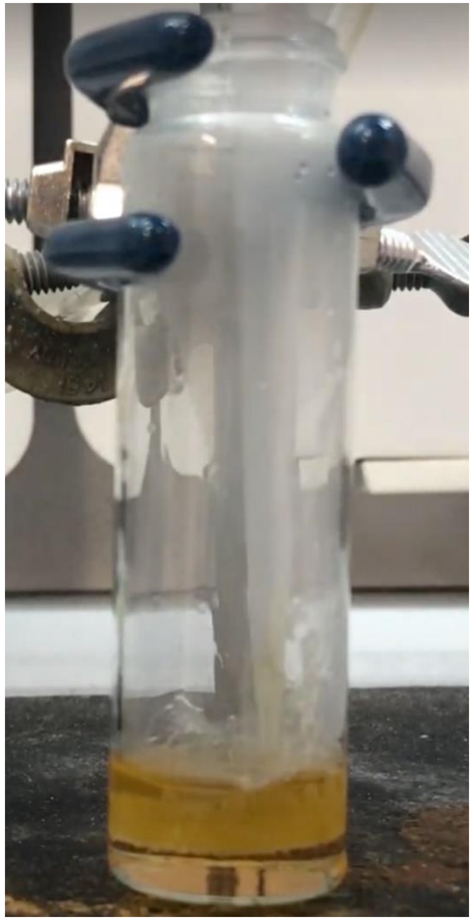


Exane BNP Parisbas

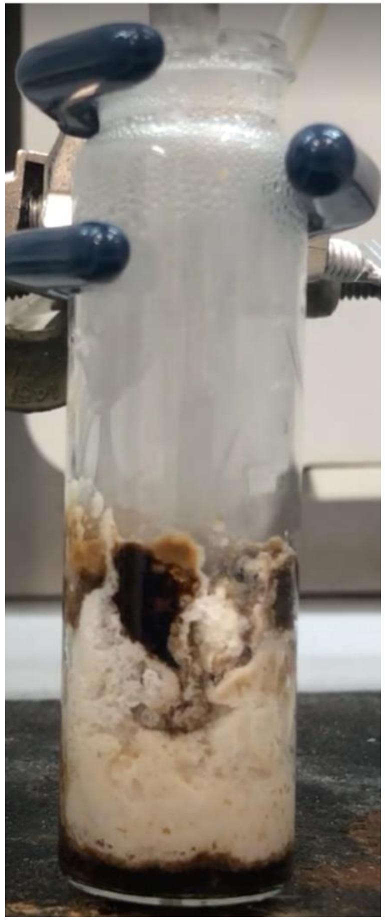
Synthesis of Cobalt-Responsive Carbon Dots



Phosphoric Acid
Sucrose
Urea



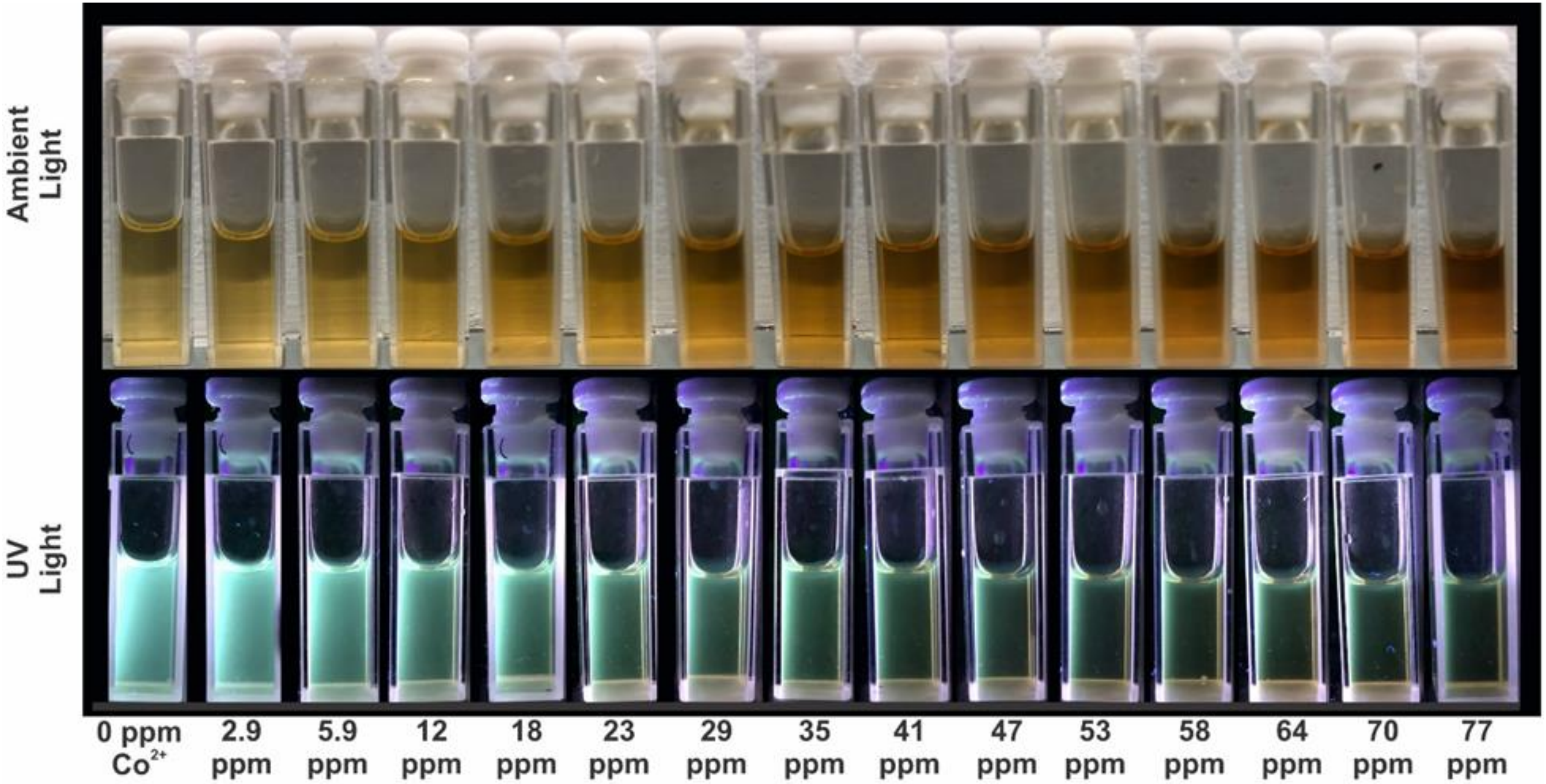
+Ethylenediamine



Localized Heating

Centrifugation, filtration, and dilution (UV Light)

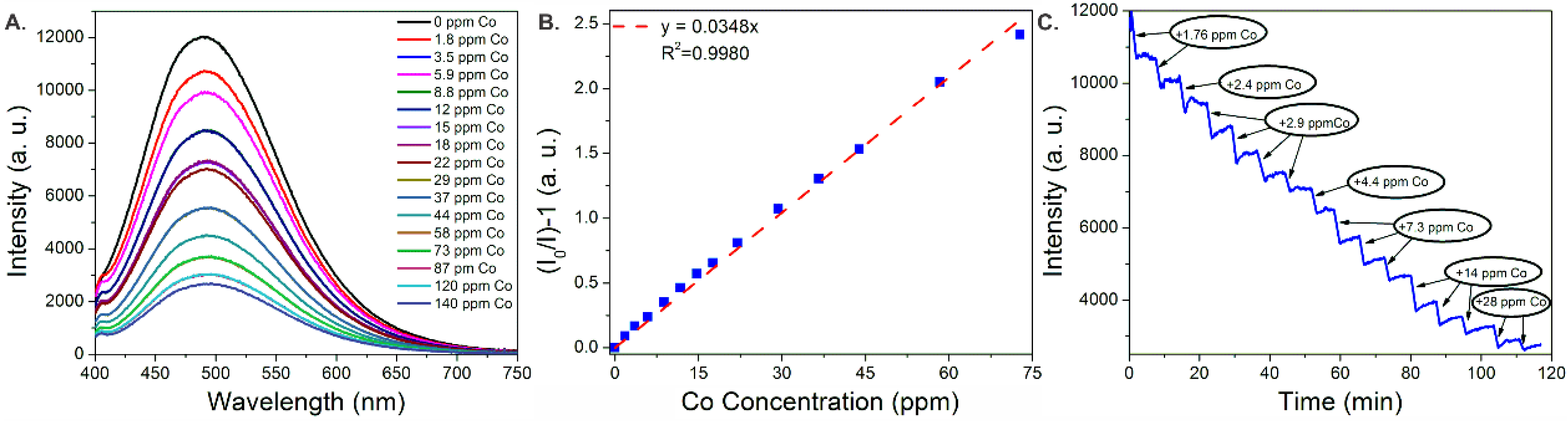
Selective Quenching Response to Cobalt



- Crucial component for <u>EV batteries</u> and <u>fuel cells</u>
- Global production is <u>monopolistic</u>, threatening supply chain stability
- Luminescent sensors can again <u>lower the costs</u> of characterization

Crawford, S.E., Kim, K,J., and Baltrus, J,P., ***J. Mater. Chem. C***, 2022, *10*, 16506-16516

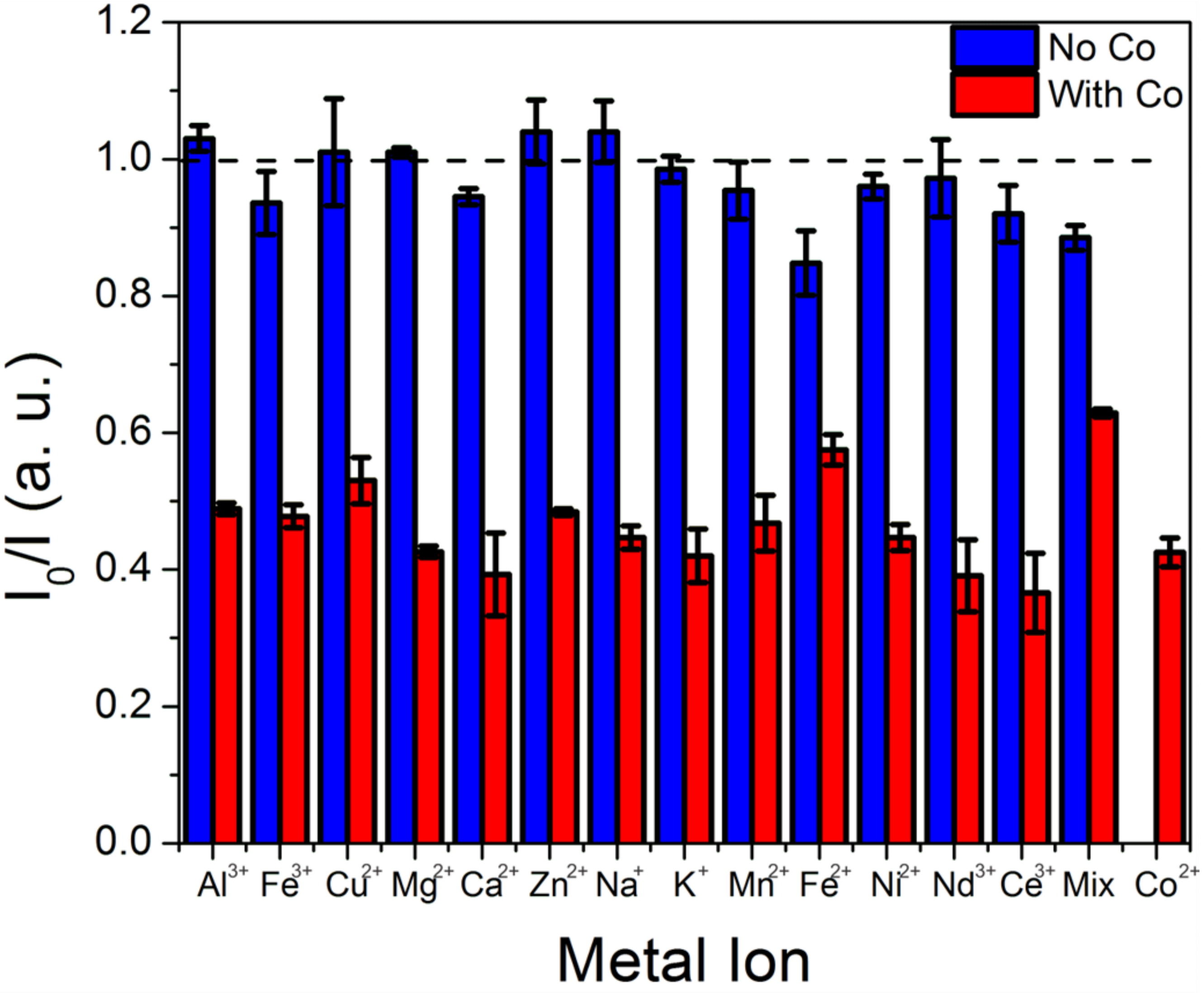
Cobalt Detection on a Portable Sensor



The portable sensor is capable of sub-ppm detection limits in water and low ppm detection limits in acid. The response to cobalt addition is nearly instantaneous

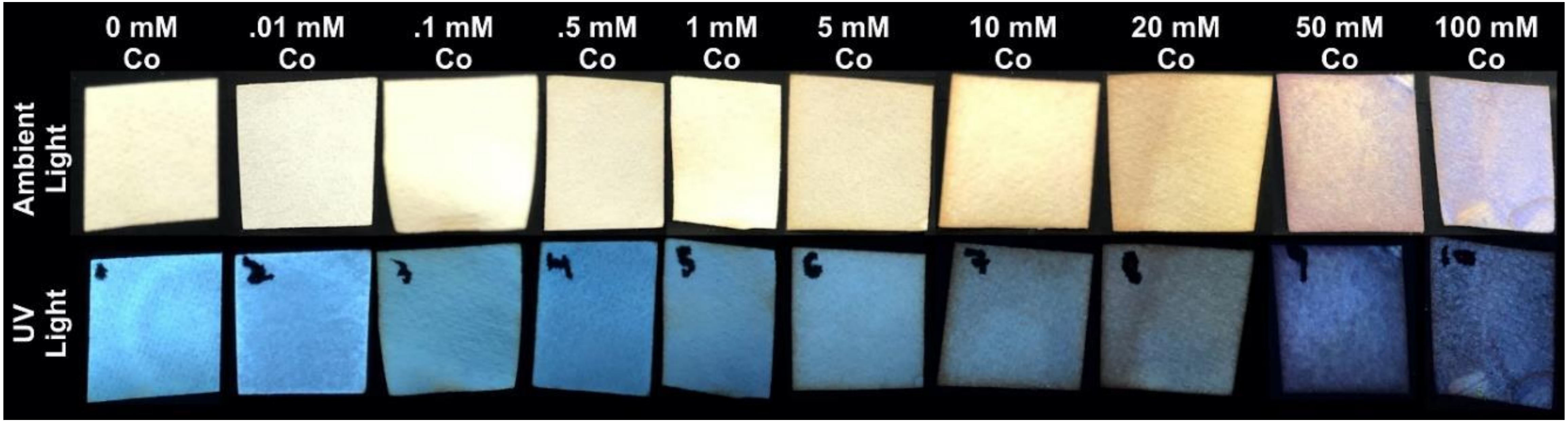
Crawford, S.E., Kim, K.J., and Baltrus, J.P., ***J. Mater. Chem. C***, 2022, *10*, 16506-16516

Cobalt Detection on a Portable Sensor

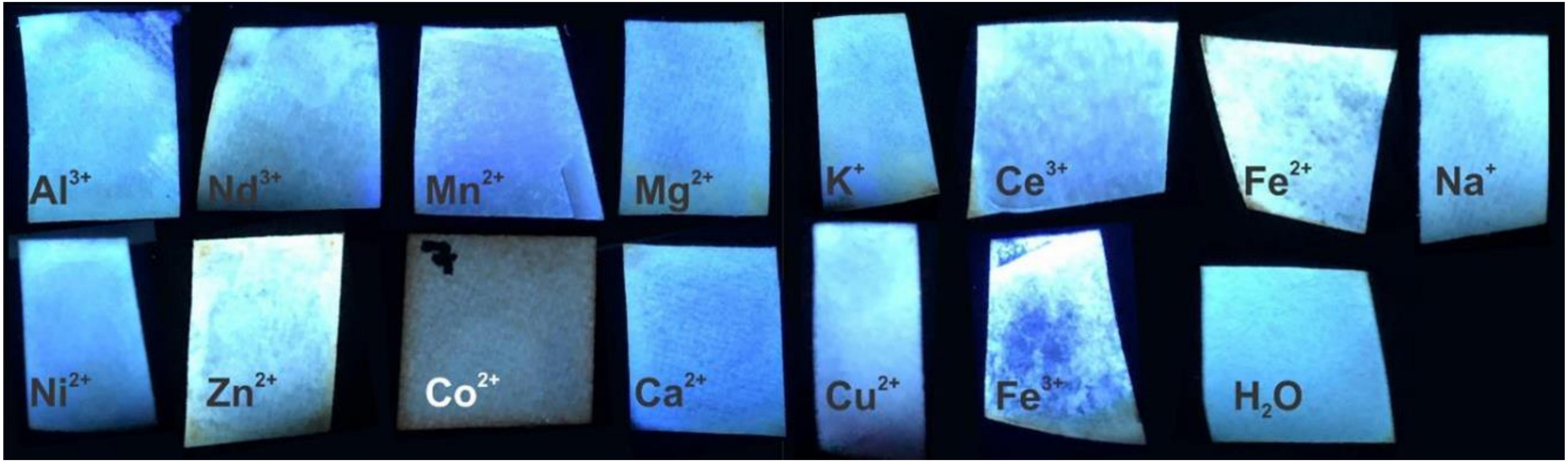


The portable sensor is **selective for cobalt** against 13 different metals commonly encountered in coal and coal utilization byproducts.

Cobalt Test Strips: Sensitivity



Cobalt Test Strips: Selectivity



Challenges and Implications of Fe(III) for REEs

NATIONAL ENERGY TECHNOLOGY LABORATORY

Removal of Iron from Pyrite-Rich Coal Refuse by Calcination and Magnetic Separation for Hydrometallurgical Extraction of Rare Earth Elements

by Tushar Gupta [1], Ahmad Nawab [2] and Rick Honaker [2,*]

[1] MP Materials Mountain Pass Mine, 67750 Bailey Rd, Mountain Pass, CA 92366, USA
[2] Department of Mining Engineering, University of Kentucky, Lexington, KY 40506, USA
[*] Author to whom correspondence should be addressed.

Minerals **2023**, *13*(3), 327; https://doi.org/10.3390/min13030327

ELSEVIER
Chemosphere
Volume 277, August 2021, 130131

The role of iron in the rare earth elements and uranium scavenging by Fe–Al-precipitates in acid mine drainage

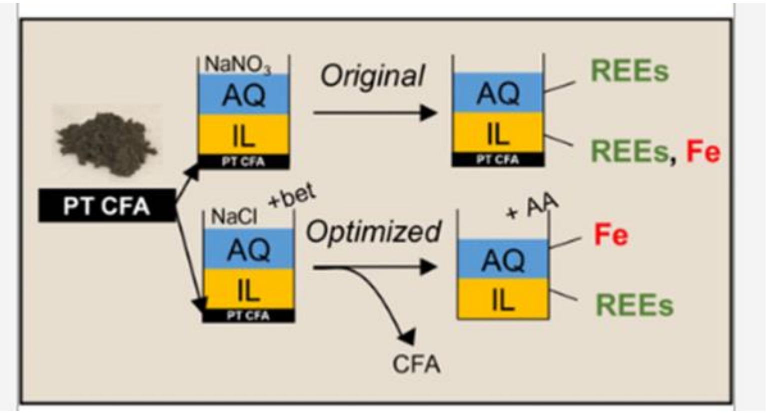
Mateus Lanna Borges de Moraes [a b], Ana Claudia Queiroz Ladeira [a]

https://doi.org/10.1016/j.chemosphere.2021.130131

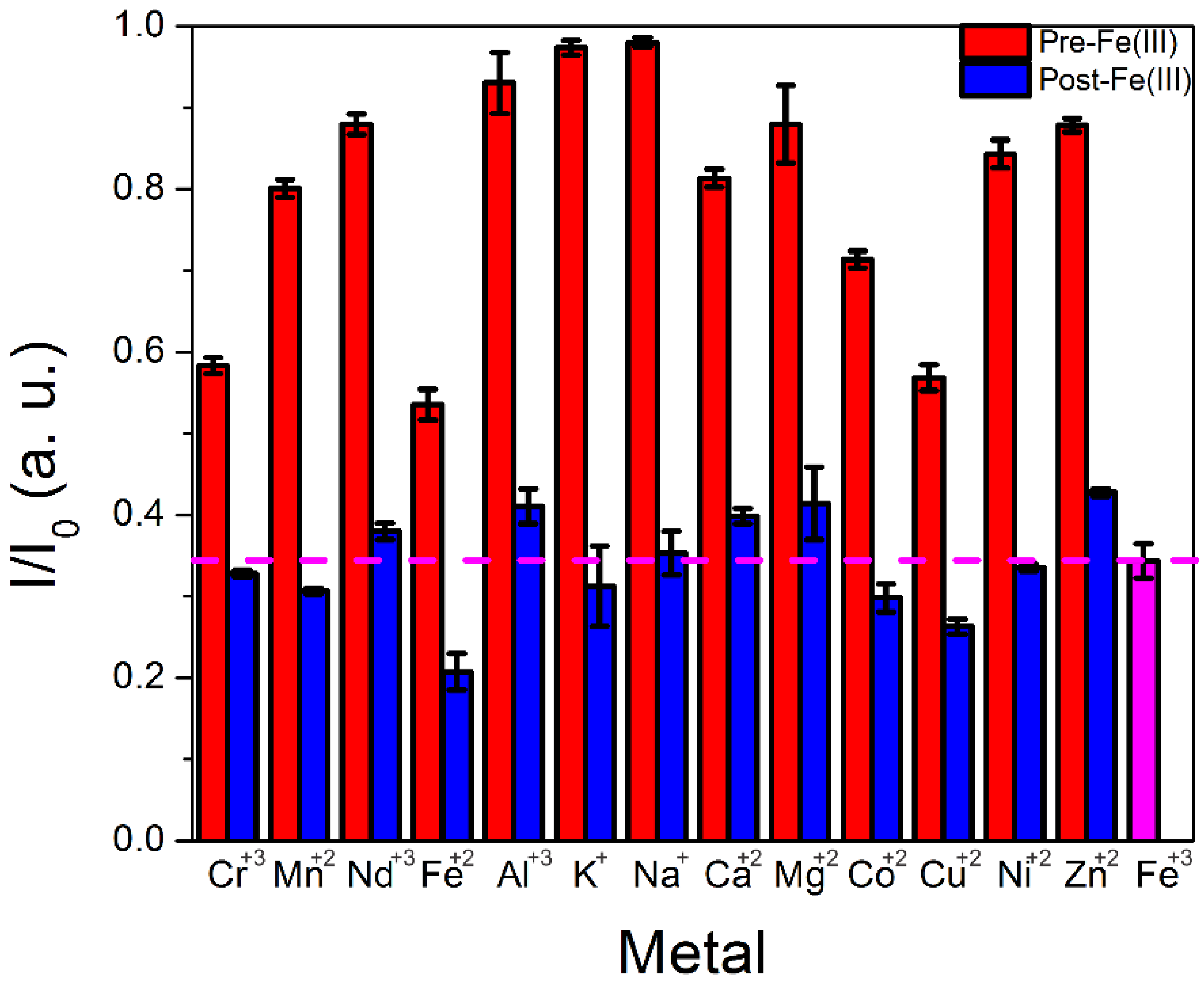
Optimization of Iron Removal in the Recovery of Rare-Earth Elements from Coal Fly Ash Using a Recyclable Ionic Liquid

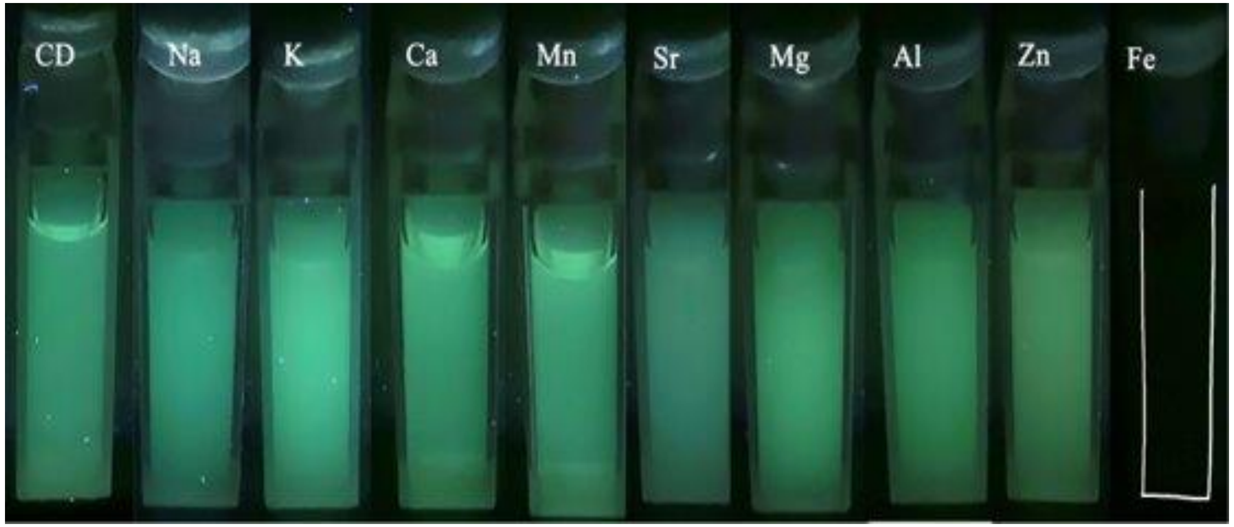
Laura Stoy, Yamini Kulkarni, and Ching-Hua Huang*

Cite this: *Environ. Sci. Technol.* 2022, 56, 8, 5150–5160
Publication Date: April 5, 2022
https://doi.org/10.1021/acs.est.1c08552

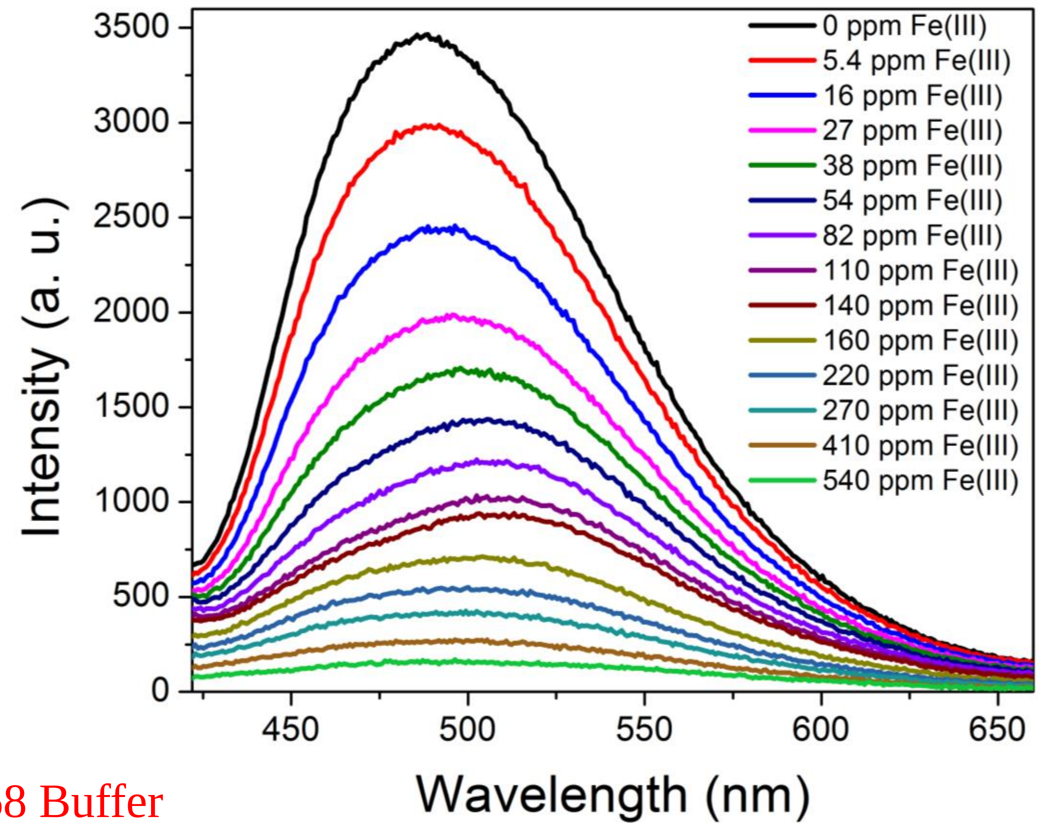


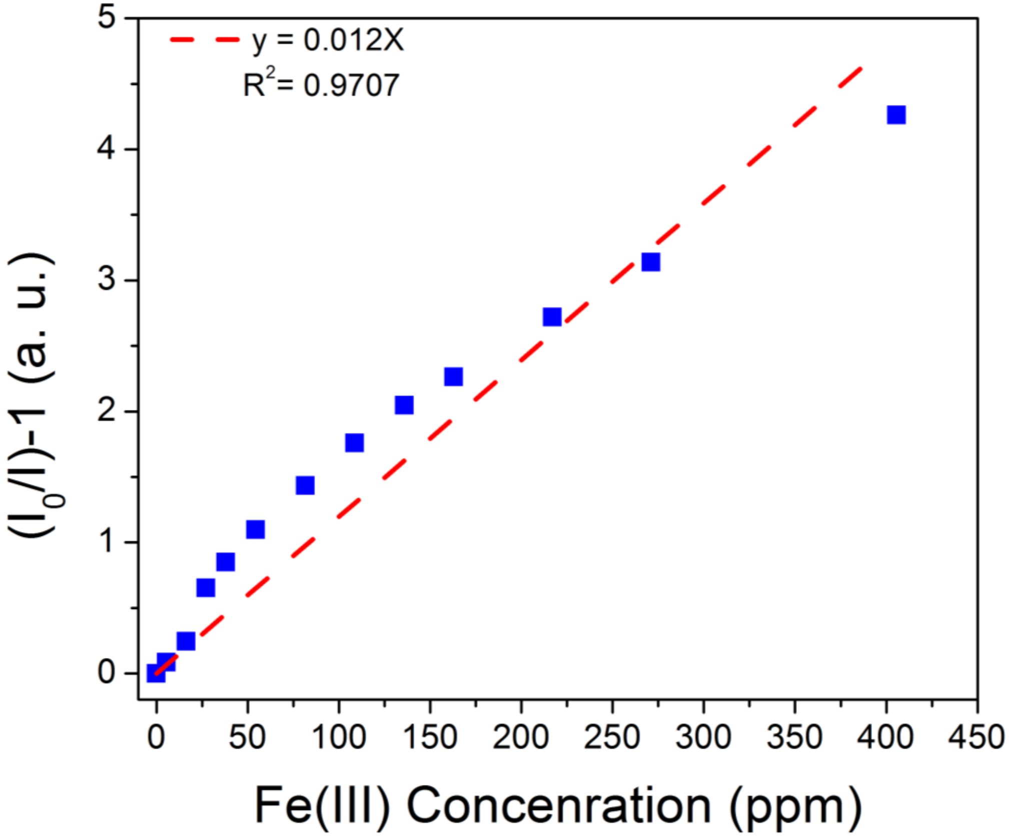
Carbon Dot Sensor for Fe(III) Detection





Sensitive Detection in Low-pH Streams





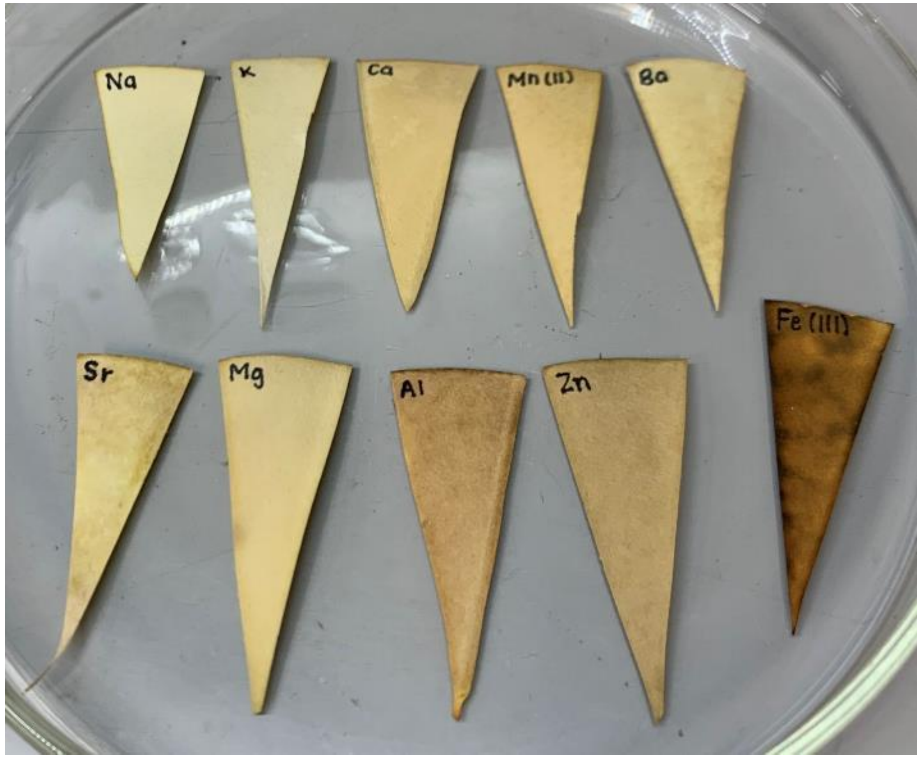
pH ~1.68 Buffer

Limit of Detection ~ 2.83 ± 0.06 ppm

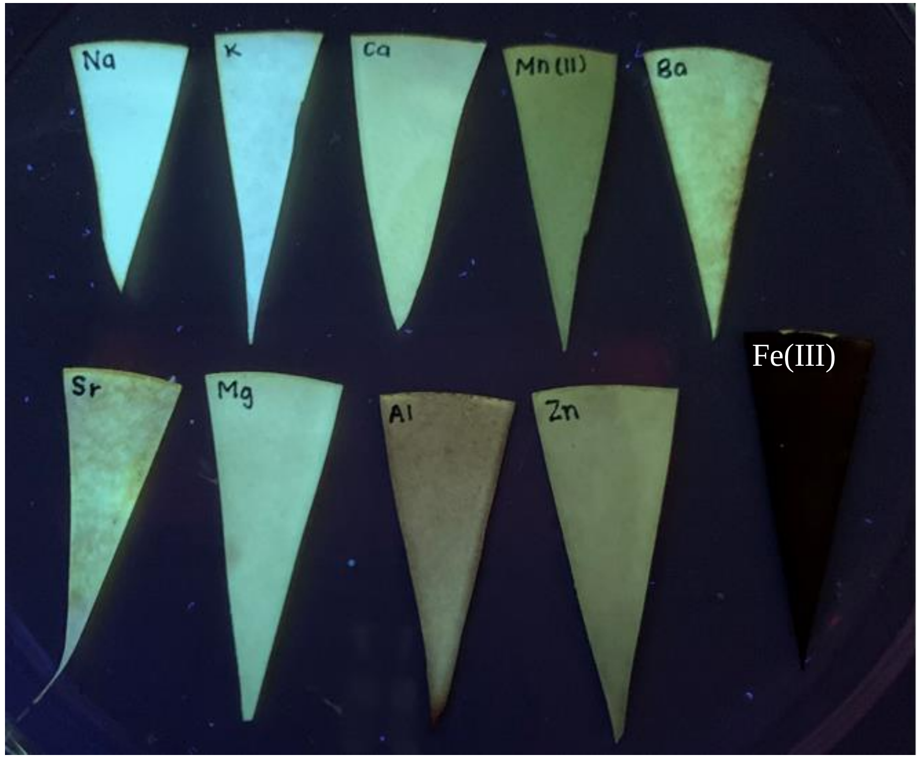
Limit of Quantification ~ 9.4 ± 0.2 ppm

Optimal laboratory conditions to replicate low pH environment where these metal ions are commonly found

Paper Test Strips: Selectivity



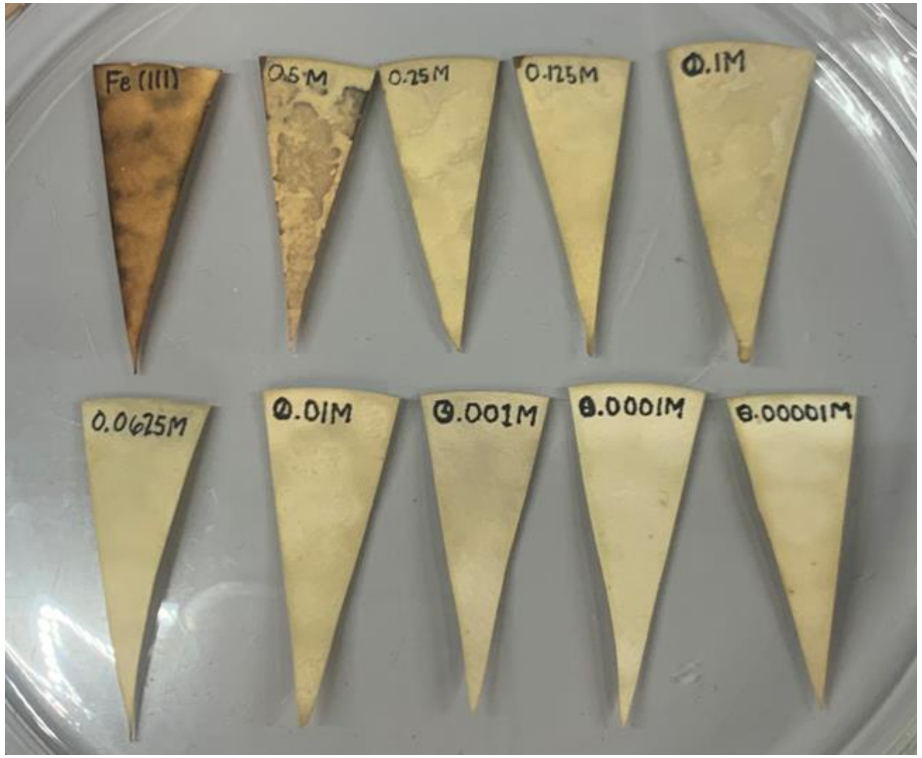
Ambient Light



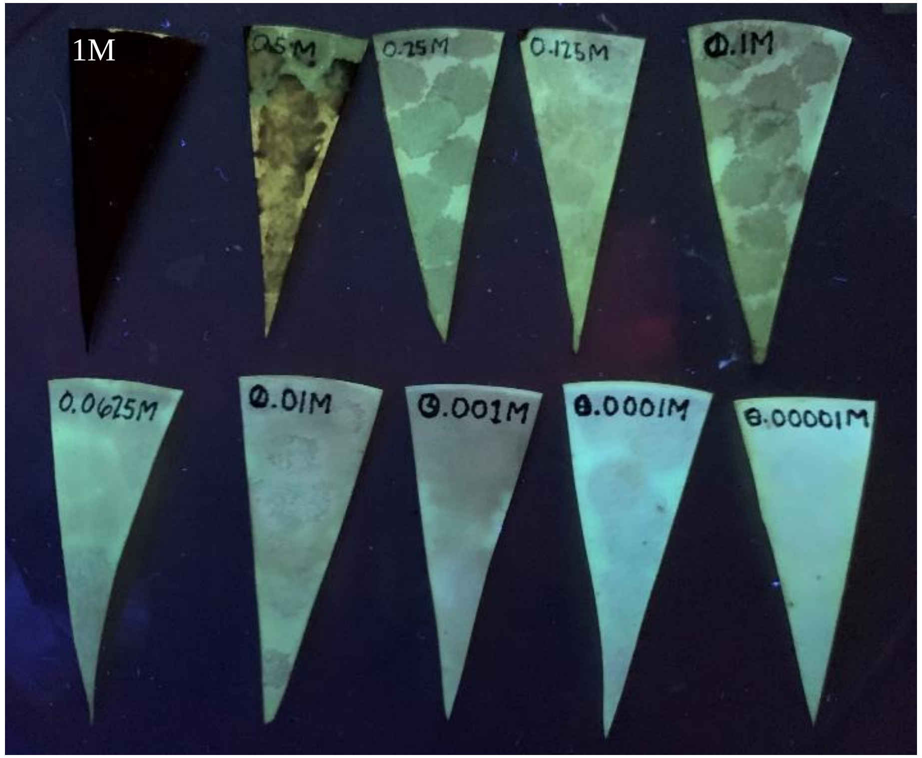
UV Light - 365 nm

Selective for Fe(III) against other metals frequently encountered in process streams (1 M samples)

Paper Test Strips: Sensitivity



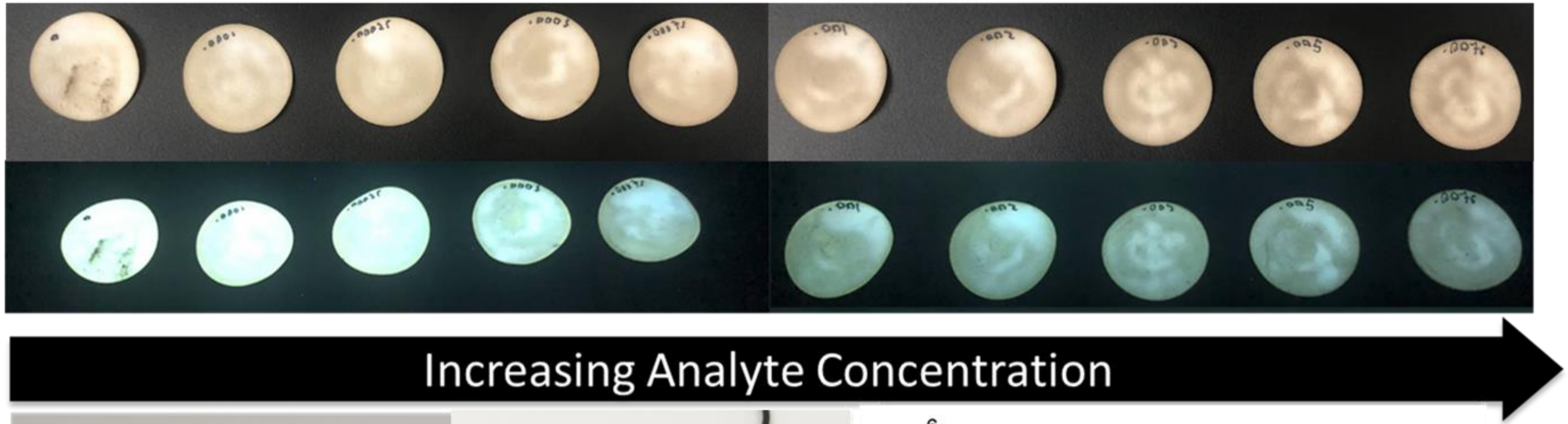
Ambient Light

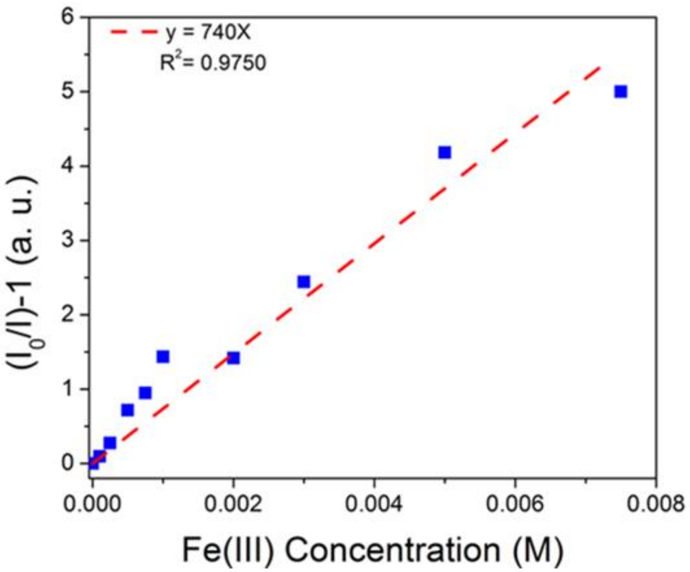


UV Light - 365 nm

Quenching correlates with Fe(III) Concentration

Technology for Test Strip Analysis





Research From 2023 Summer Student

Ariana Adkisson

Concluding Thoughts

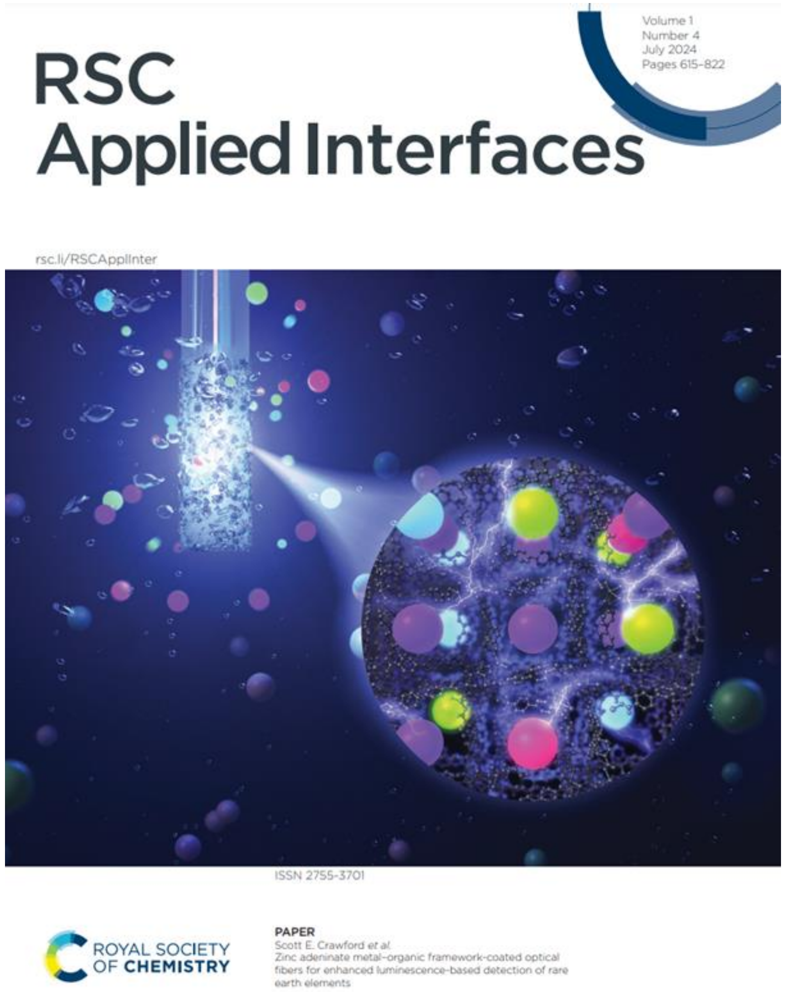
NATIONAL ENERGY TECHNOLOGY LABORATORY

- Luminescent techniques can offer significant time and financial savings relative to other analytical methods for metals characterization

- Low part-per-million (or better) detection limits of high value metals are achievable using a low-cost, home built portable luminescent spectrometer

- Requires innovations in both the sensing platform and materials

- MLEF program has been a major contributor to this project!



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