Luminescence-Based Sensing of Rare Earth Elements Using Zinc Adeninate Metal-Organic Frameworks

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Critical Mineral Resources from Coal

- Projected **increase in demand** for REEs driven by wind power, electric vehicles, and advanced electronics
- Global REE trade is **monopolistic** with ~85-95% of trade controlled through China
- Domestic mining requires **environmentally harsh chemicals and practices** making it impractical
- Coal is naturally REE-rich, and its **utilization byproducts are further enriched**.

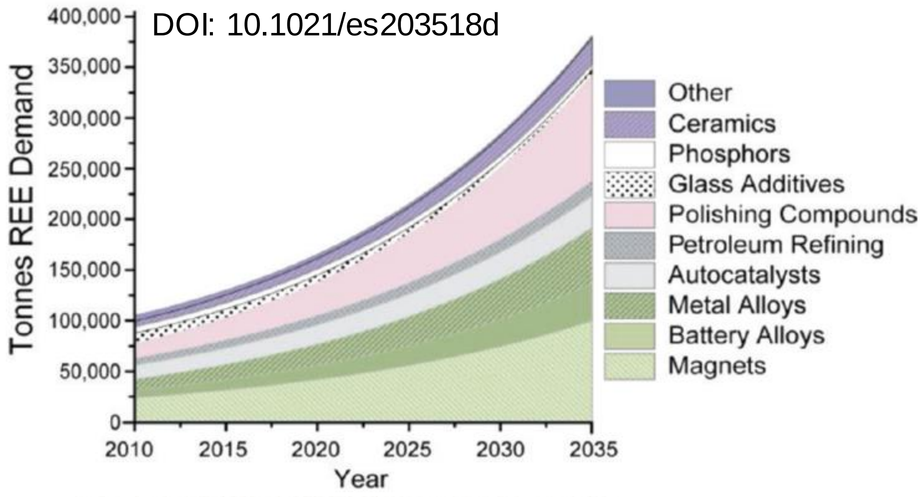
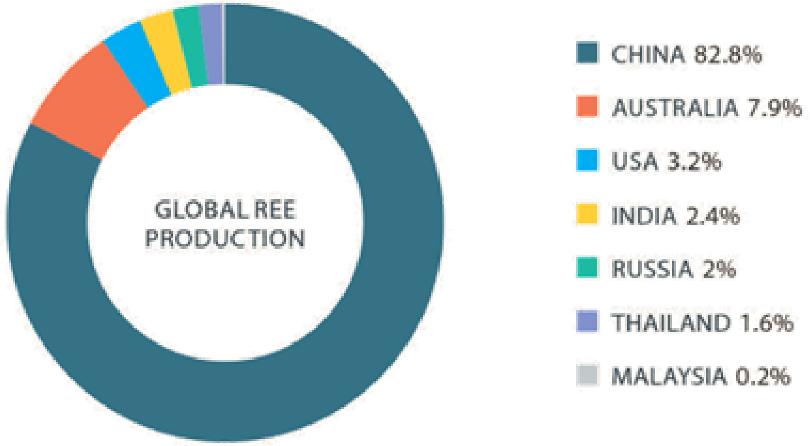


Figure 2. Global REE production 2015 (USGS, 2016).



http://minerals.usgs.gov/minerals/pubs/mcs/2015/mcs2015.pdf

REE Content in Coal Resources

~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

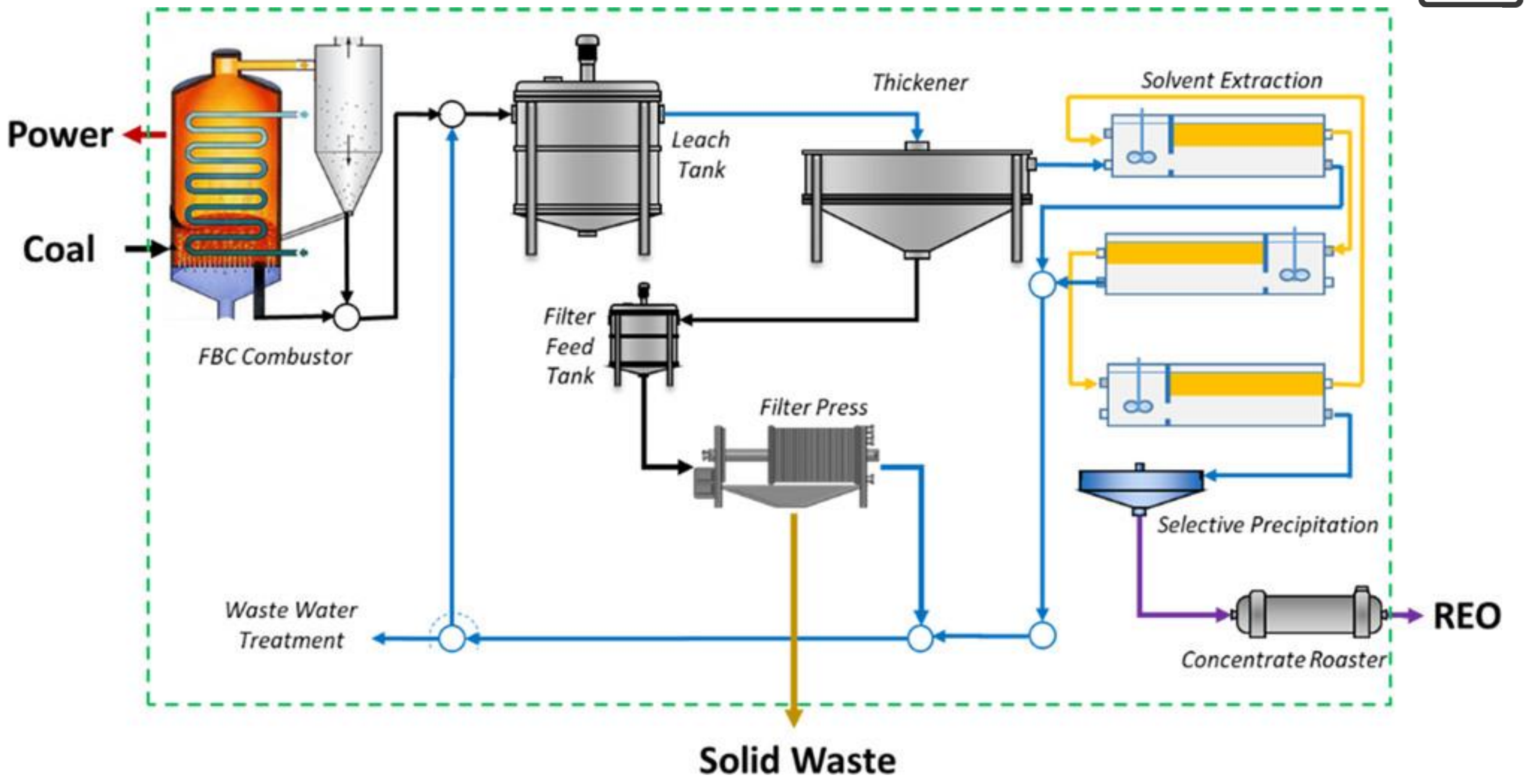
Coal Rock Refuse
(~250 ppm REE)

DOI: 10.1016/j.coal.2011.05.006

Coal Fly Ash
(~450 ppm REE)

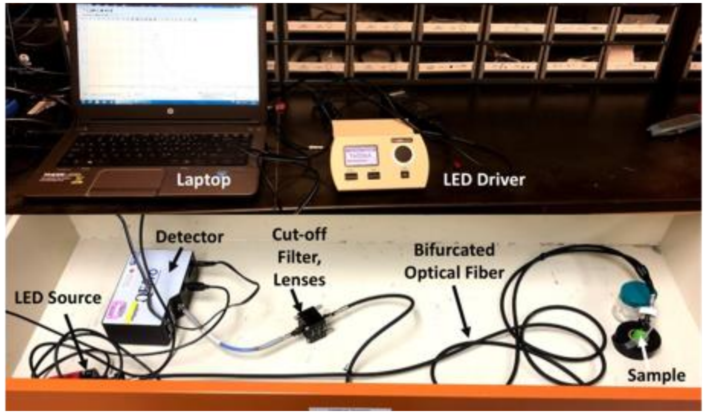
DOI: 10.1007/s11356-015-4111-9

Multiple Processing Steps Required



DOI: 10.1021/acs.energyfuels.9b00295

Rapid Characterization Methods Needed

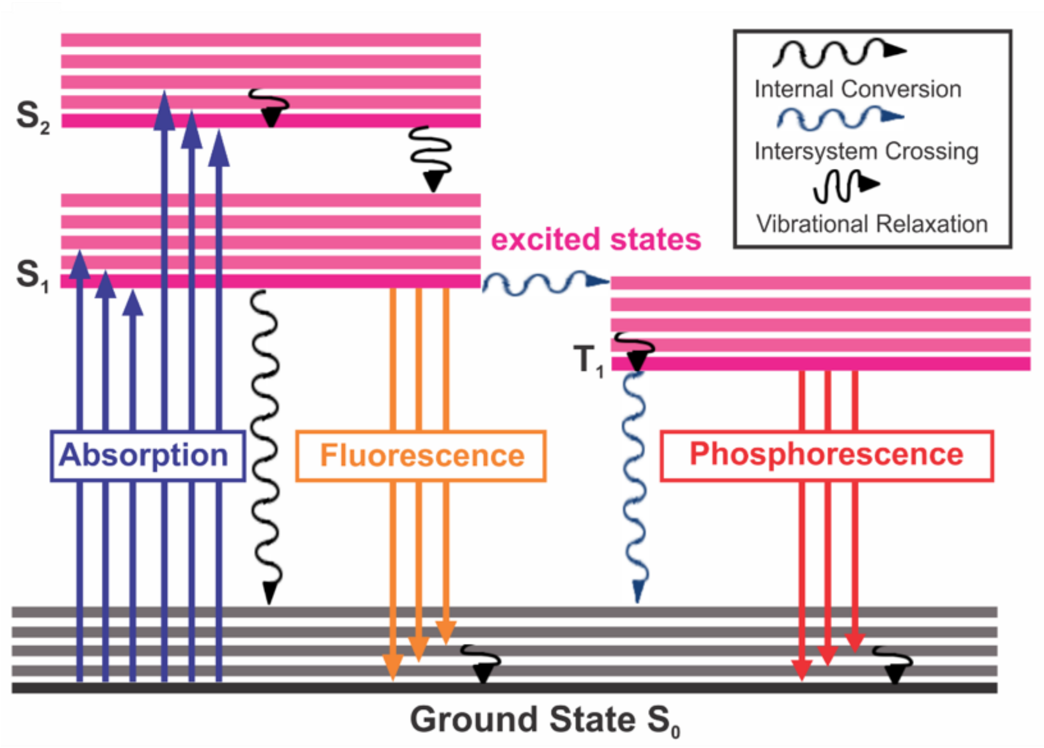


Technique	Instrument Cost	Detection Limit	Portable?
Inductively-Coupled Plasma Mass-Spectrometry	~\$180k	Part-per-trillion	No
X-Ray Fluorescence Spectroscopy	~\$13-17k	10s of part-per-million	Yes
Laser-Induced Breakdown Spectroscopy	~\$30-50k	10s of part-per-million	Yes
Luminescence Spectroscopy	~\$18-35k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

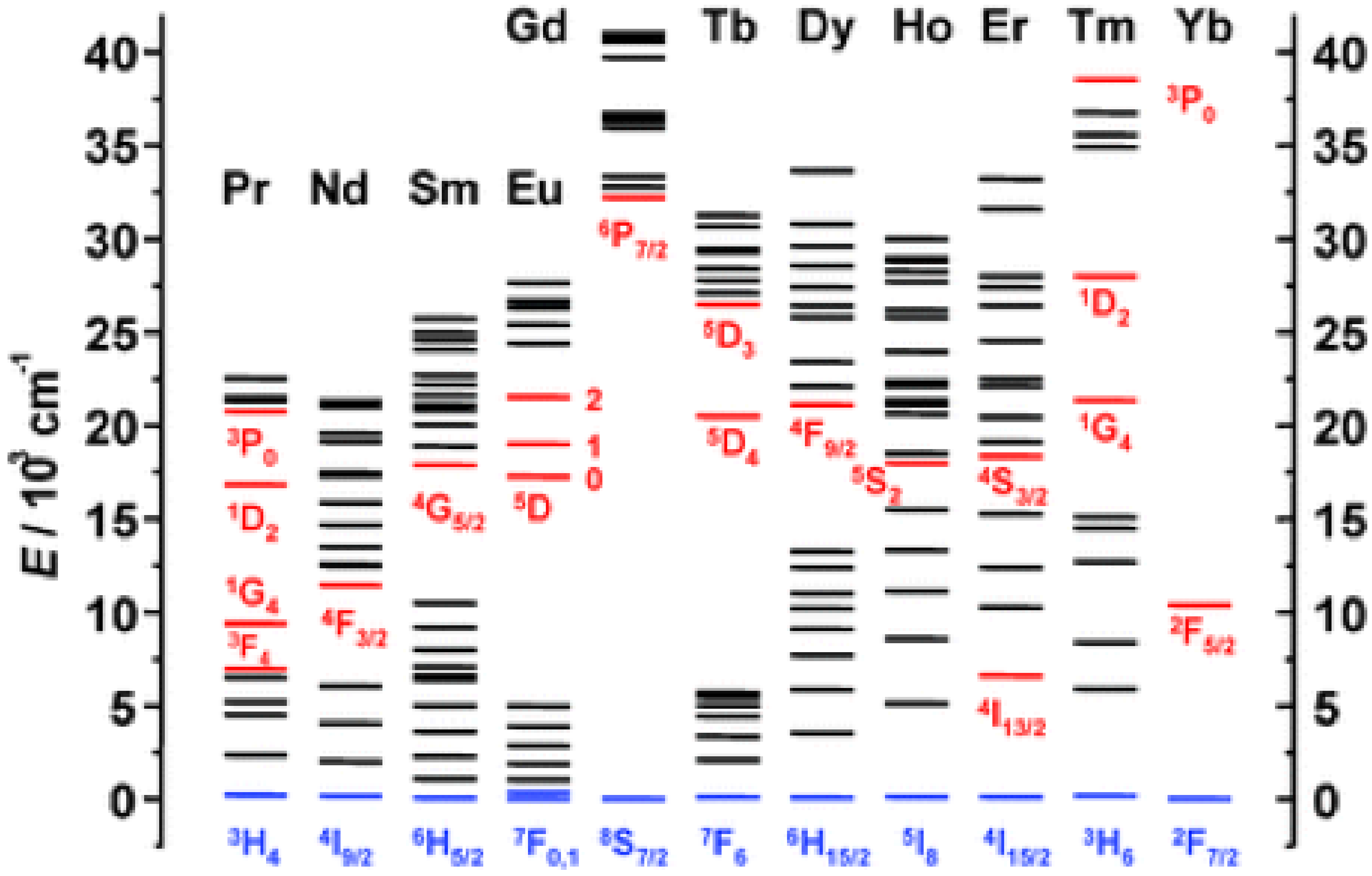
Goal: Develop Luminescent REE Sensor

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



DOI: 10.1039/c3cs60232j

Certain REEs Are Inherently Emissive!

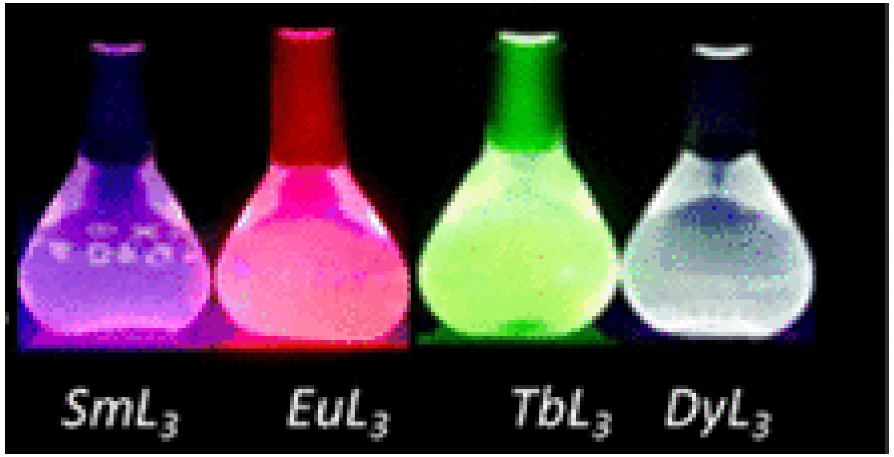


F-orbital transitions in REEs give rise to element-distinct, narrow emission bands, providing an additional sensing mechanism!

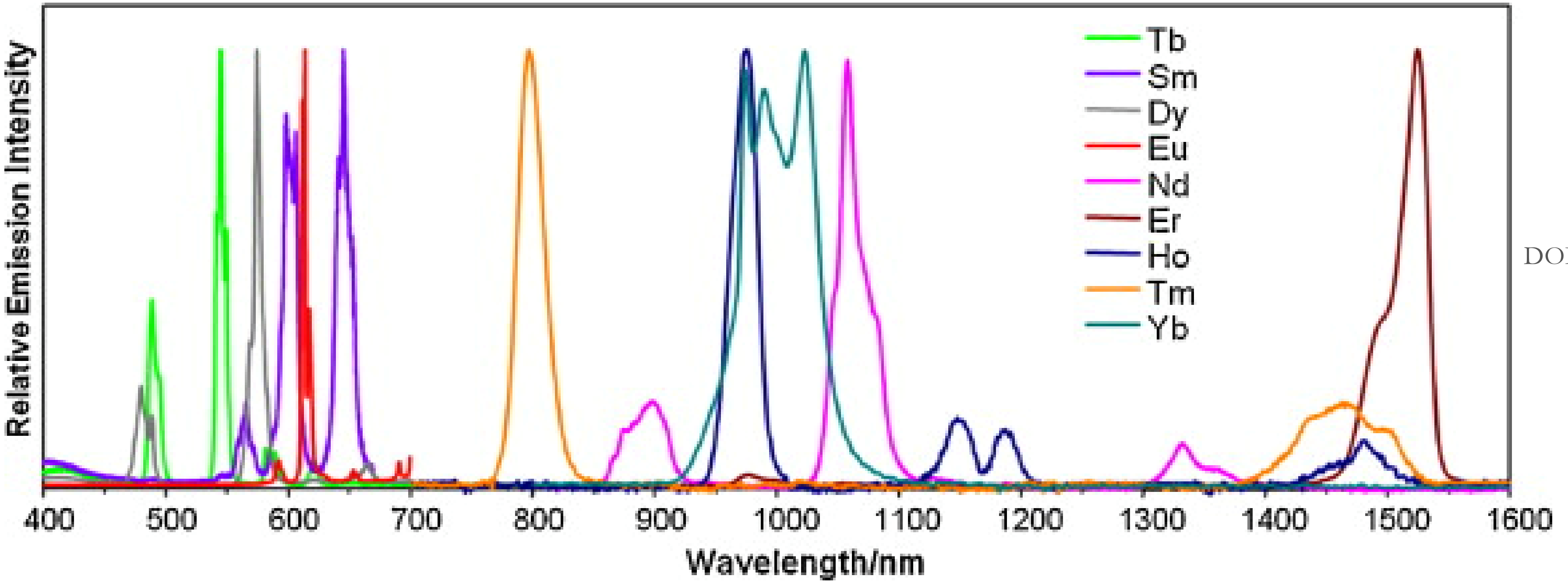
DOI: 10.1039/B406082M

Intense REE-Centered Emission

Raymond Lab, Cal Berkley

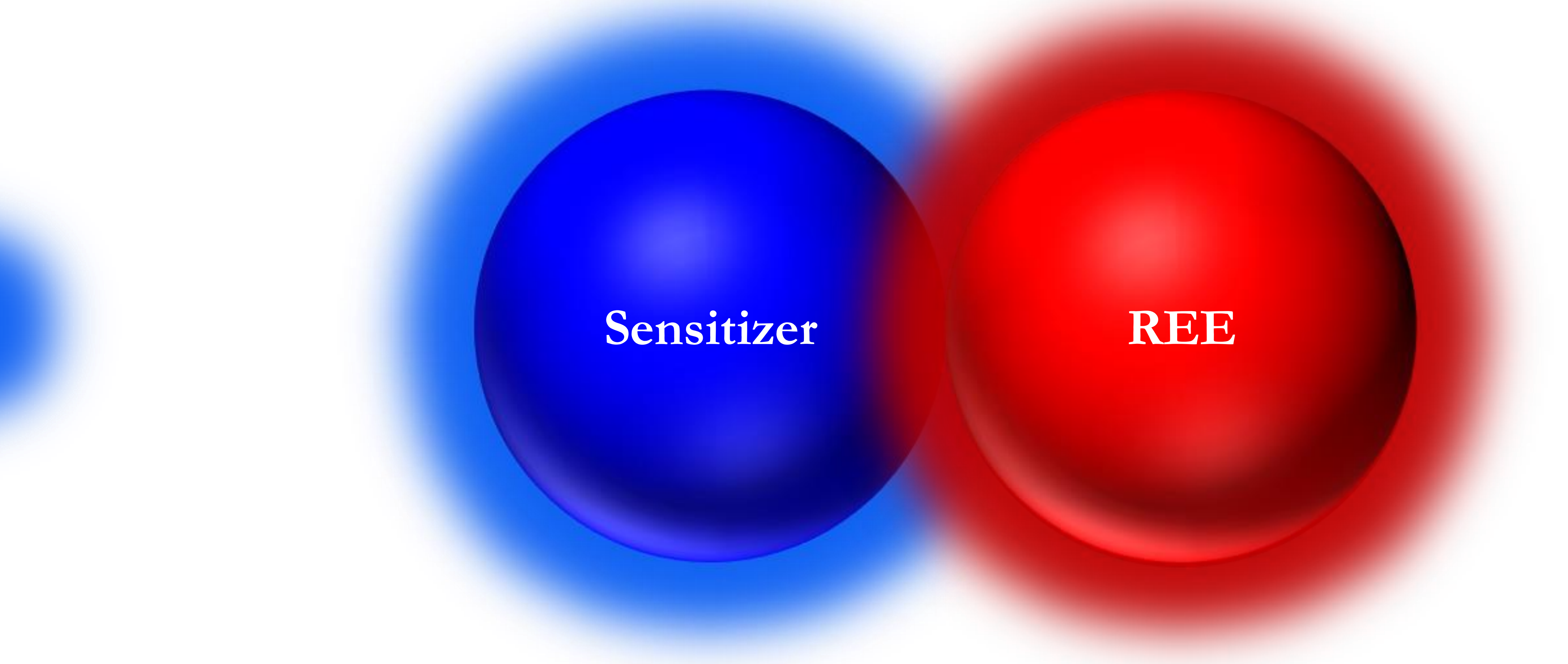


DOI: 10.1021/acs.inorgchem.7b02861

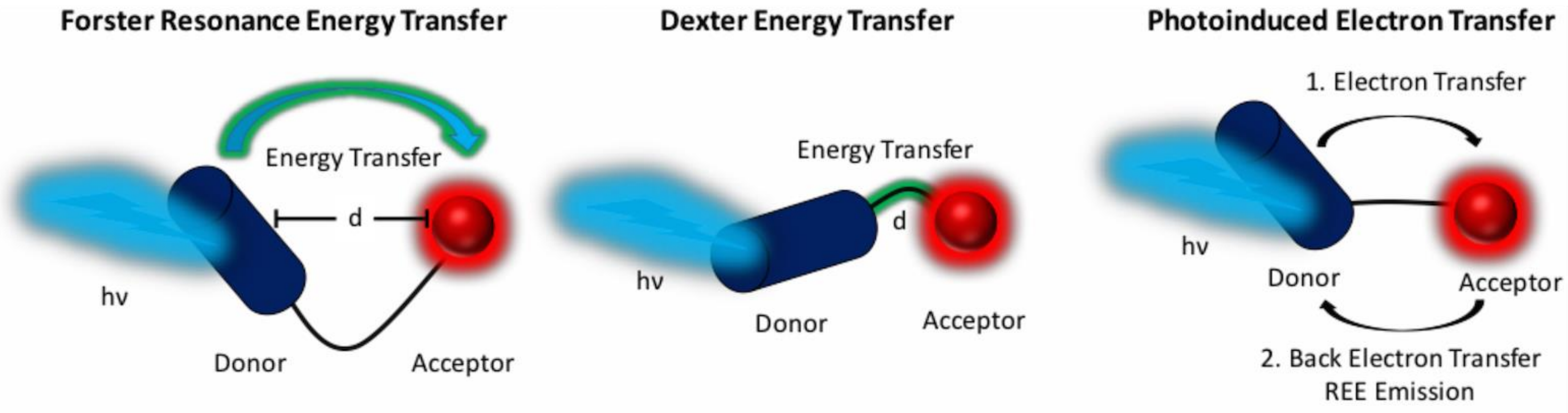


DOI: 10.1016/j.crci.2010.05.007

A Sensitizer Material is Required



Sensitization Mechanisms



- **Through Space; Dipole-Dipole Coupling**
- **Efficiency Decays with distance as d^{-6}**
- **Spectral Overlap Required**

- **Through bond; double electron exchange**
- **Efficiency Decays with distance as e^{-2d}**
- **Spectral Overlap Required**

- **2 distinct electron transfer steps**
- **Observed in Eu(III) and Yb(III)**
- **No Spectral Overlap Required**

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

J. Mater. Chem. C. Review on REE Sensing

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Journal of
Materials Chemistry C

ROYAL SOCIETY OF CHEMISTRY

REVIEW

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View Journal

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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

Rare earth elements (REEs) are widely used in high-performance technologies including wind turbine magnets, electric vehicle batteries, lighting displays, circuitry, and national defense systems. A combination of projected increasing demand for REEs, monopolistic economic conditions, and environmental hazards associated with the mining and separation of REEs has led to significant interest in recovering REEs from alternative sources such as coal waste streams. However, rapidly locating high-value waste streams in the field remains a significant challenge primarily because of slow analytical methods, and existing techniques with low limits of detection such as inductively-coupled plasma mass spectrometry suffer from high equipment and operating costs and a lack of portability. Alternatively, luminescence-based sensors for REEs present a potential path for sensitive, portable, low-cost detection. The development and design of materials suitable for the luminescence-based detection of REEs are crucial to realizing this potential. Here, we review a broad range of materials used (or that have the potential to be used) for REE luminescence-based detection, including organic compounds, biomolecules, polymers, metal complexes, nanoparticles, and metal–organic frameworks. A general overview of REE optoelectronic properties and luminescent sensing protocols is first presented, followed by analyses of material-specific sensing mechanisms, emphasizing sensing figures of merit including sensitivity, selectivity, reusability and portability. The review concludes with a discussion of remaining barriers to luminescent REE sensing, how each sensor class may be best deployed, and directions for future material and spectrometer design. Taken together, this review provides a broad overview of sensing materials and methods that should be foundational for the continued development of high-performance sensors.

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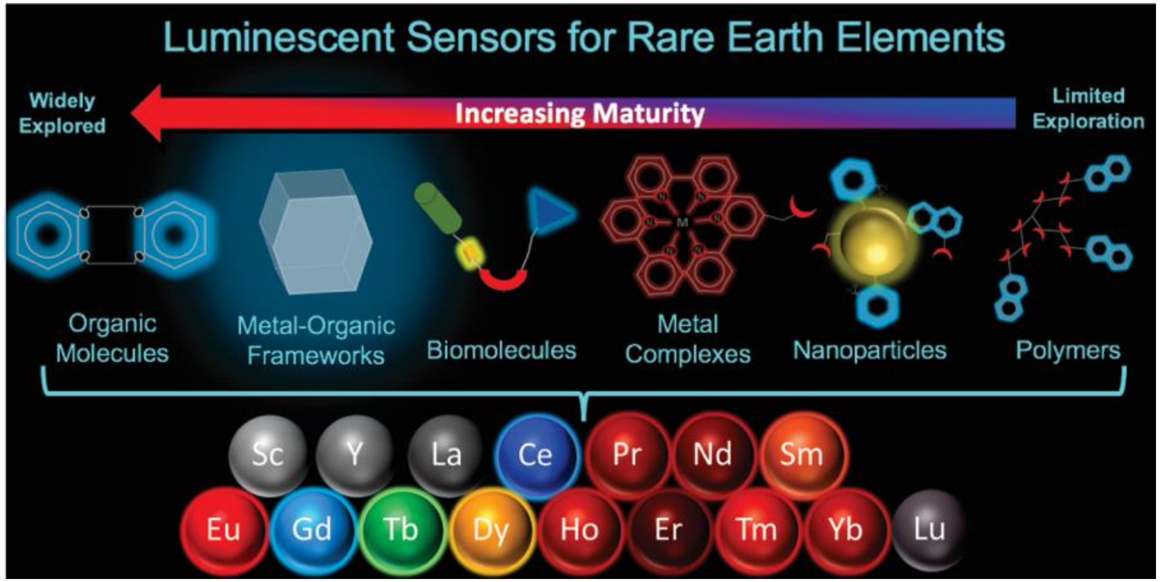
DOI: 10.1039/d0tc01939a

rsc.li/materials-c



Opportunity for Material Science Solution

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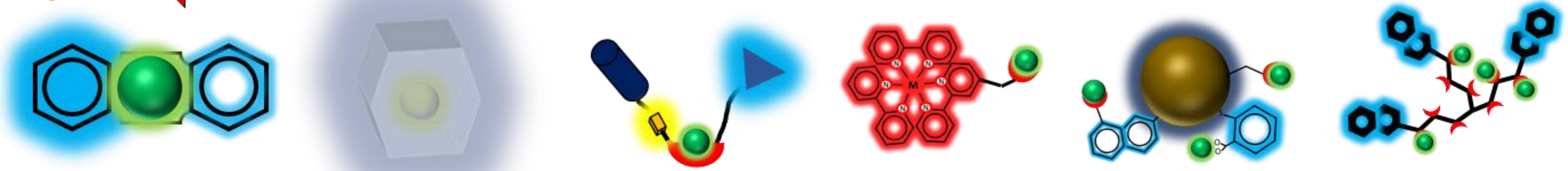
Widely Explored ← Increasing Maturity — **Limited Exploration**



	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?	√	√	?	?	√	√

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

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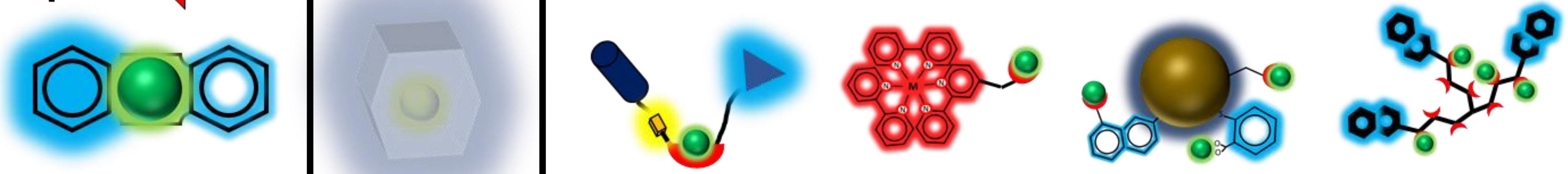
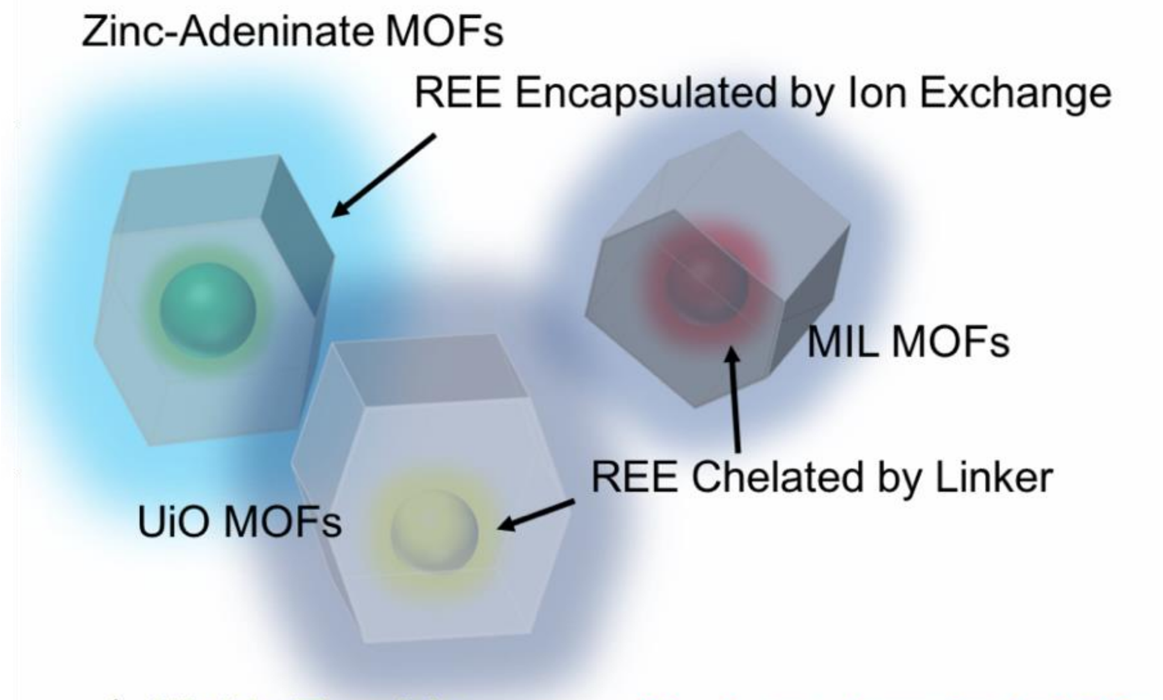


	Organic Compounds	MOFs	Biomolecules	Metal Complexes	Nanoparticles	Polymers
Sensitive?	√	√	√	√	?	?
Selective?	√	X	√	X	?	?
Water Compatible?	X	√	√	X	X	X
Easy to Synthesize?	X	√	X	X	√	X
Incorporated into Portable Sensors?	√	√	?	?	√	√

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

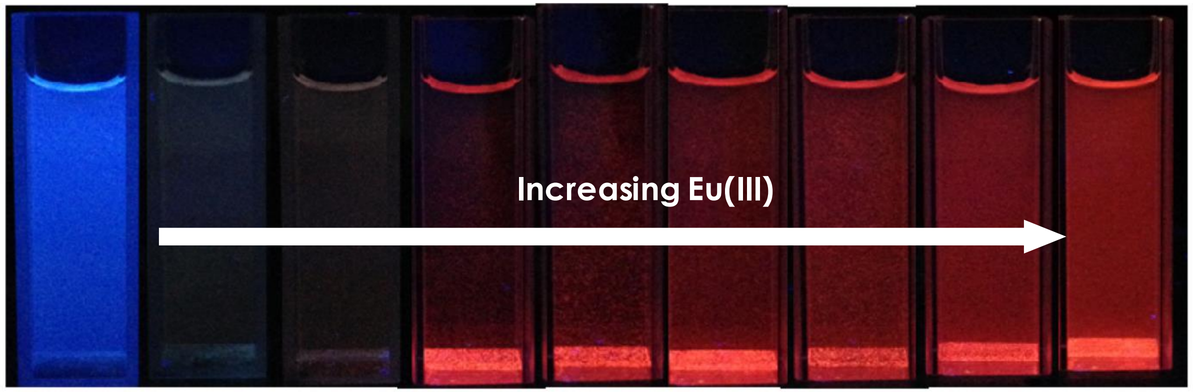
MOFs as REE Sensors

Metal-Organic Framework REE Sensors

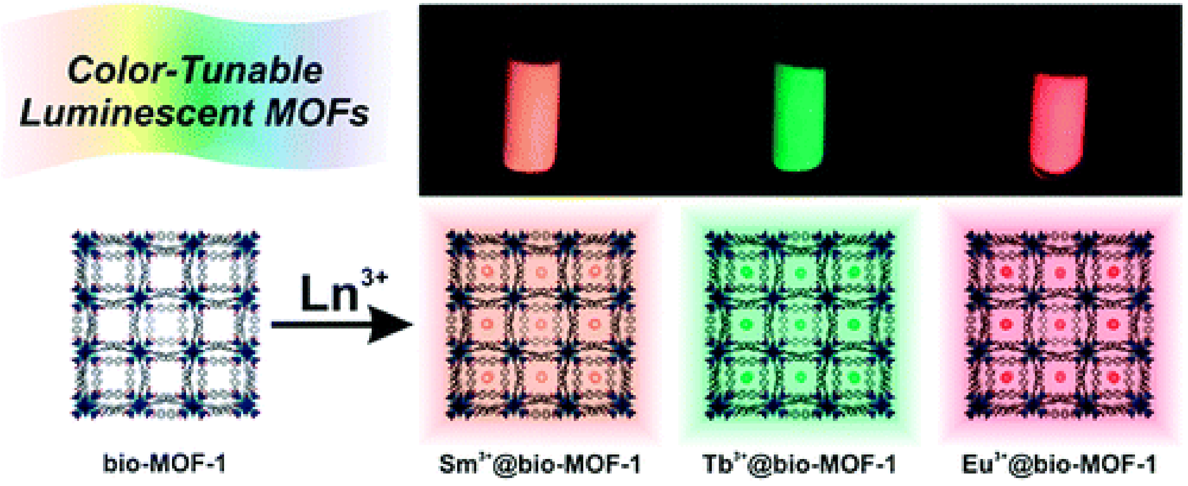


- ✓ Highly Tunable
- ✓ Easy Synthesis
- ✓ Facile Sensor Integration
- ✓ Dispersible in Water & Organics

X Long term instability

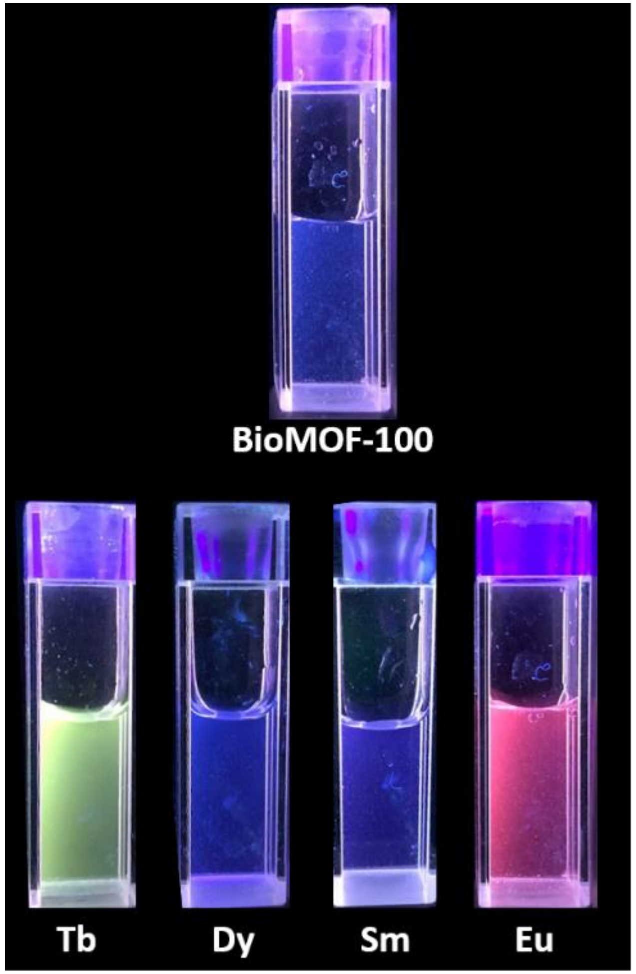


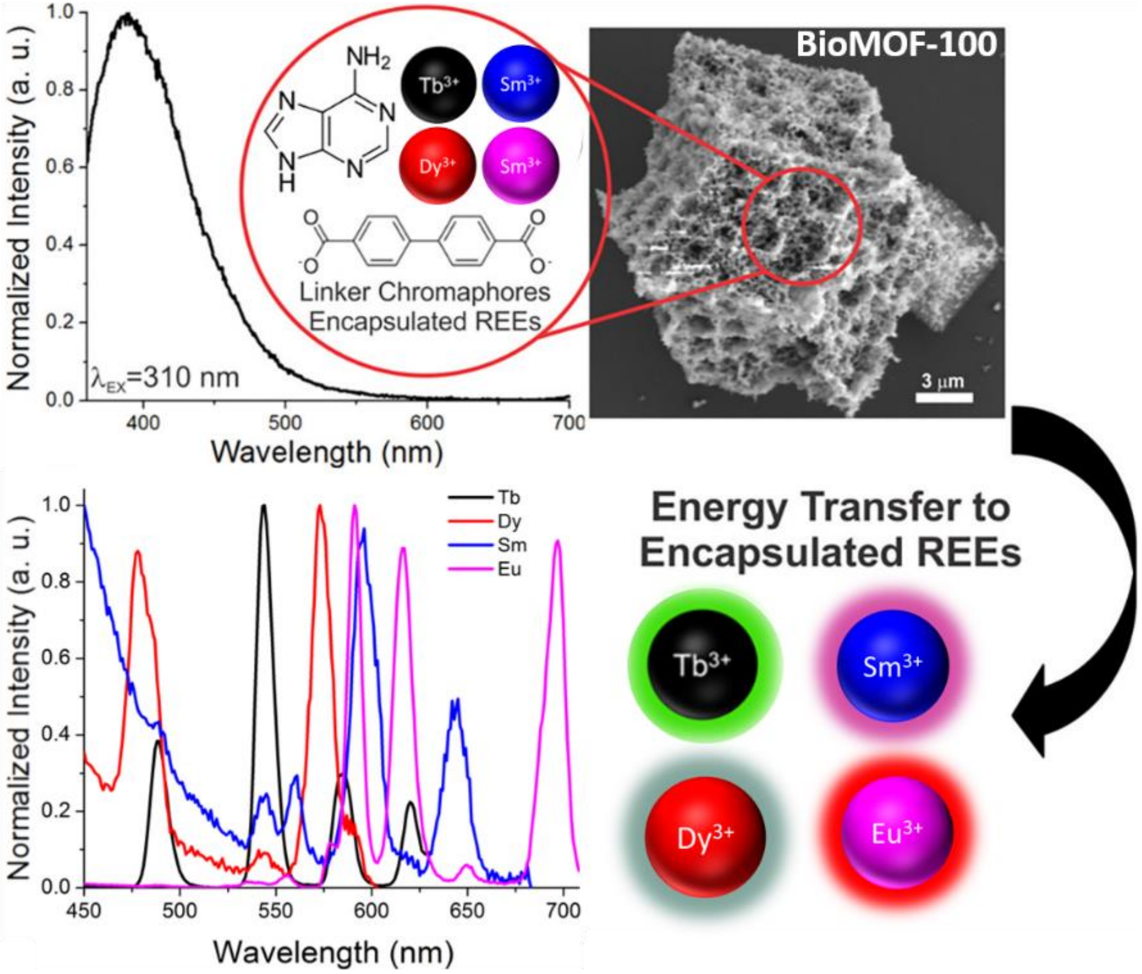
DOI: 10.1021/acs.cgd.7b00219



DOI: 10.1021/ja109103t

Initial Effort: BioMOF-100, an Anionic MOF

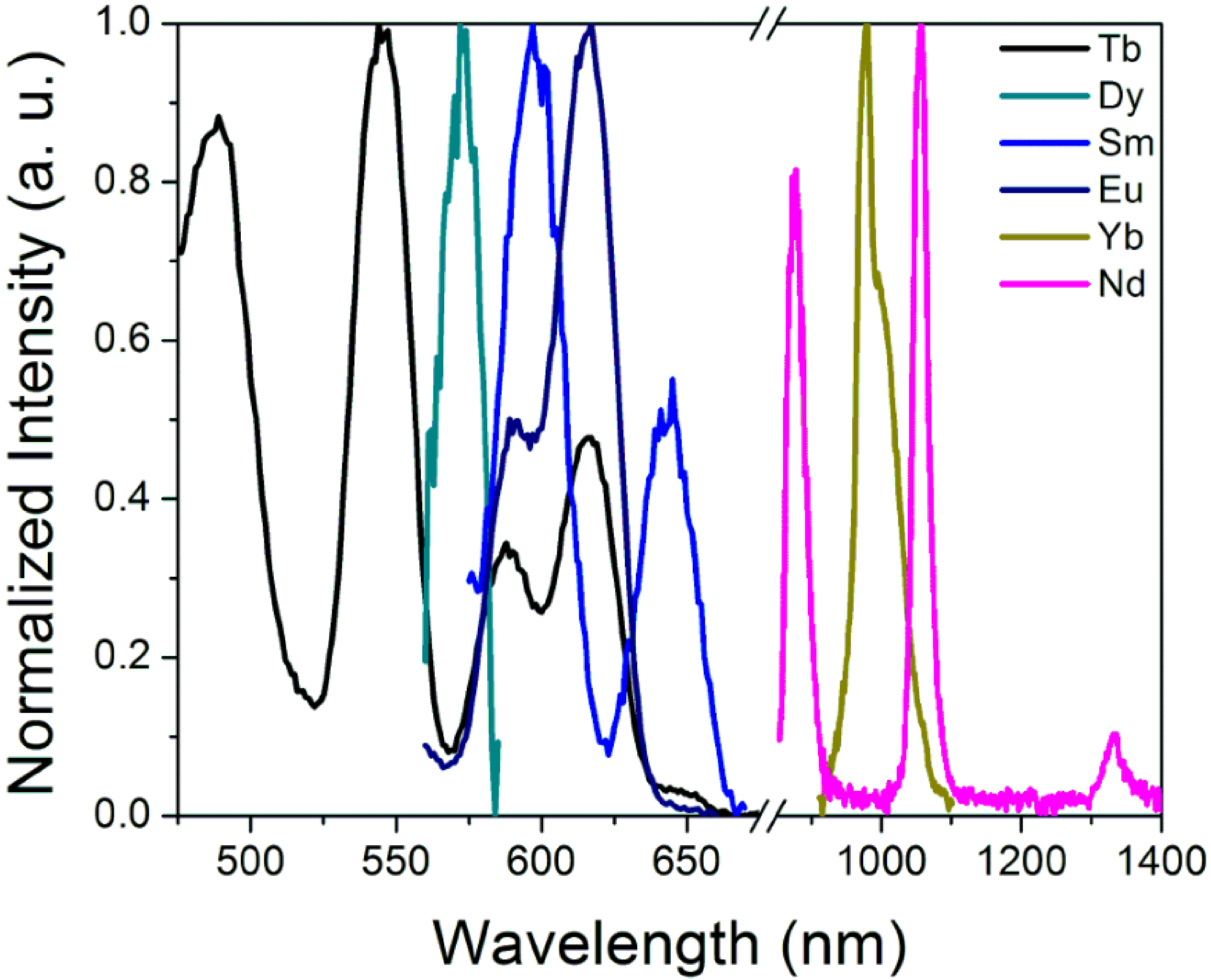


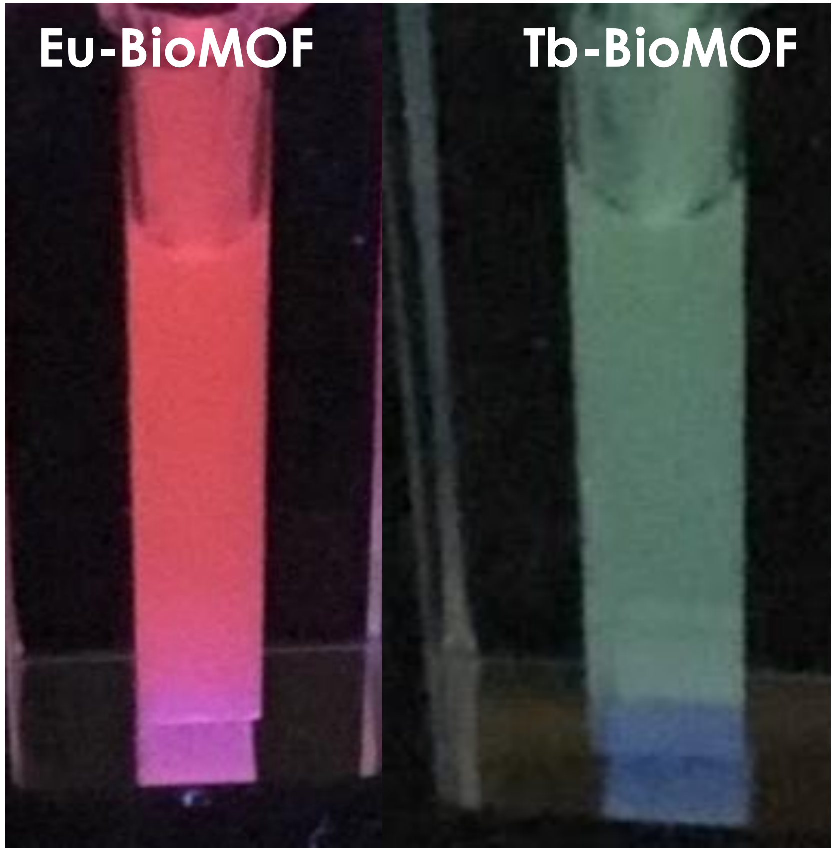


1. REE encapsulated via cation exchange
2. Organic chormophoric linkers are excited by UV light
3. Energy is transferred from chromophore to REEs
4. REE centered emission is observed

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

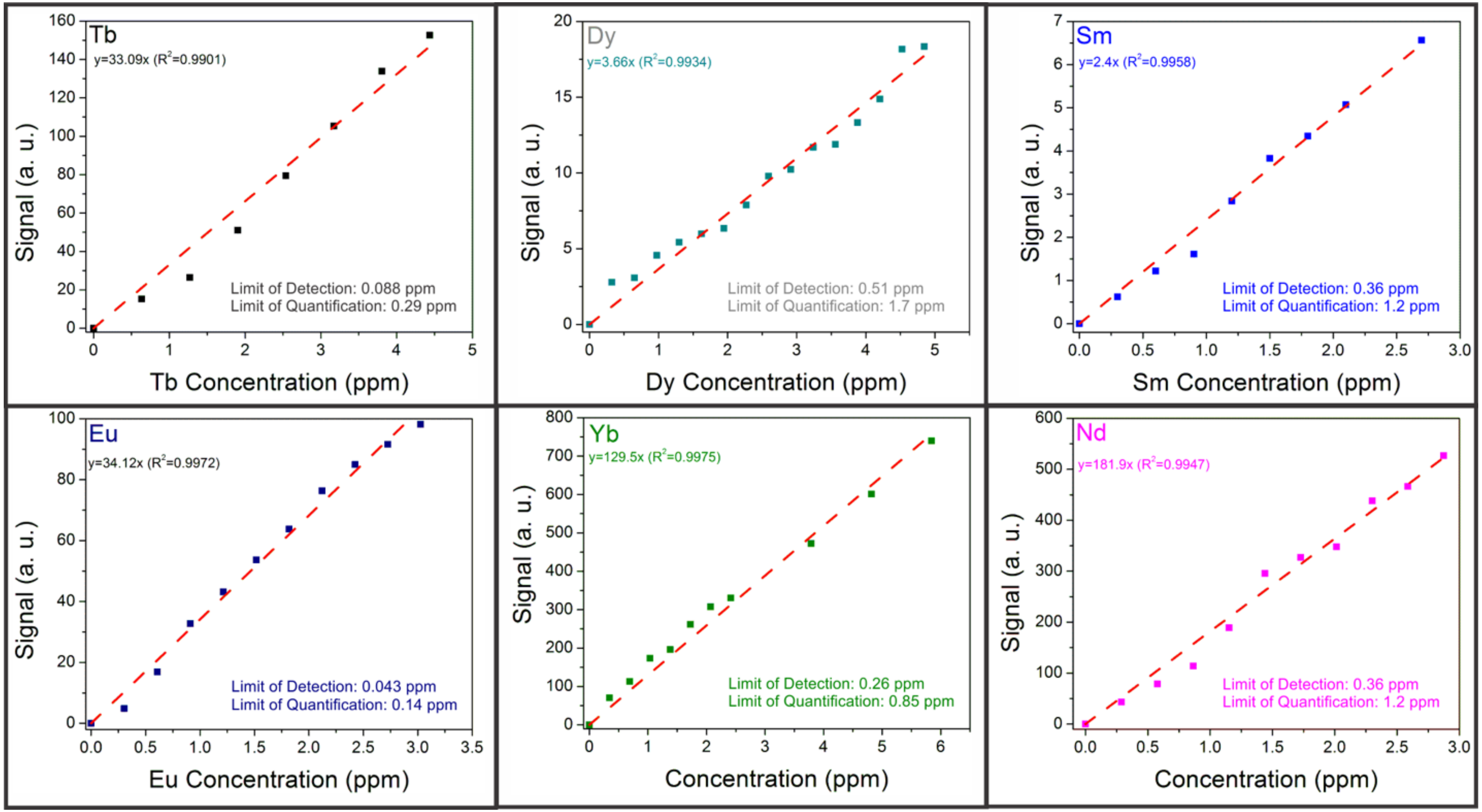
Sensitization of 6 REEs with One Material!





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

Sub-ppm Limits of Detection for 6 REEs!



Sub-ppm Limits of Detection for 6 REEs!

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REE	LOD (ppm)	LOQ (ppm)	λ_{EM} (nm)[a]	fwhm (nm)[b]
Tb	0.088	0.29	545	22
Dy	0.51	1.7	572	18
Sm	0.38	1.2	597	24
Eu	0.043	0.14	617	36
Yb	0.28	0.85	980	54
Nd	0.36	1.2	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.

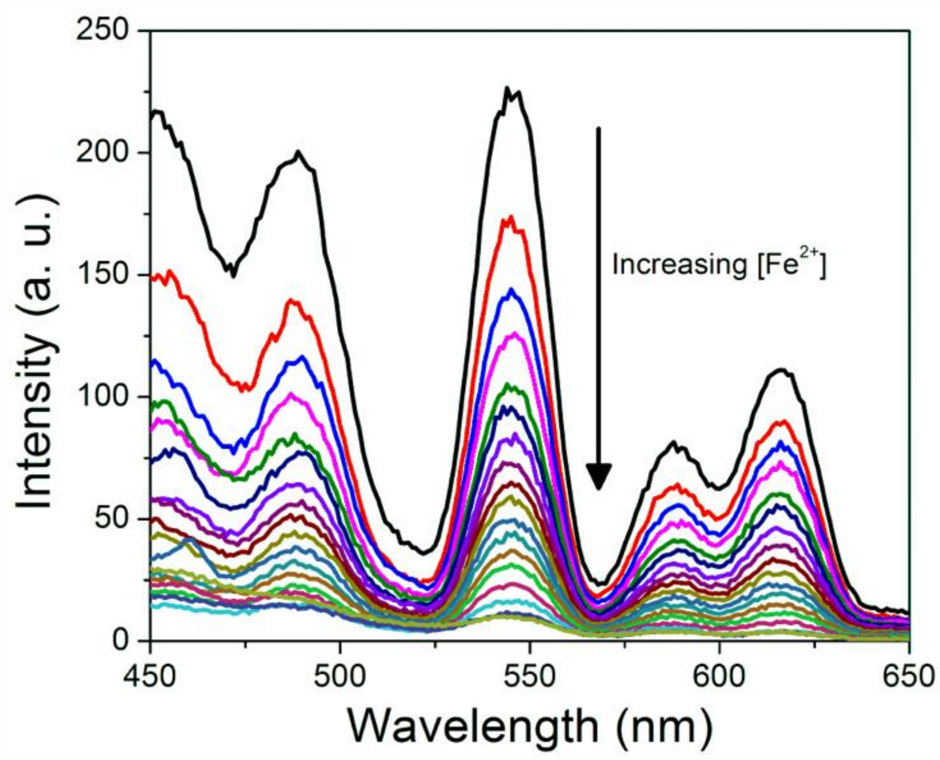
Crawford*, Gan, Lemaire, Millstone, Baltrus, and Ohodnicki, *ACS Sensors* **2019**, *4*, 1986

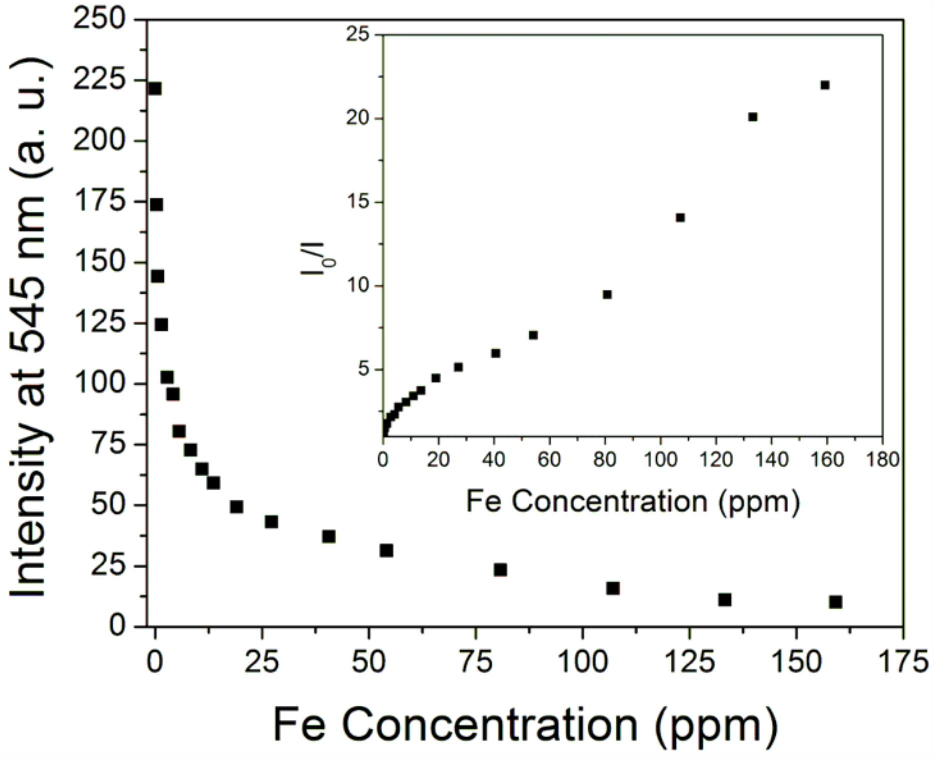
Selectivity is a Significant Challenge

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

Secondary Metal Quenching

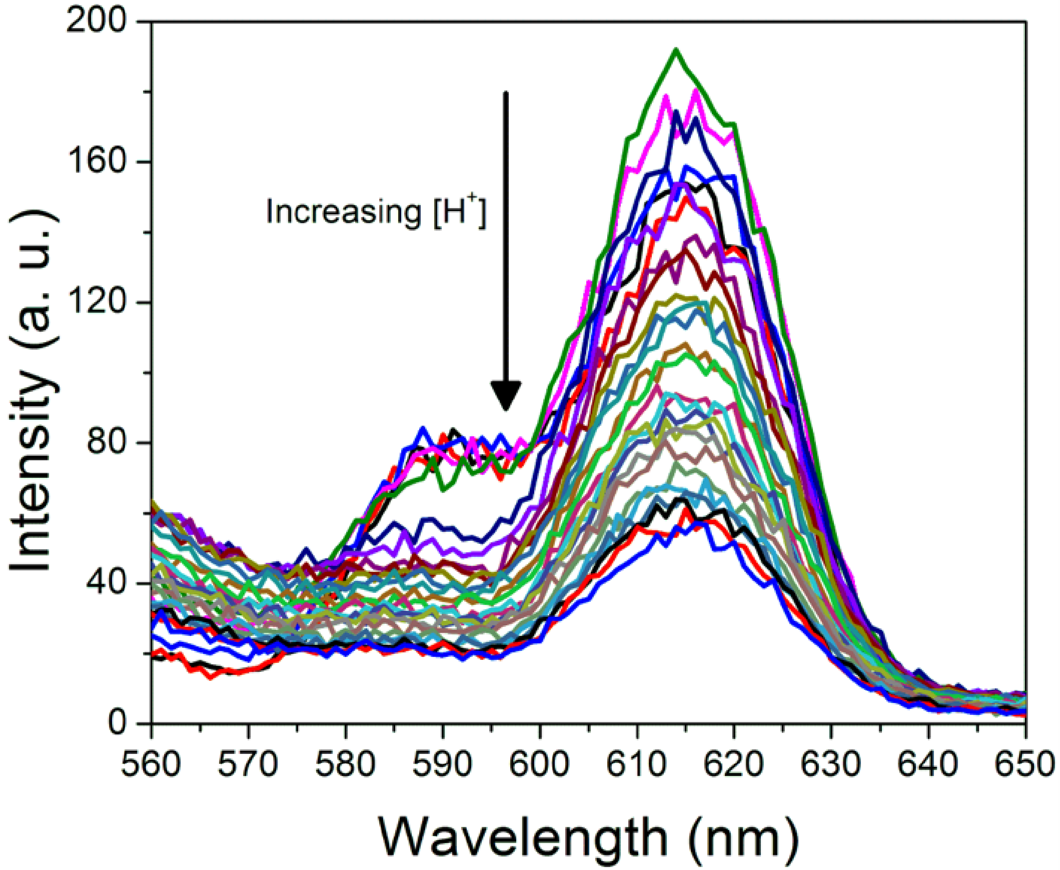


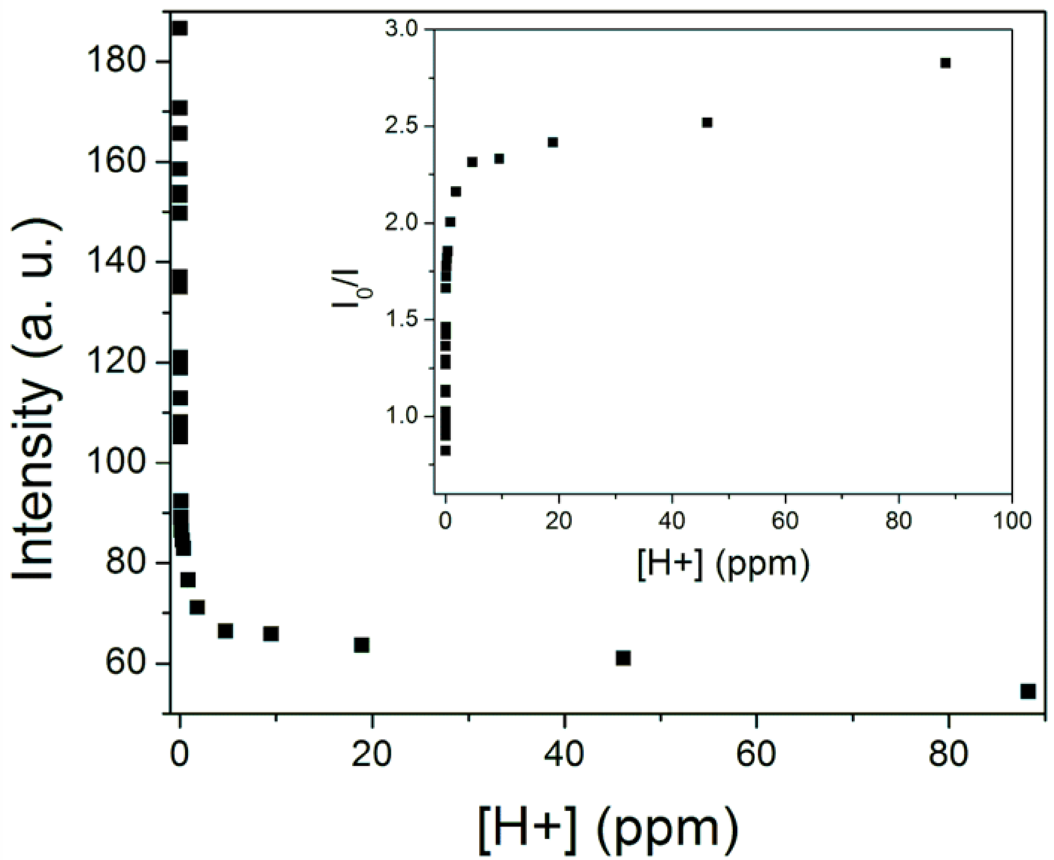


Fe (II) sulfate is used as a representative AMD secondary metal. Quenching behavior is observed for all BioMOF-100/REE systems, with element-specific differences in the quenching profiles.

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

Acidic Conditions also Reduce Signal





Similarly, the addition of HCl leads to a decrease in emission for BioMOF-100/REE systems. Eu^{3+} shows the highest resistance to quenching from proton addition, with signal detected at 90 ppm H^+ (pH 1.1)

One Alternative: Measure Post-Extraction

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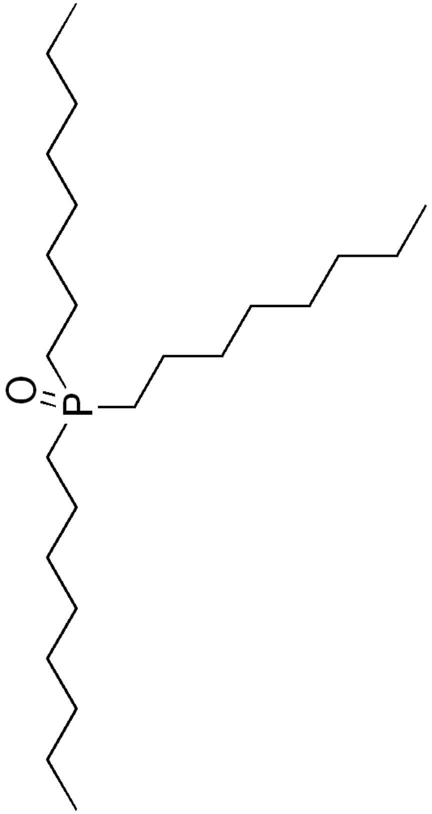

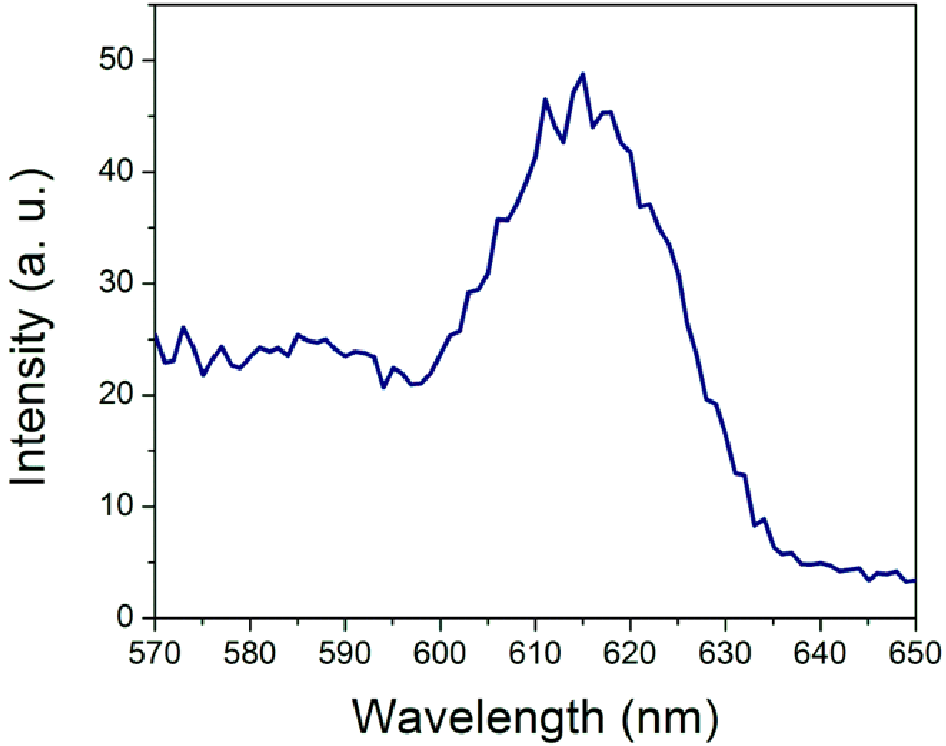

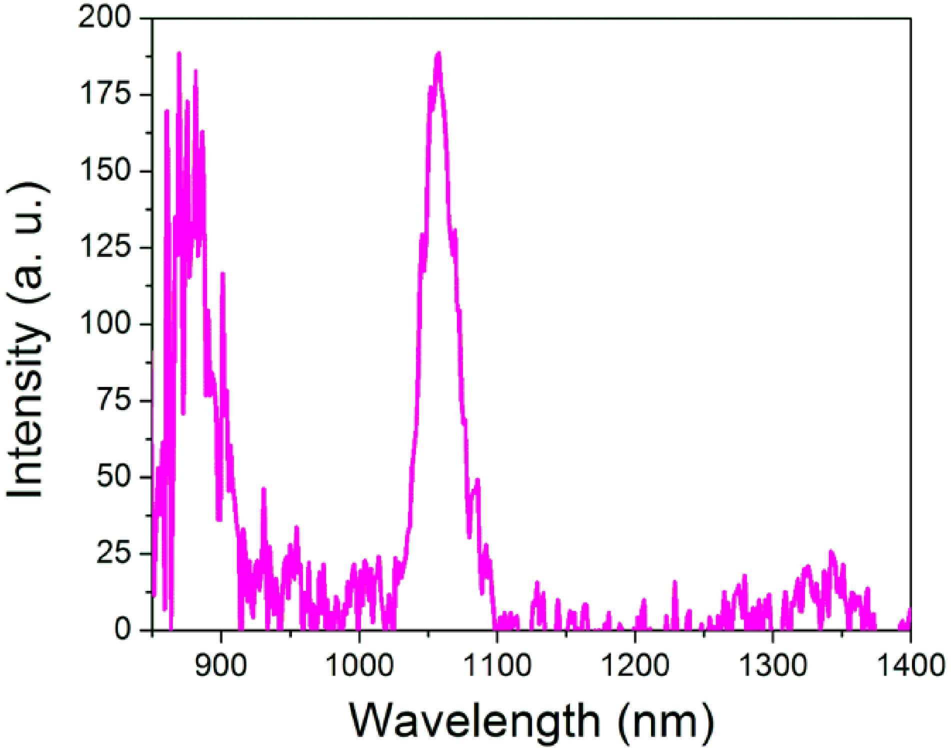

Triocylphoshpine-oxide

DOI 10.1039/JA9900500371

A representative visible-emitting REE (Eu) and NIR-emtting REE (Nd) both exhibited detectable emission in hexanes post-extraction using BioMOF-100

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

Choice of Linker Influences Selectivity

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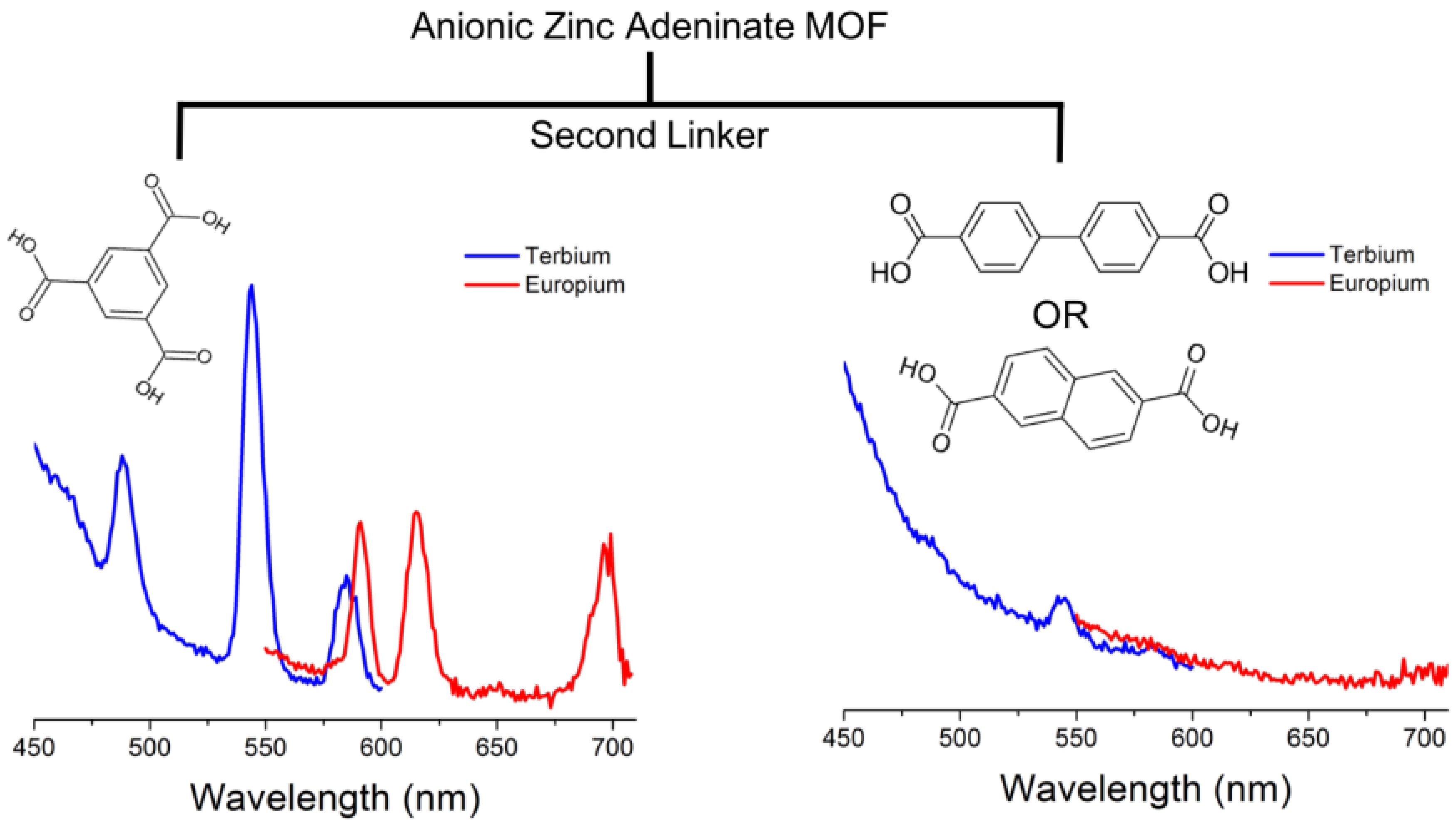

Emission in Acid Mine Drainage Matrix: 3.3 pH, [Ca] = 59 ppm, [Mn] = 29 ppm, [Al] = 10 ppm

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

Detecting Down to <10 ppb REEs

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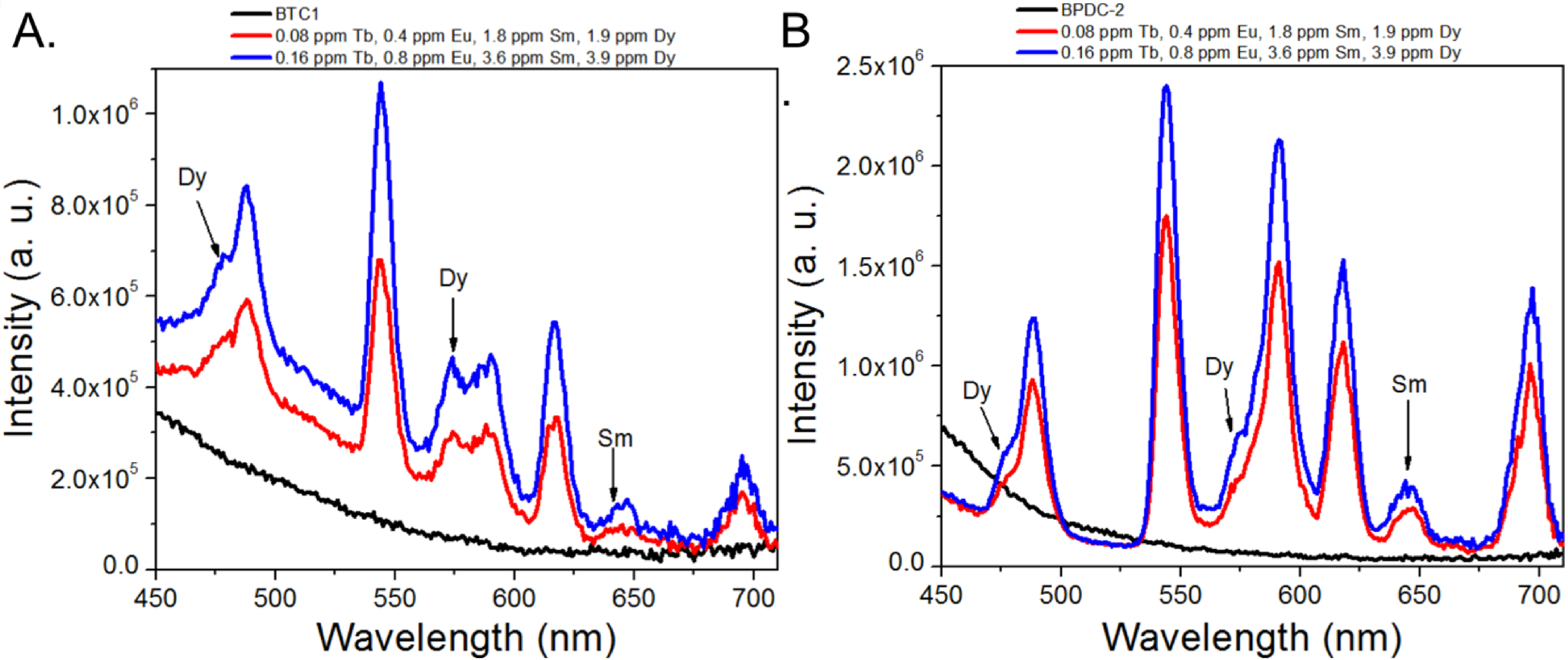
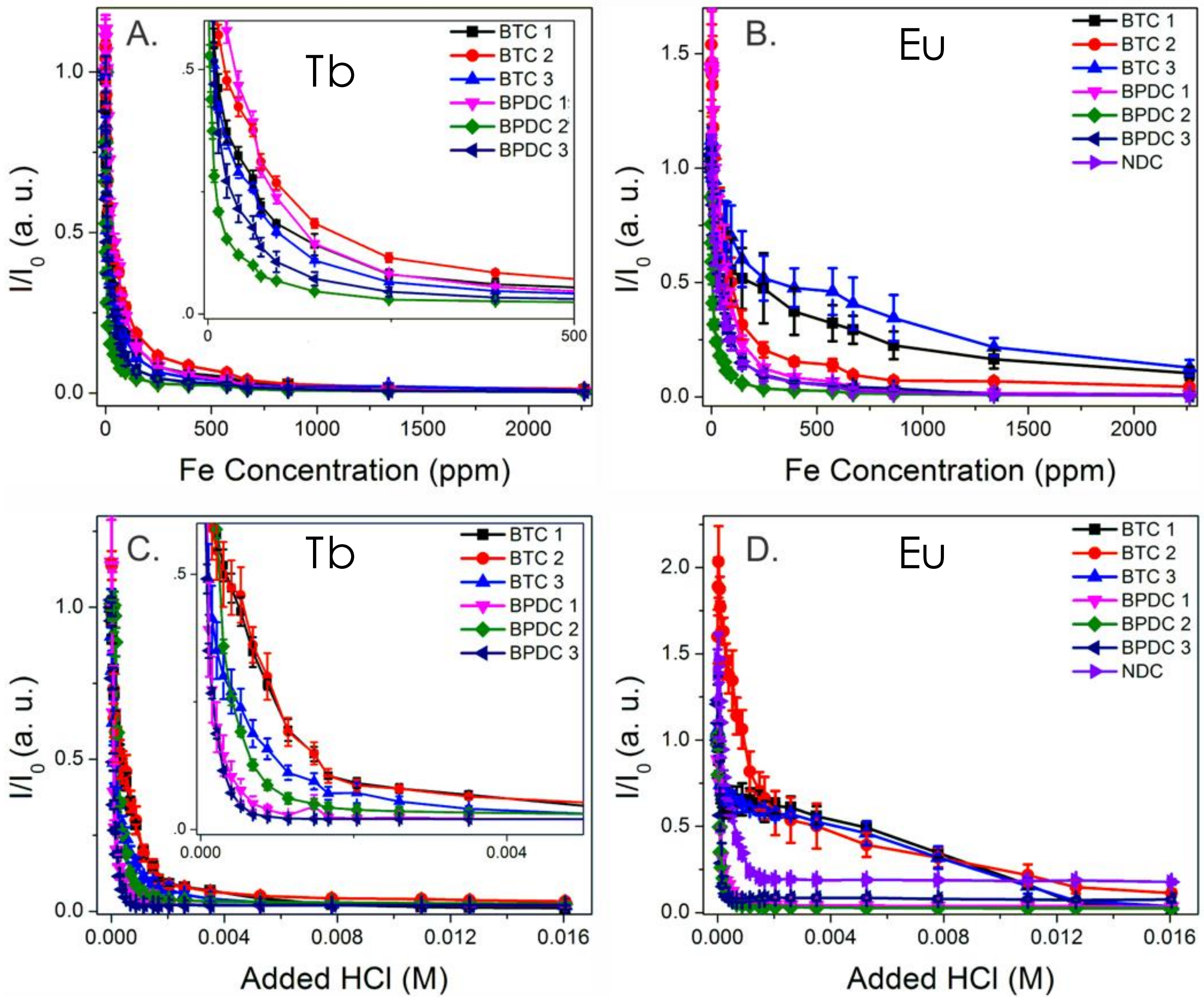
MOF		Tb (ppb)	Dy (ppb)	Sm (ppb)	Eu (ppb)
$[Zn_3(ad)(\mathbf{BTC})_2(DMA), 5.75DMF, 0.25H_2O]$	LOD	8 ± 1	**170 ± 10**	600 ± 90	70 ± 10
	LOQ	27 ± 4	**550 ± 30**	2000 ± 300	220 ± 40
$Zn_7(Ad)_4(\mathbf{BTC})_4(DMF)O, 4DMA, 3DMF_4, H_2O$	LOD	13 ± 2	390 ± 60	1000 ± 100	74 ± 3
	LOQ	44 ± 8	1300 ± 200	3400 ± 500	240 ± 10
$Zn_3(Ad)(\mathbf{BTC})_2(H_2O)\cdot DMA\cdot xDMF\cdot yH_2O$	LOD	10 ± 1	230 ± 30	490 ± 30	46 ± 2
	LOQ	33 ± 5	800 ± 100	1600 ± 100	152 ± 6
$[Zn_8(ad)_4(\underline{BPDC})_6O\bullet DMA, 8DMF, 11H_2O]$	LOD	8.3 ± 0.8	190 ± 20	190 ± 30	44 ± 3
	LOQ	28 ± 2	630 ± 80	**600 ± 100**	150 ± 10
$Zn_8(ad)_4(\underline{BPDC})_6O_2 \bullet 4DMA, 49DMF, 31H_2O$	LOD	**5.7 ± 0.6**	200 ± 30	270 ± 10	**18 ± 4**
	LOQ	**18 ± 2**	700 ± 100	900 ± 40	**60 ± 10**
$\{DMA_2[Zn_6(\mu_4\text{-}O)(ad)_4(\underline{BPDC})_4]\}_n$	LOD	10 ± 2	190 ± 30	**184 ± 6**	20 ± 3
	LOQ	33 ± 6	620 ± 80	610 ± 20	67 ± 9
$Zn_8(ad)_4(\underline{\mathbf{NDC}})_6(OH)2\bullet 2DMA, 35DMF, 23H_2O$	LOD	-	-	-	30 ± 1
	LOQ				98 ± 3

Sensitization of Multiple REEs



Selectivity Influenced by Linker, Structure



- BTC linker generally is more robust vs. quenching than BPDC, NDC
- Certain structures are more selective than others even with the same linker (e.g., BTC-3 vs. BTC-2 with Eu)

Does it Matter? Tests in AMD Matrix

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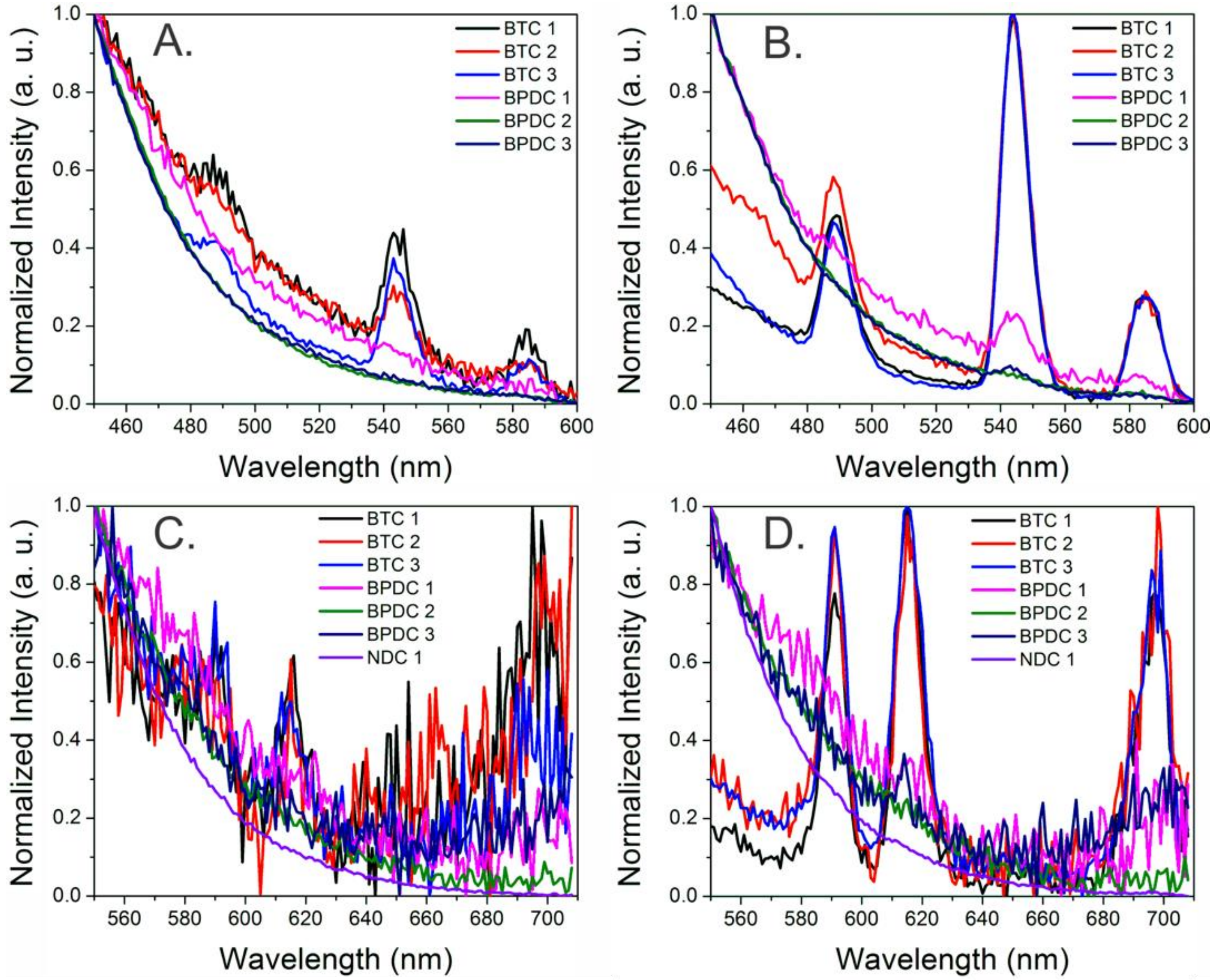
0.7 ppm Tb

7 ppm Tb

0.7 ppm Eu

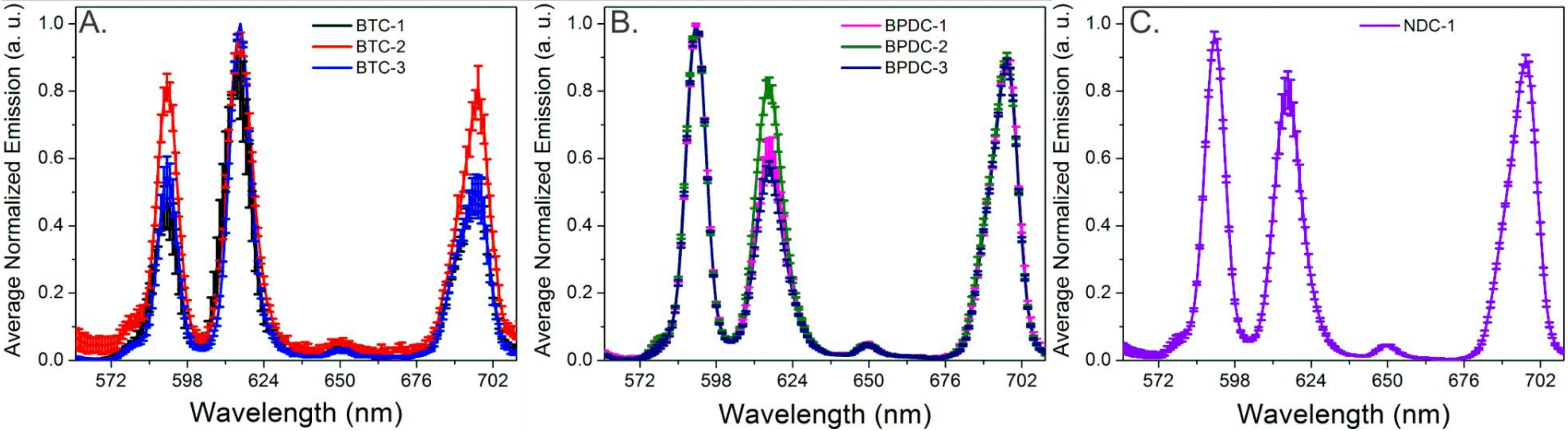
7 ppm Eu



BTC MOFs sensitize Tb, Eu even in an acid mine drainage matrix

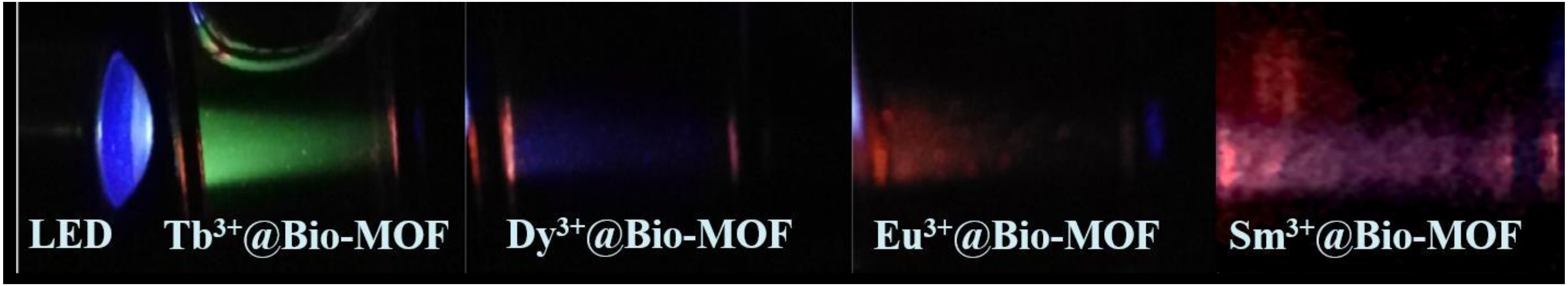
pH = 3.3
[Ca] = 59 ppm
[Mn] = 29 ppm
[Al] = 10 ppm
[Fe] = 320 ppb

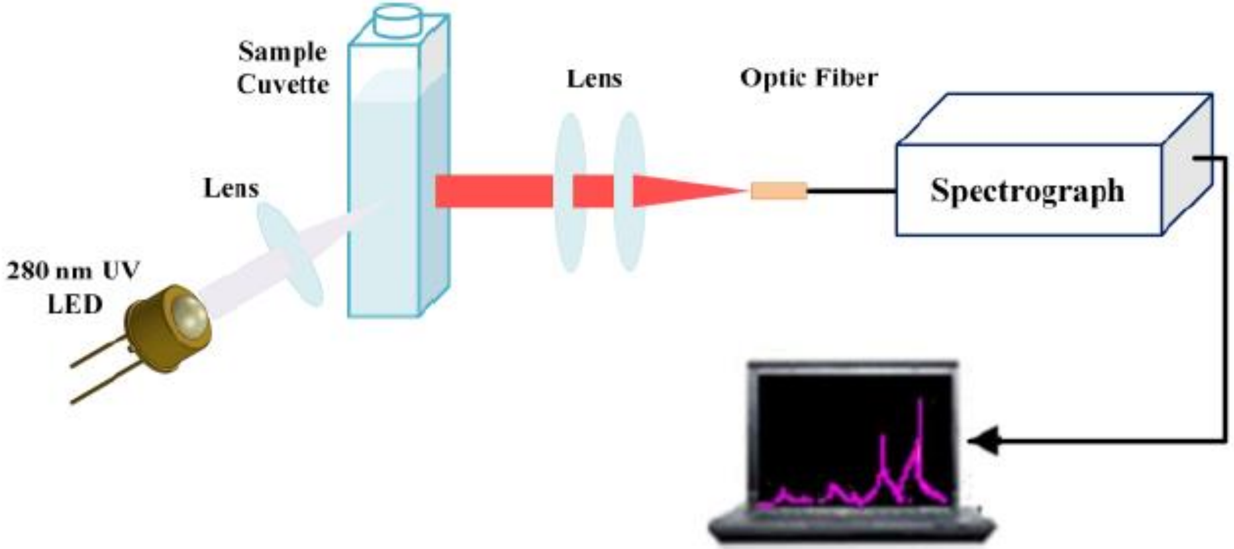
Linker-Dependent REE Coordination

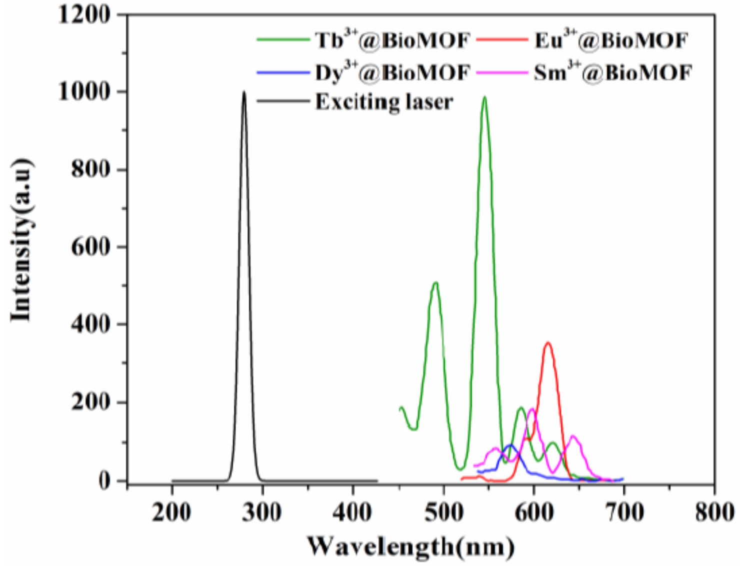


BTC MOFs exhibit enhanced Eu hypersensitive transition peak at 617 nm relative to the BPDC and NDC MOFs, indicating linker-dependent REE coordination.

Development of Low-Cost Sensor



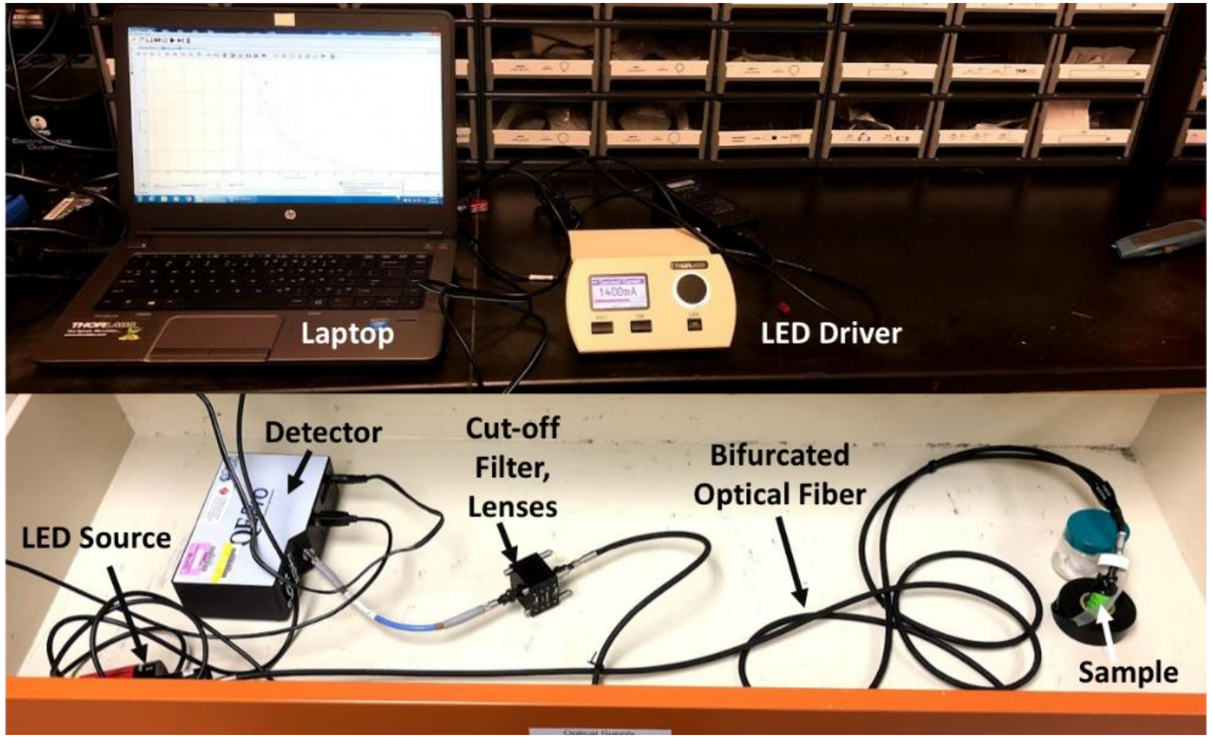


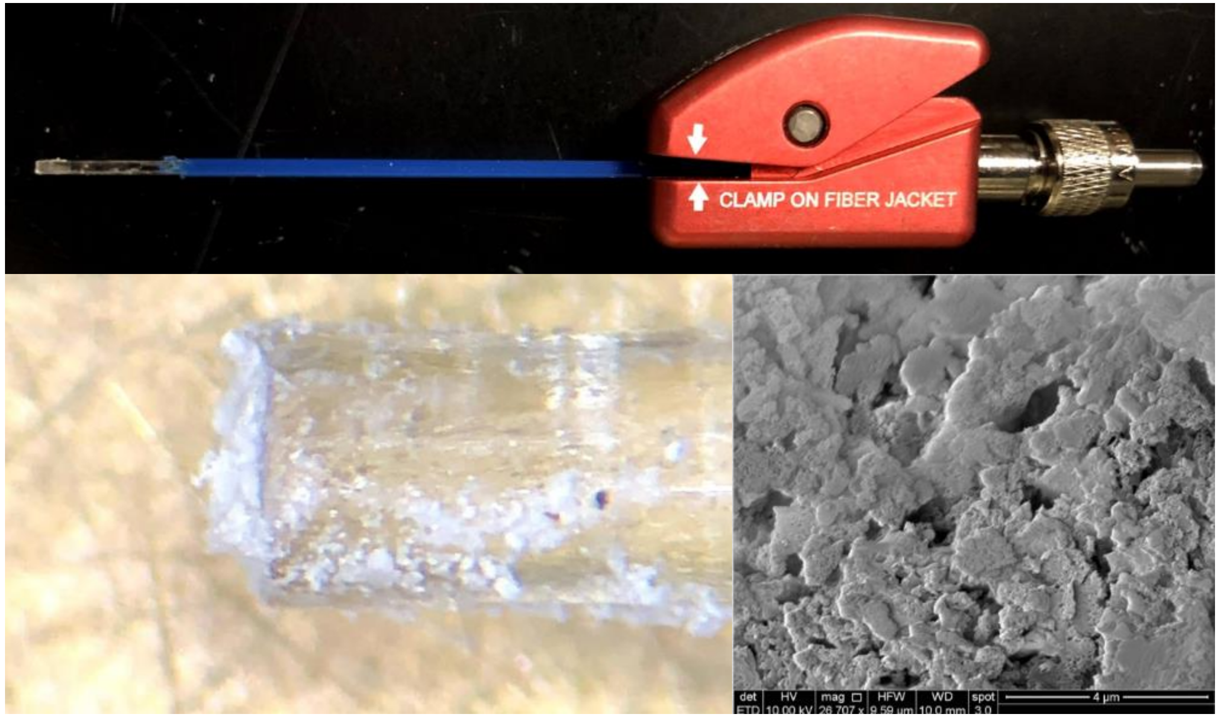


Lan, H., Crawford, S., Splain, Z., Boyer, T., Ohodnicki, P., Baltrus, J., Zou, R., Wang, M., Chen, K.; *CLEO: QELS_Fundamental Science* **2019**, JW2A-14

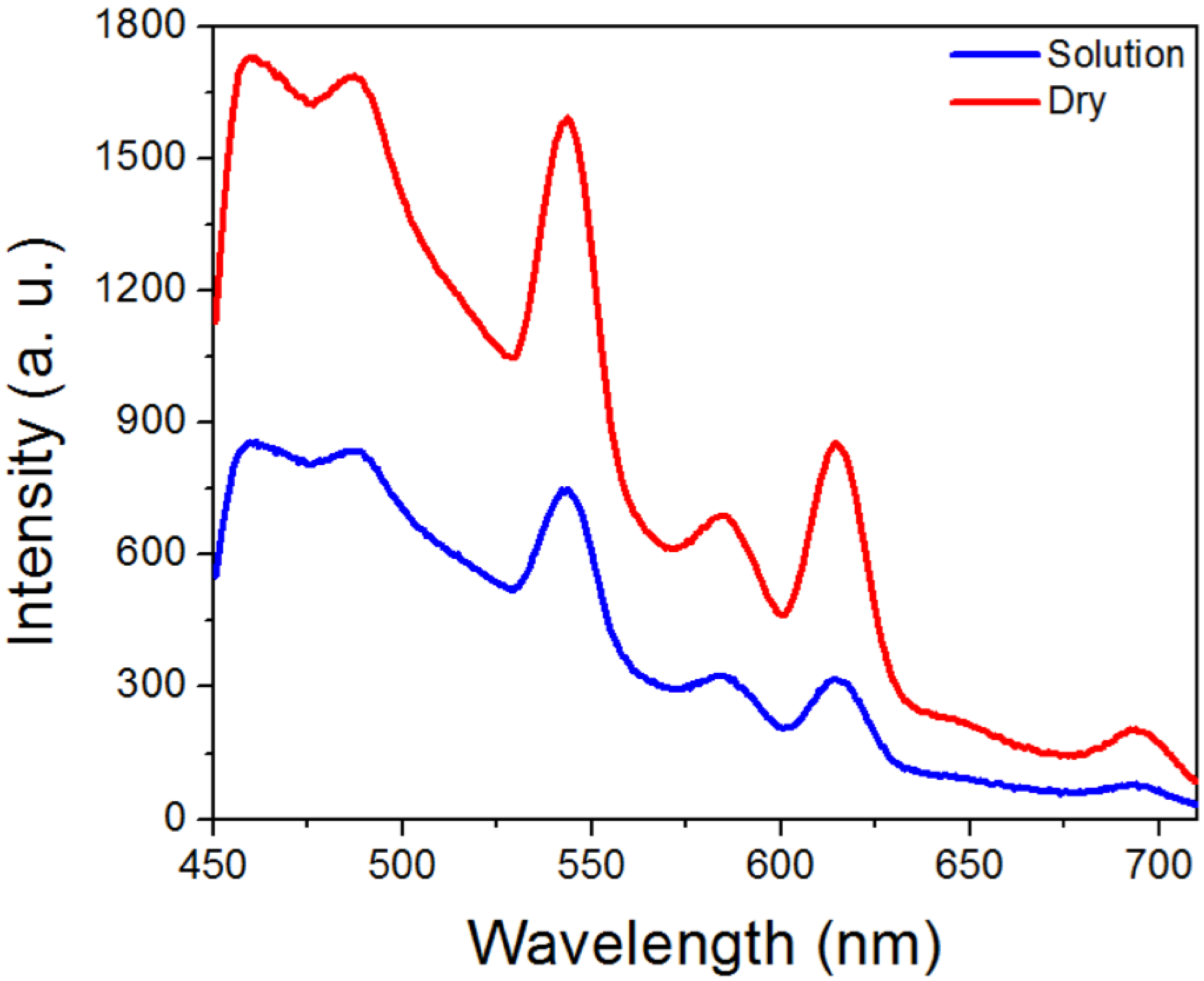
Integration onto Portable Sensor

- Rapid detection (minute time-scale)
- 10s of part-per-billion detection limits for Tb, Eu
- Reusable tip/Inexpensive tip replacement ($0.06/MOF-coated tip)



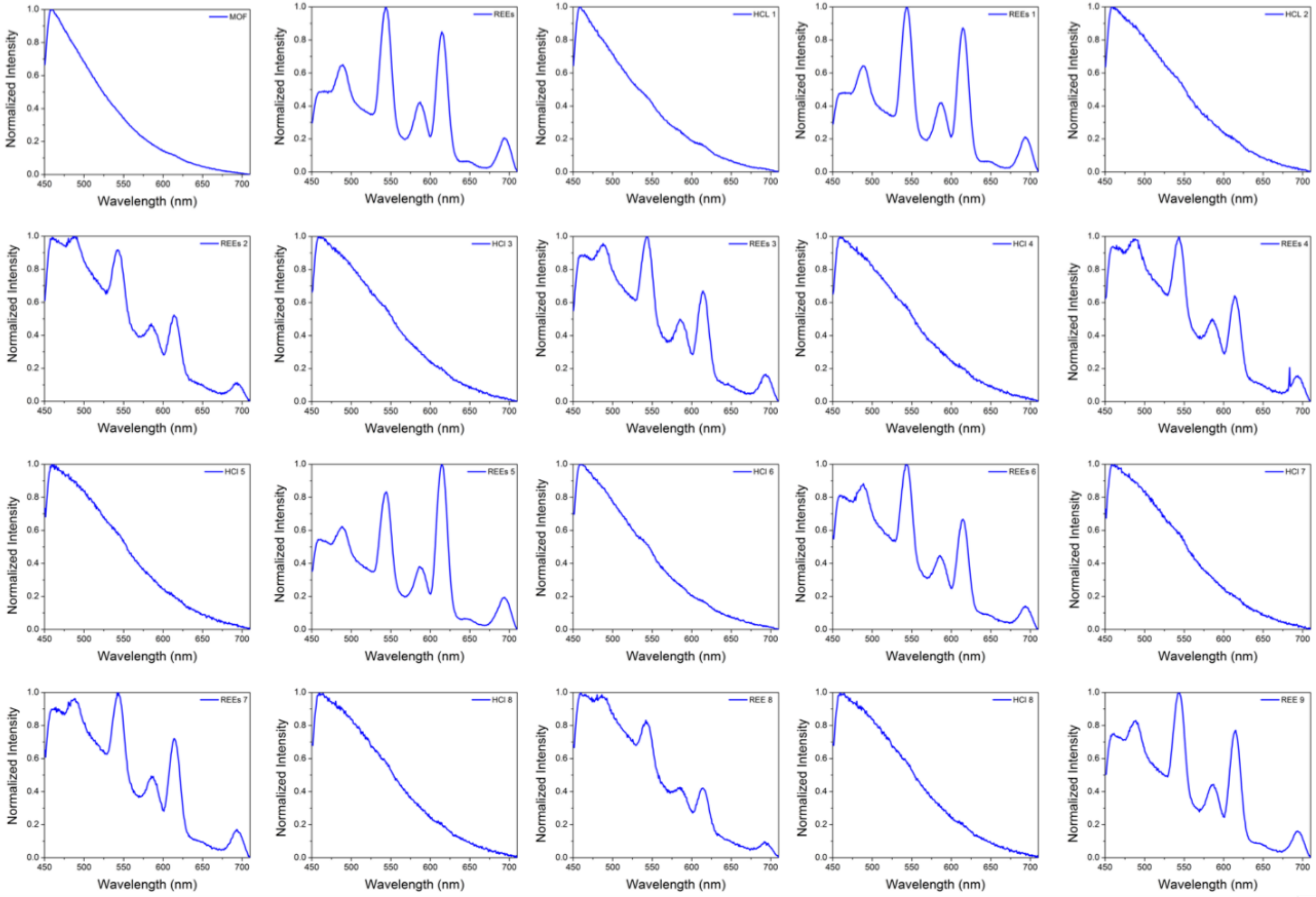


Signal Enhancement from Drying



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

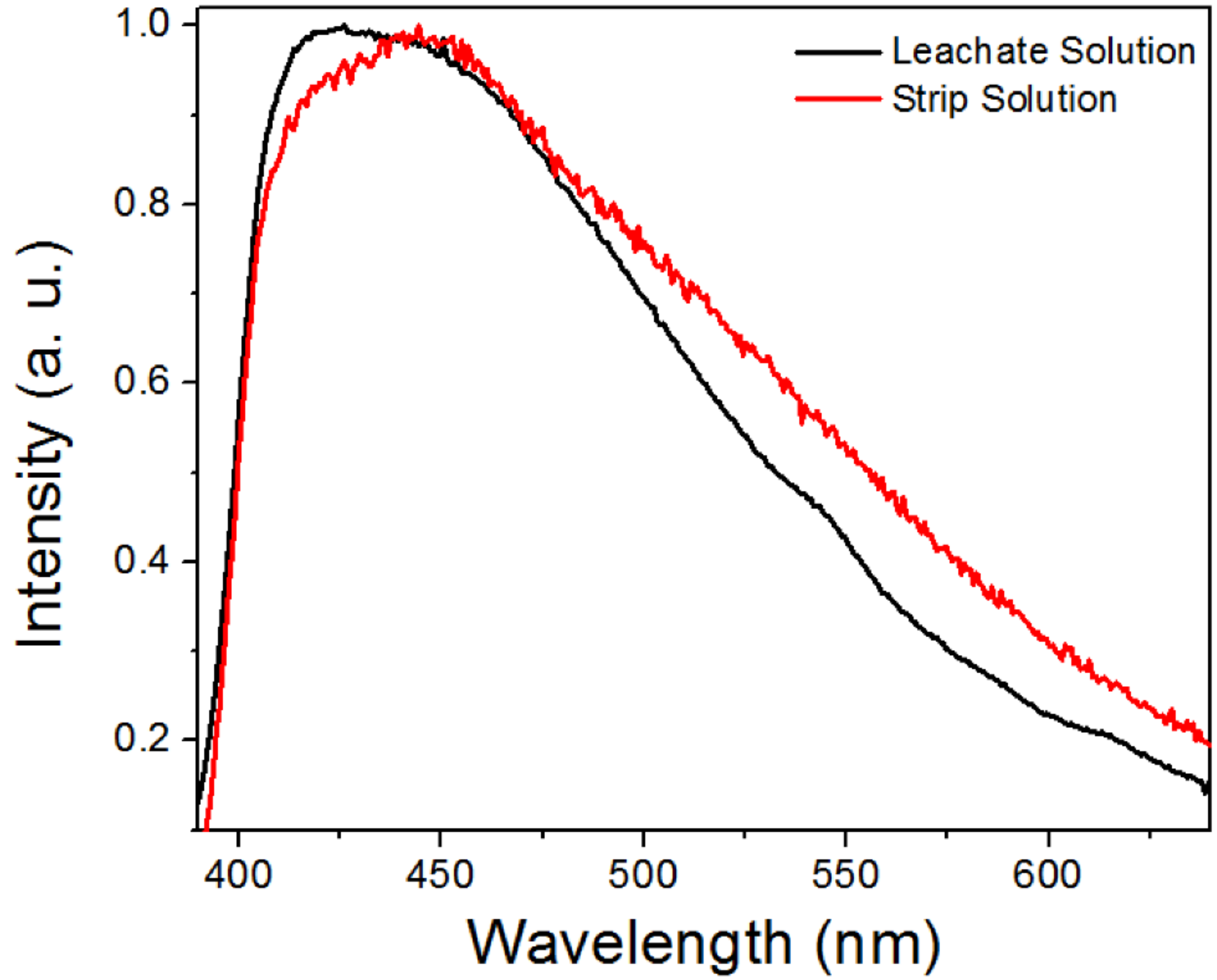
Sensitive, Reversible Sensing



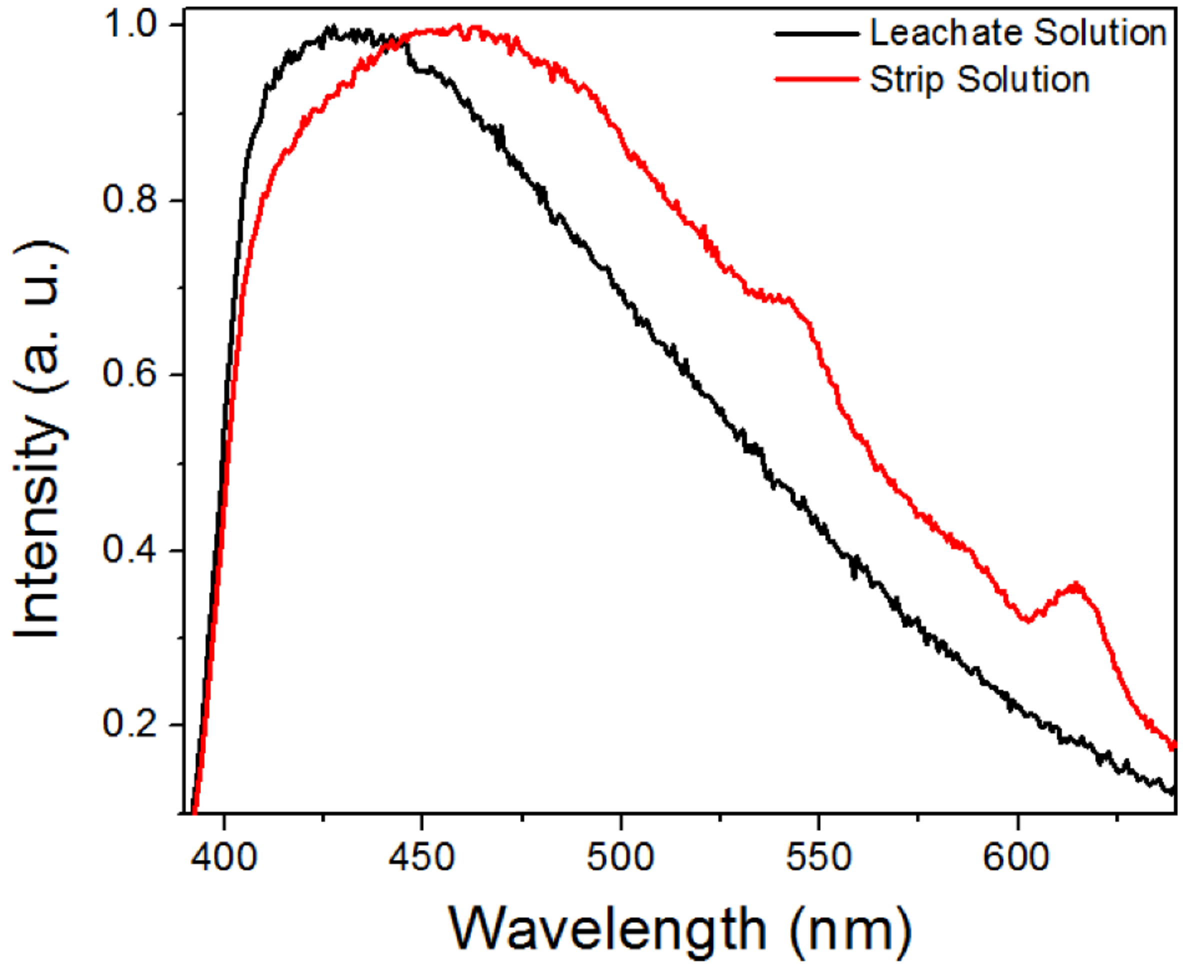
Qualitative regeneration of signal across multiple cycles using dilute acid

Performance in Simulated Process Stream

T = 0 hours



T = 27 hours



Concluding Thoughts

- Metal-Organic Frameworks (MOFs) exhibit significant promise as rare earth element sensors, with limits of detection now down to **sub-10 ppb in water**
- Correlating MOF structure (pore dimensions, emission properties, pore functionality, charge) with REE uptake and sensitization will aid in the rational design of MOF-based sensors
- Zinc-Adeninate MOFs with BTC linkers may help overcome selectivity challenges in harsh matrices
- Inexpensive portable sensors may be developed with low cost (<$20k) for field use, with some advantages over conventional commercial spectrometers

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