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research & innovation

Synthesis and Evaluation of Optically Detectable, Highly Water-Soluble Zwitterionic Dipicolinic Acid (DPA) – Based Tracers for Hydrocarbon Reservoir Surveillance

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Aramco Americas, Aramco Research Centers – Boston

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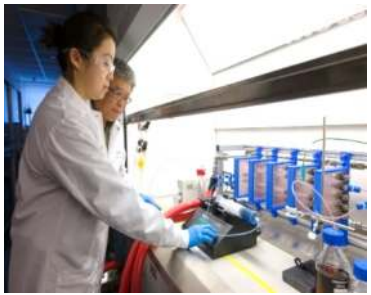
Reservoir Engineering Technology - Boston

Specialized NanoMaterials Synthesis

20 L batch reactor system

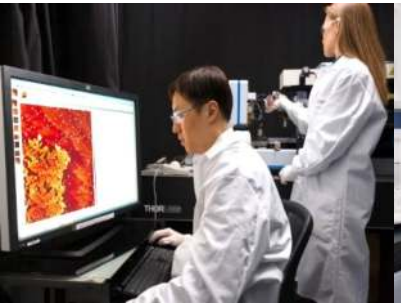


Continuous-flow micro-reactors

Vacuum gas manifold

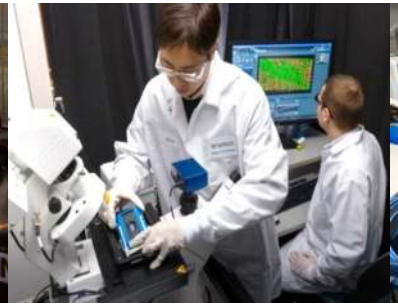
Large-scale CEOR formulation screening

Advanced NanoMaterials Imaging and Characterization

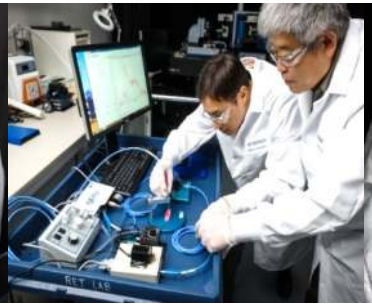


Atomic force microscope

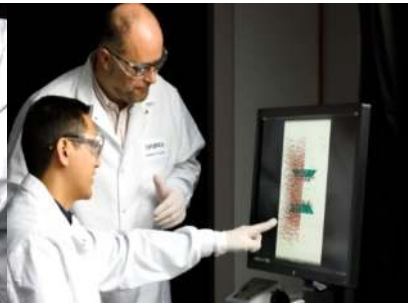
High field NMR spectroscopy



Imaging reservoir-on-a-chip



Miniature spectrometers



Molecular-dynamical modeling

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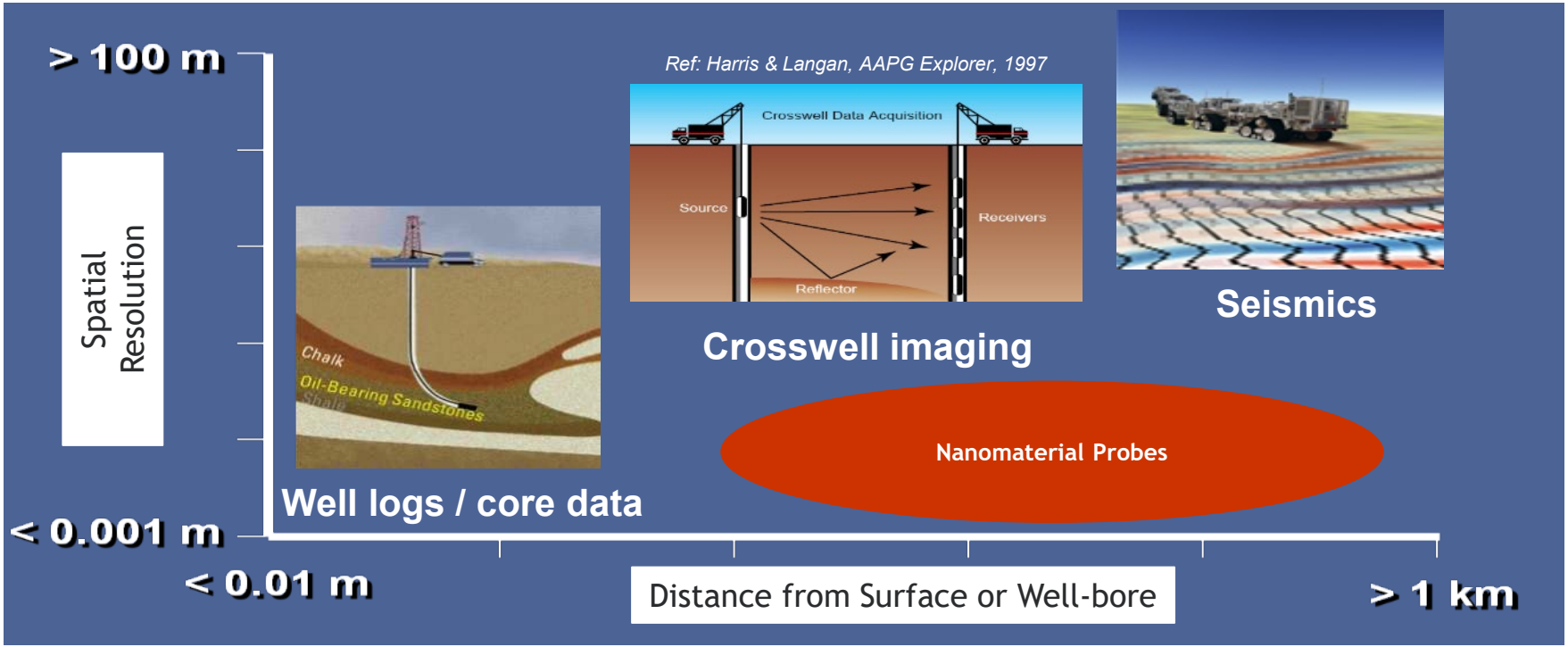
The ‘Measurements Gap’

Problem for Effective Reservoir Management



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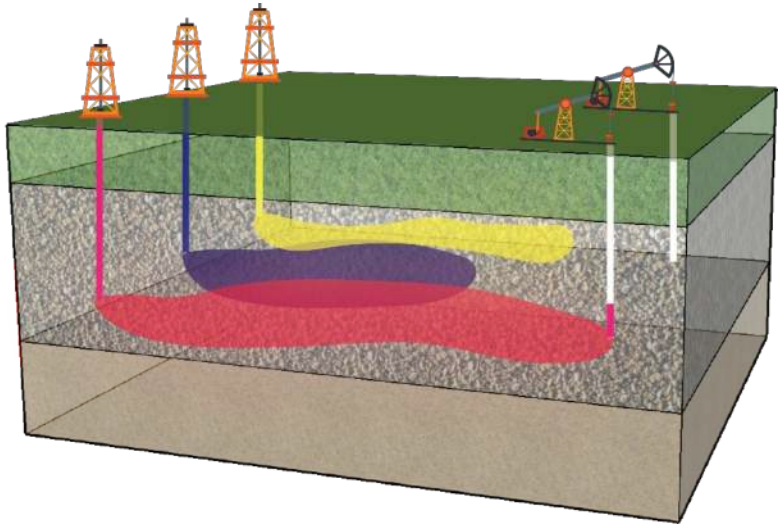
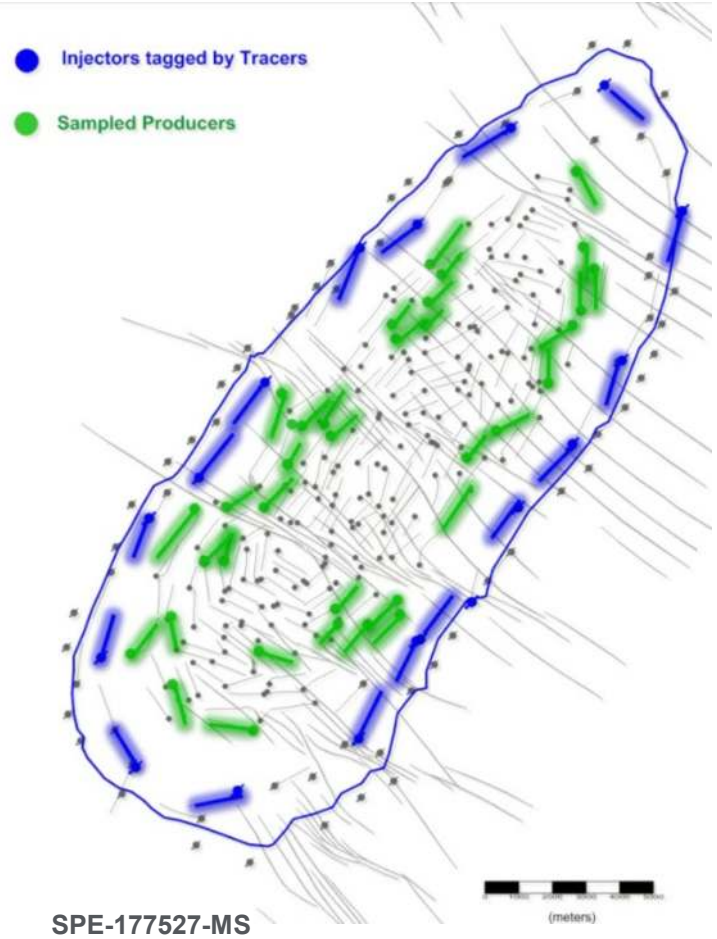
Tracers in Hydrocarbon Reservoirs

The Need for Many Unique Tracers



- Direct Communication Between Injector and Producer
- Exact Breakthrough Times Between Injector and Producer
- Identification of Natural Fractures, Thief Zones and Faults
- Extent of Formation Layering
- Swept Pore Volume and Sweep Efficiency
- Conformance Gel Treatment Volume Estimation

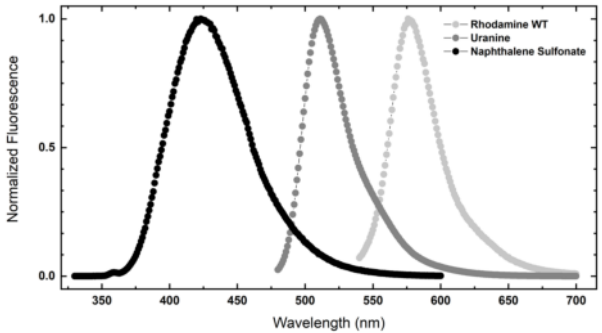


SPE-177527-MS

Use of Optically Detectable Tracers in Hydrology

Challenges in Multiplexing

Barcode by Spectral Characteristics

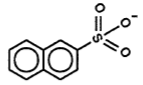
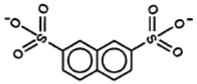
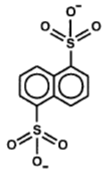
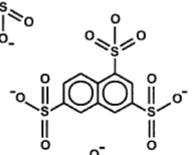
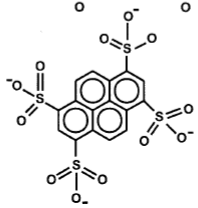


Features & Shortcomings

- Spectral overlap limits number of unique tracers
- Differential degradation behavior

- Highly stable to 250ºC – refractory nature of naphthionate and pyrene analogs
- 200ppt LOD using fluorescence (HPLC)
- Suffers from high background (UV excitation)

Barcode by HPLC Retention Time

2-naphthalene sulfonate		*220 / 336*
2,7-naphthalene disulfonate		*226 / 339*
1,5-naphthalene disulfonate		*218 / 334*
1,3,6-naphthalene trisulfonate		*228 / 342*
1,3,6,8-pyrene tetrasulfonate		*346 / 386*

Rose *et al*, Geothermics 30 (2001) 617-640
Magal *et al*, Journal of Hydrology 358 (2008) 124-133

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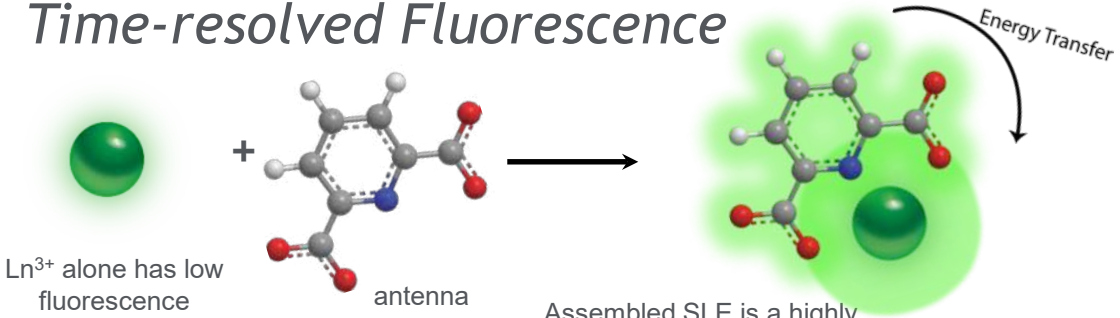
Addressing Difficult Matrices with High Background

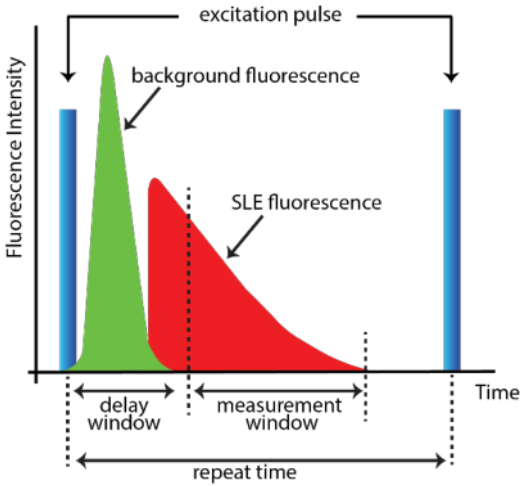
Time-resolved Fluorescence

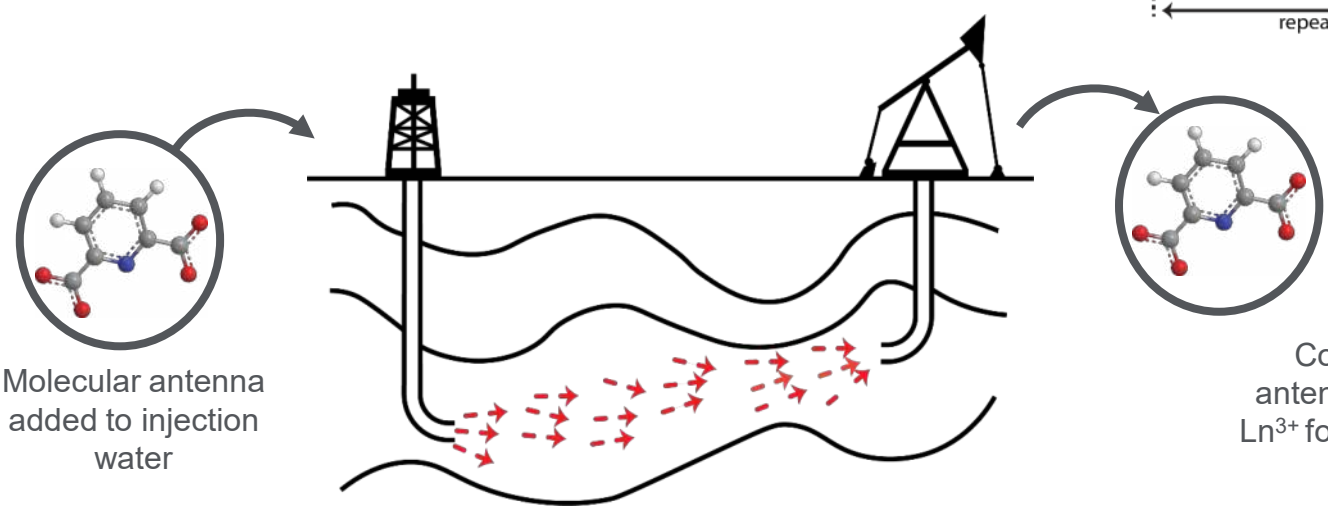


Ln^{3+} alone has low fluorescence intensity

antenna

Assembled SLE is a highly fluorescent complex





Molecular antenna added to injection water

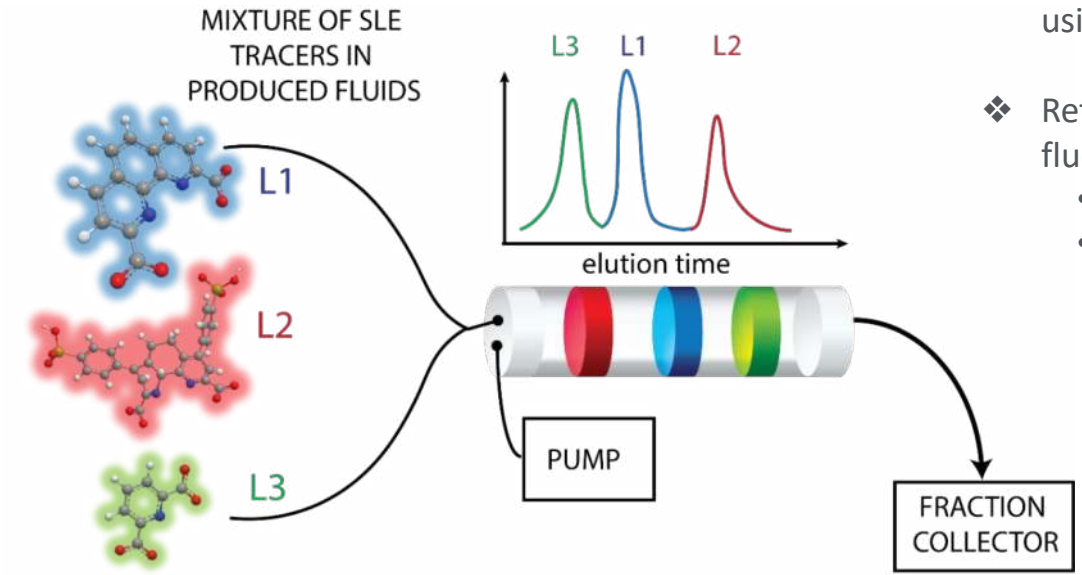
Highly mobile molecular antenna in retrieved in produced water

Collected molecular antenna is combined with Ln^{3+} for fluorescence-based quantification

Barcode Separation and Detection

Chromatographically Distinct Lanthanide Sensitizers

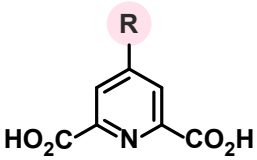
HPLC Separation and Detection



- Separate molecules by polarity/affinity for a stationary phase and read out the code using the assay
- Retention time indicates the code and the fluorescence indicates the concentration
  - Still beats the background oil signal
  - Still field-deployable

Tracer Candidates Performance

Phased Qualifications – from the Lab Bench to the Field



R
—Cl
—CH_2OH
—CO_2H
⋮

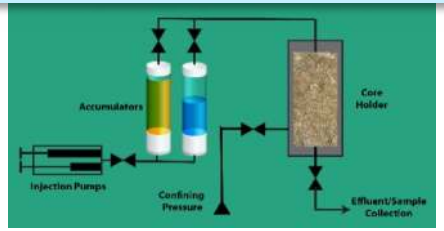
→ *Behavior in reservoir conditions not generalizable*

Non-uniformity: Chemically distinct R groups

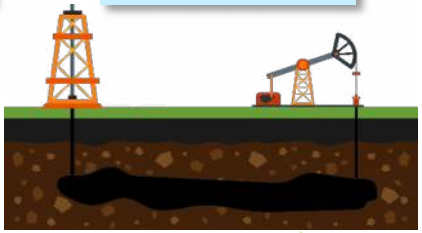
Syntheses & Characterizations

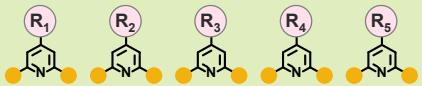
Thermal Stability

Coreflood with & without Residual Oil



Field Validation



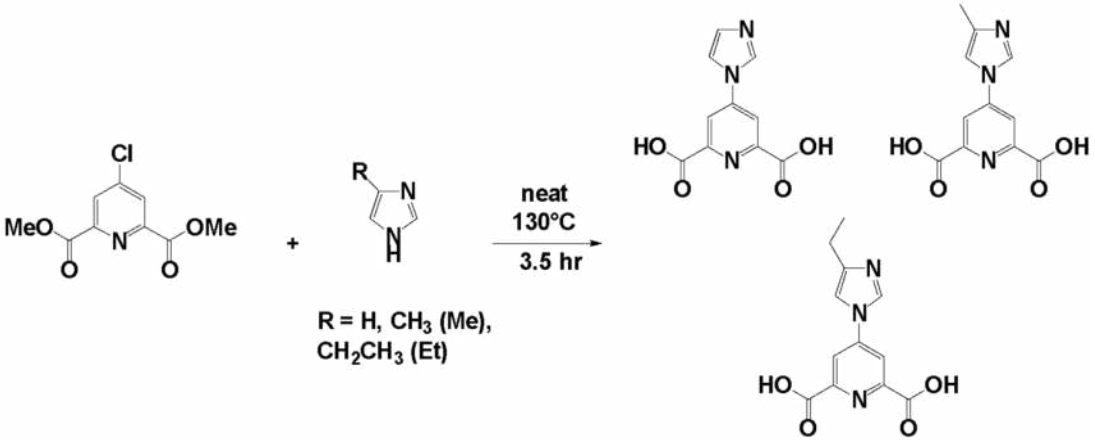


Disqualification X *Cost vs Luminosity* X *Degradation* X *Retention*

Contributors: Gawain Thomas, Sehoon Chang, Hooisweng Ow, Rena Shi, Bora Yoon, Hsieh Chen and Wei Wang

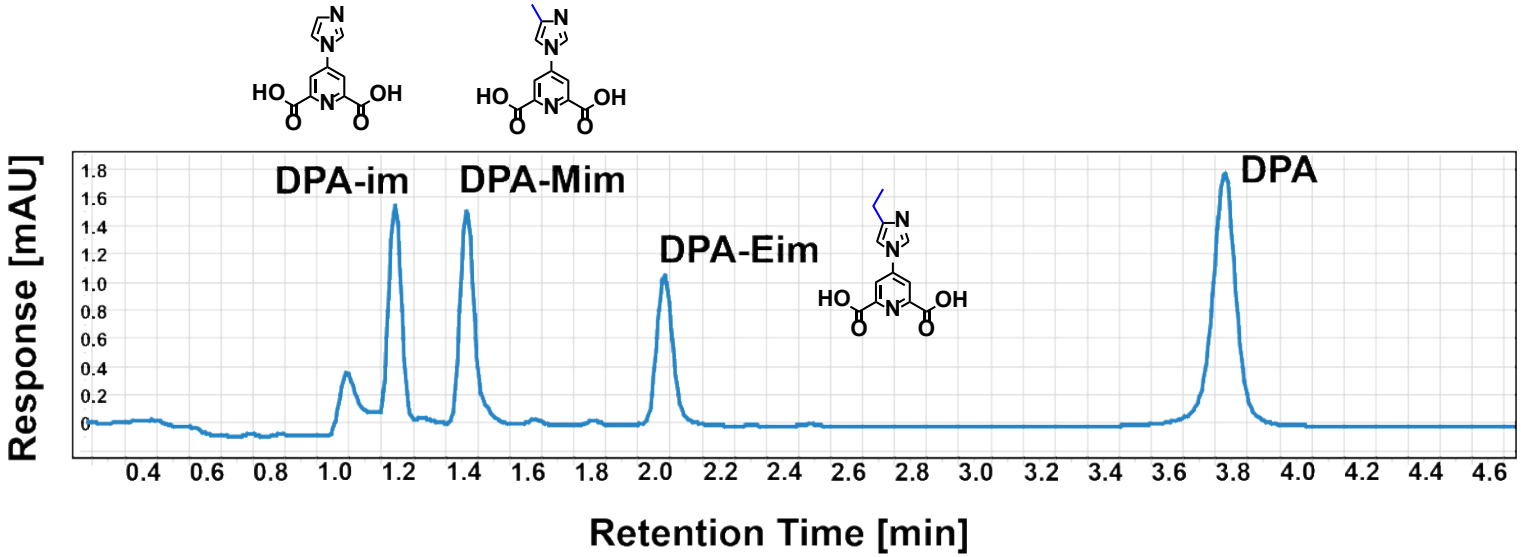
Imidazoles Substituted Analogs

Synthetic Pathway



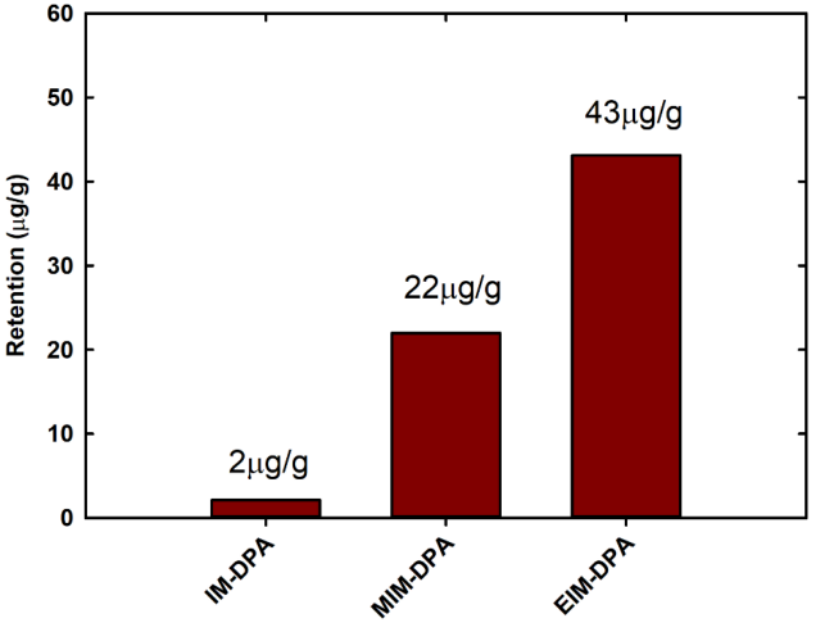
- Direct substitution enabled through 4-chloro precursor
- Solvent-free batch synthesis of imidazole-based analogs of DPA
- Further expansion possible through variation of imidazole “R” groups

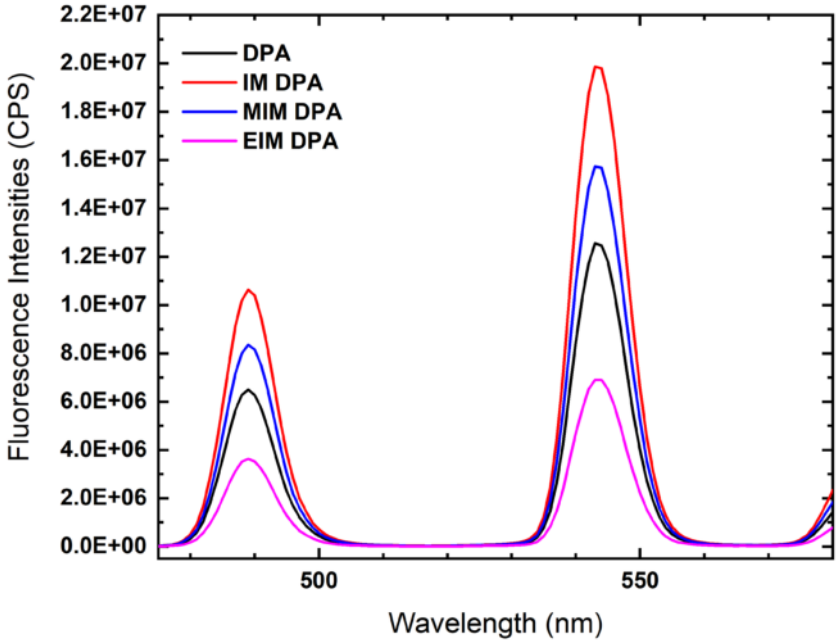
HPLC Separation



- Analogs readily separable by HPLC
- Retention times scale with hydrophobicity of substituents

Retention & Photophysics

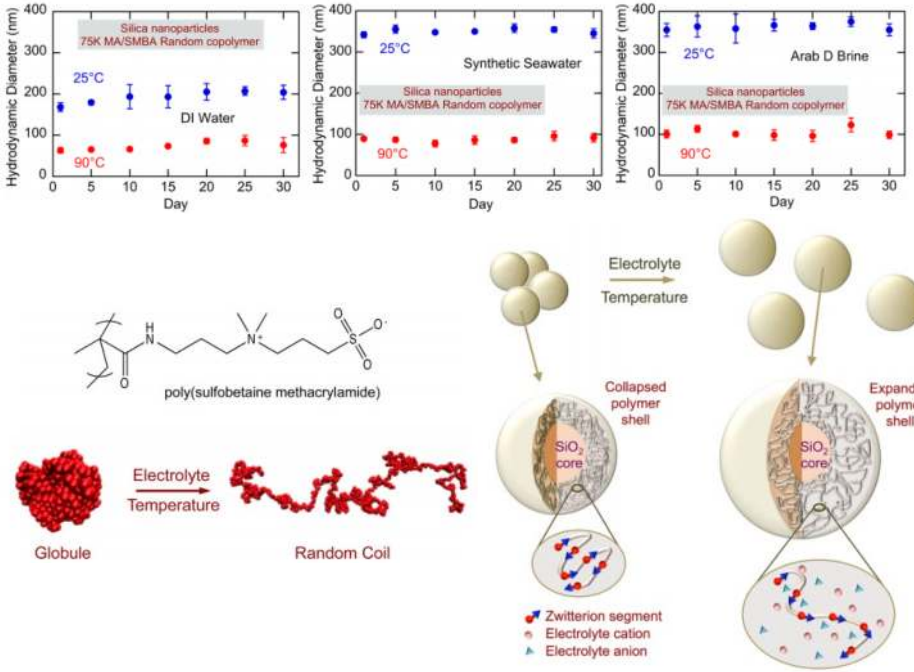




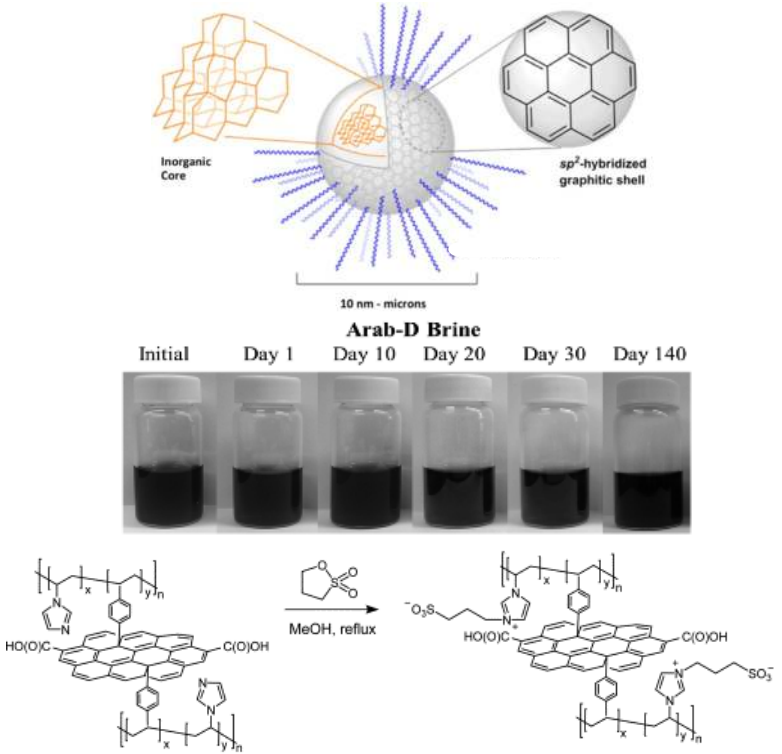
- Retention to rocks increases with the hydrophobicity of Imidazole substituent
- Fluorescence intensities decreased with increasing hydrophobicity

Polyzwitterions Improves Solubility in High Temperature Brine

Precedent in Literature



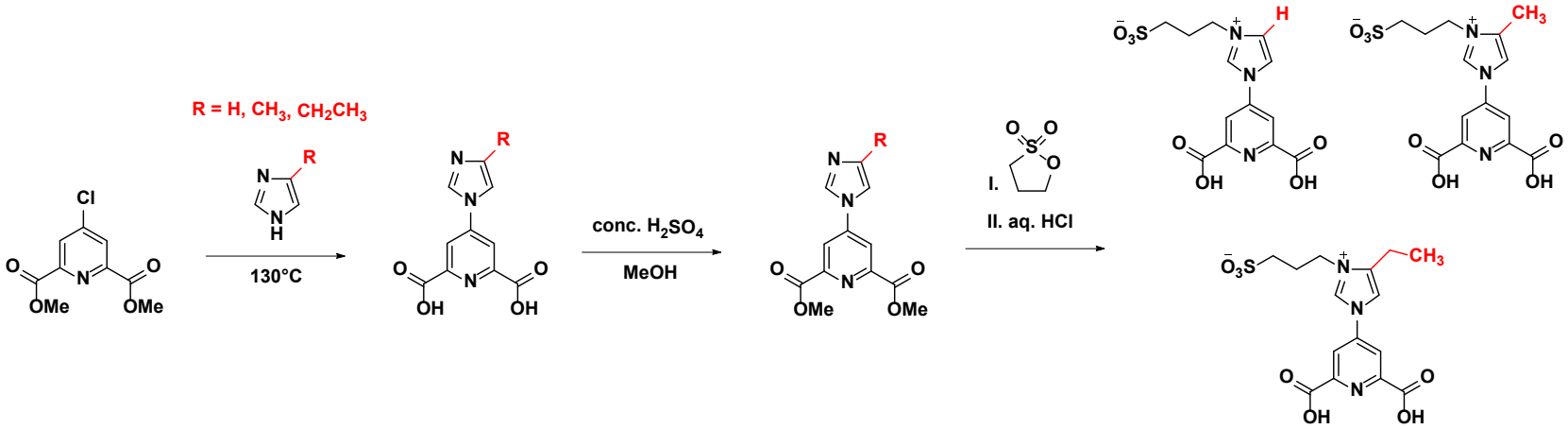
ACS Appl. Mater. Interfaces 2015, 7, 19651−19658



Zuniga, C.A.; Goods, J.B.; Cox, J.R.; Swager, T.M.
ACS Appl. Mater. Interfaces, **2016**, *8*, 1780.

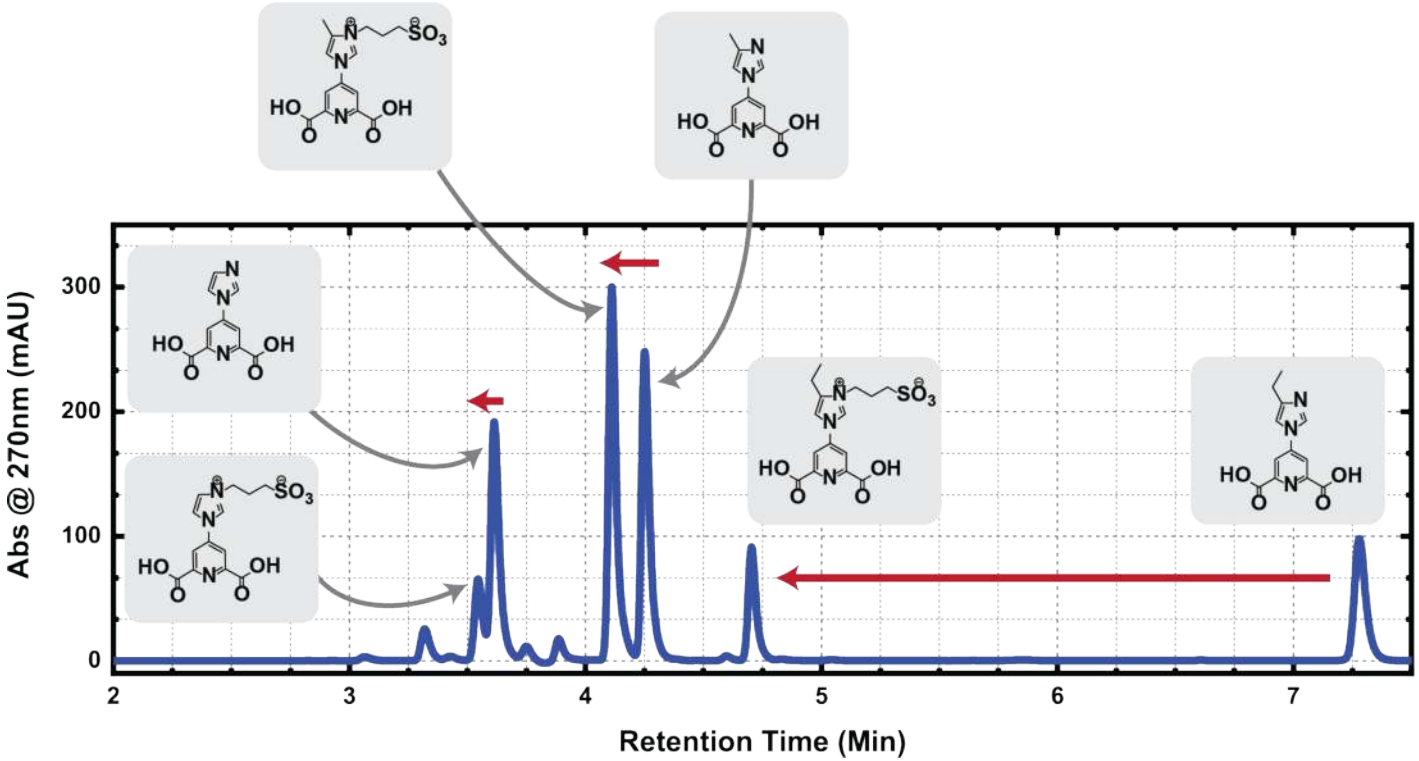
Sulfonated Analogs

Synthetic Pathway



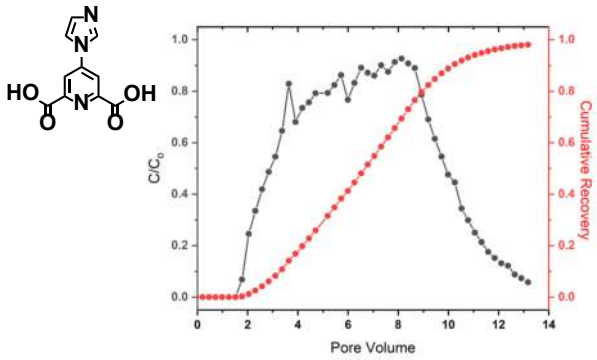
HPLC Separation

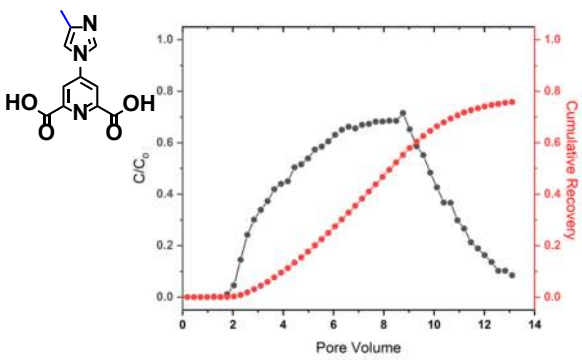
Sulfonated Analogs with Shorter Retention Time

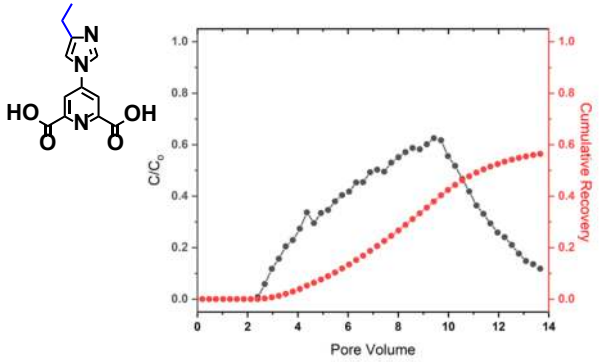


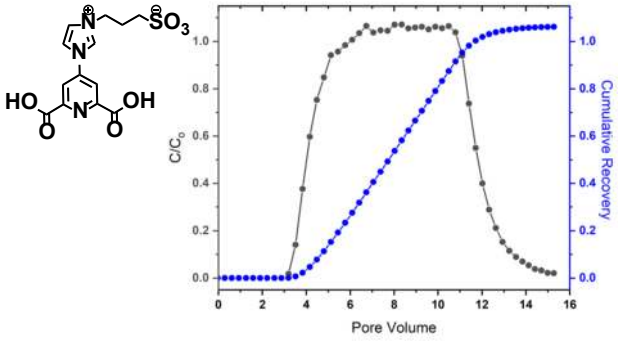
Coreflood Recovery

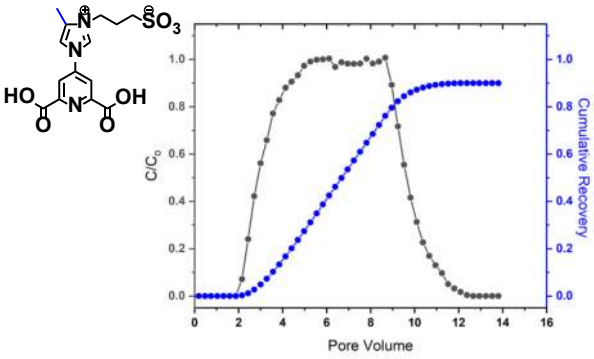
Sulfonation Improves Recovery

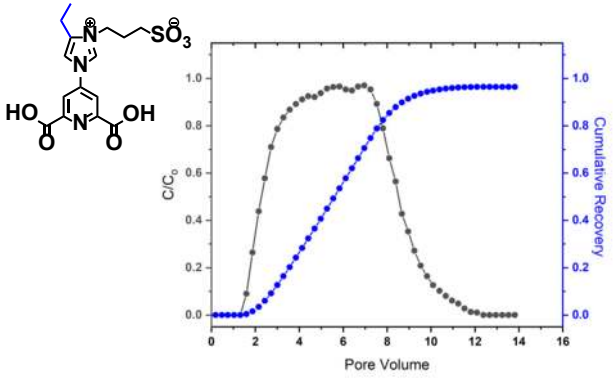






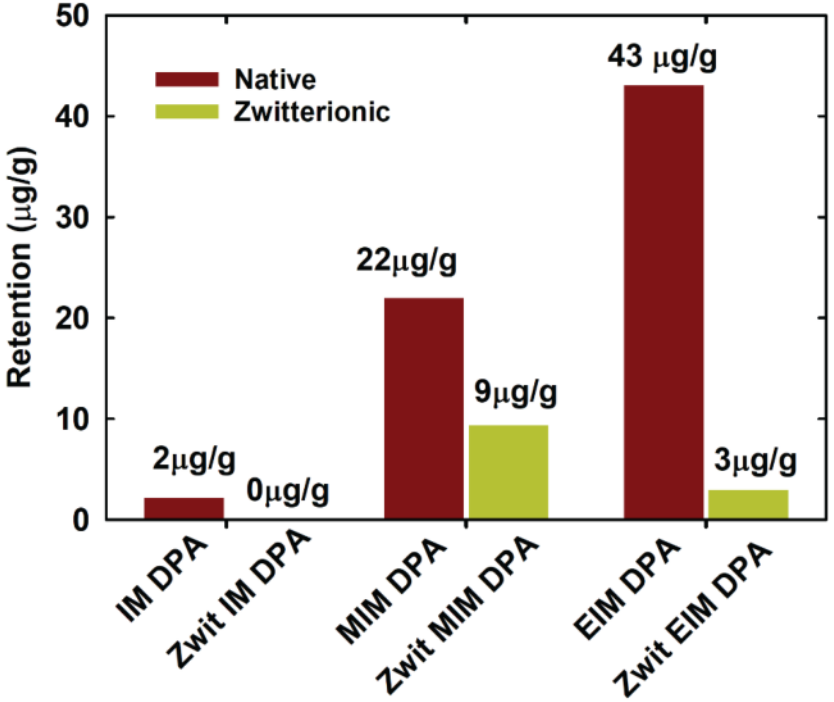




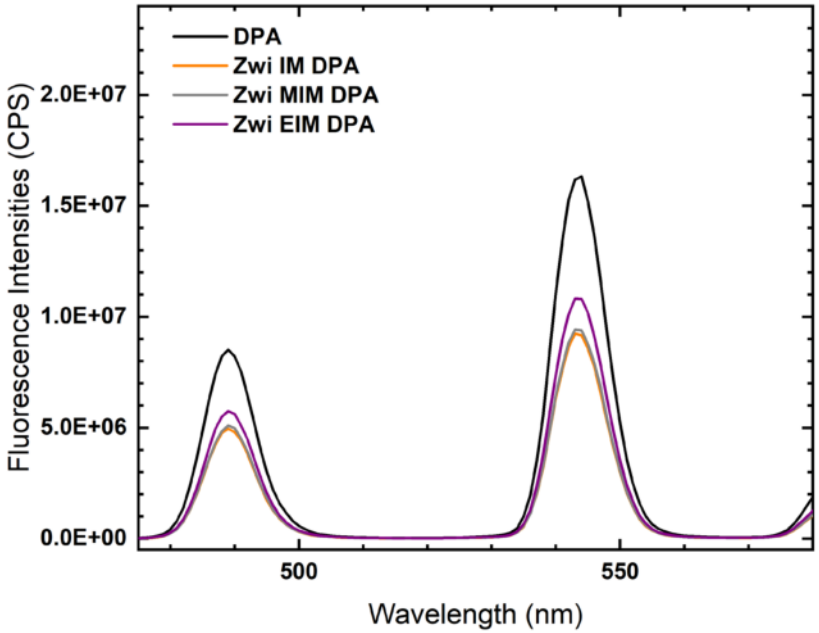


Retention & Photophysics

Summarized Retention to Rocks from Coreflood Studies



1µM DPA variants with 10µM terbium chloride



Fluorescence intensities of all sulfonated variants appear to have been normalized

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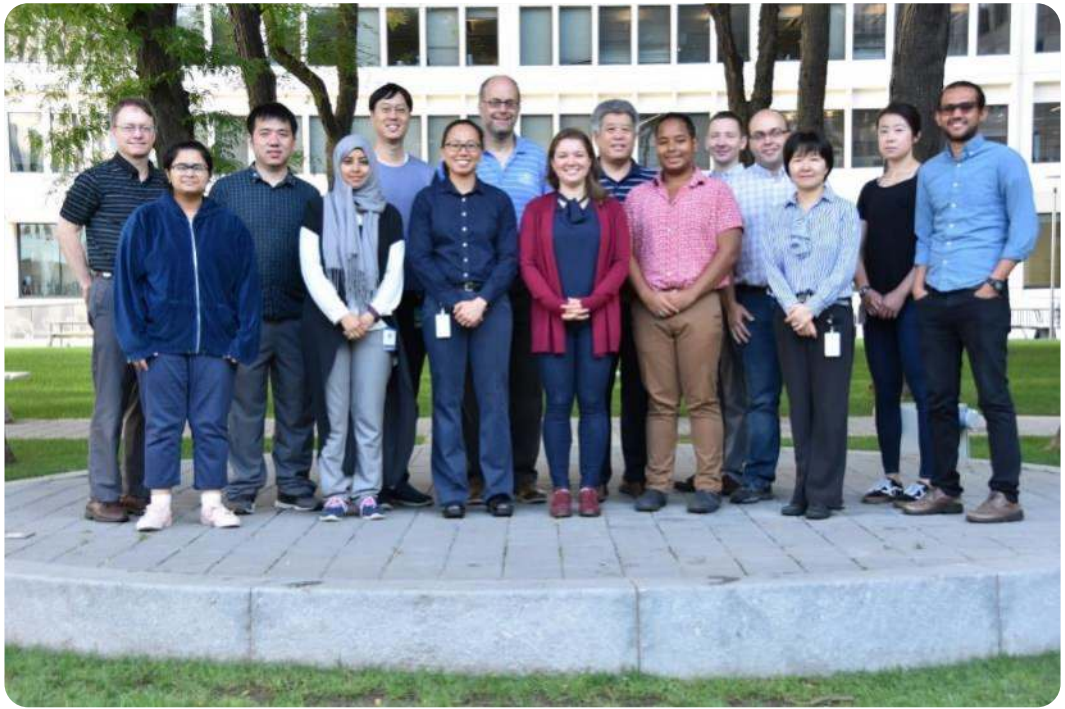
Conclusion

- DPA functionalized with increasingly hydrophobic imidazole substituents exhibits increasing retention to carbonate rocks
- Sulfonation of these DPA analogs dramatically reduces their retention
- HPLC retention time corroborates rock retention observations

Future Work

- Optimize synthetic pathway to reduce intermediate esterification step
- Complete photophysical characterizations

Acknowledgement



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