Building Hybrid Materials to Protect Reagents from Oxidative Damage.

Peter Zalupski, Mitchell Greenhalgh, Bruce Mincher
Idaho National Laboratory

Michael Schultz, Andrew Knight, U of Iowa

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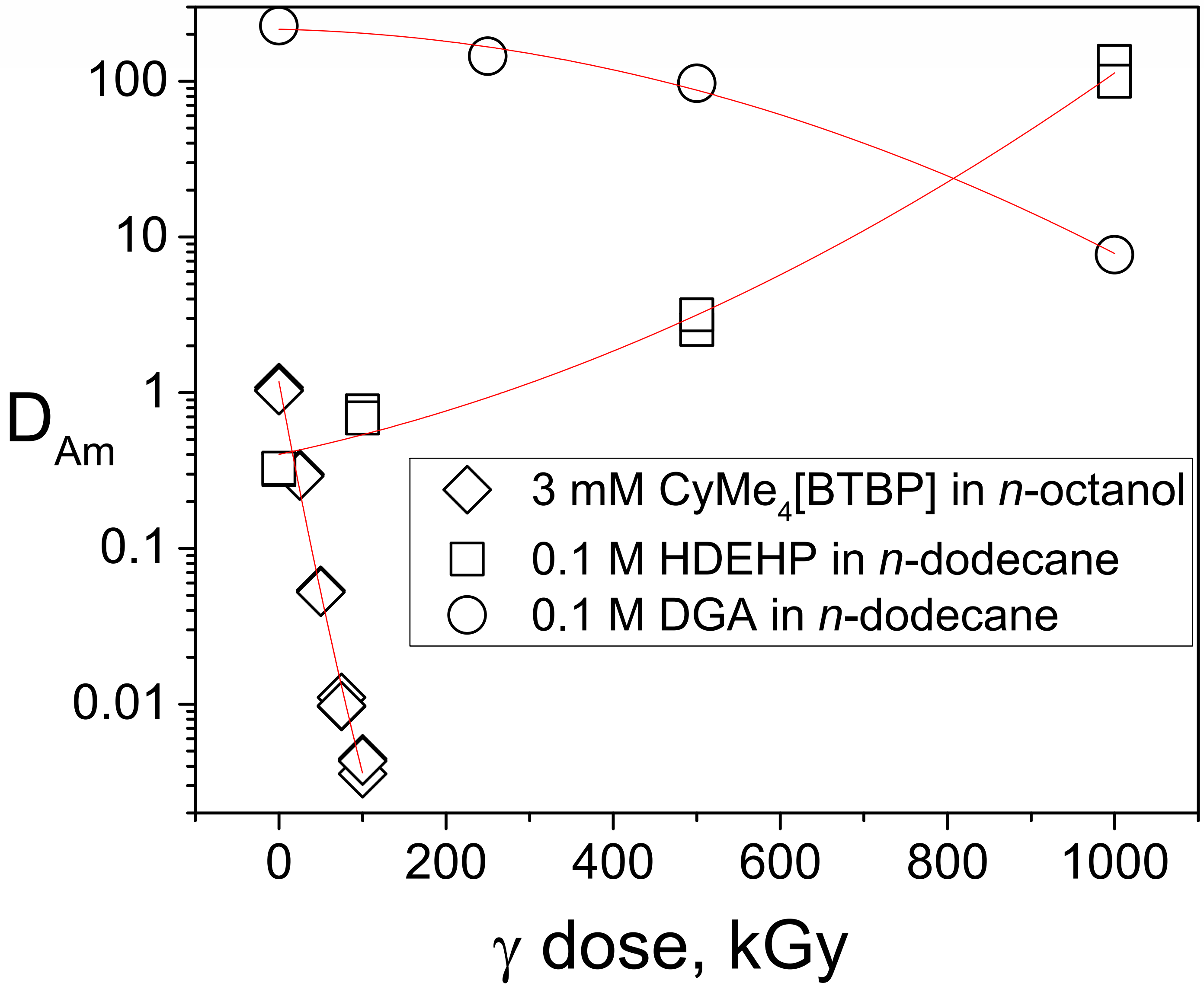
Radiolysis – the "scourge" of separations?

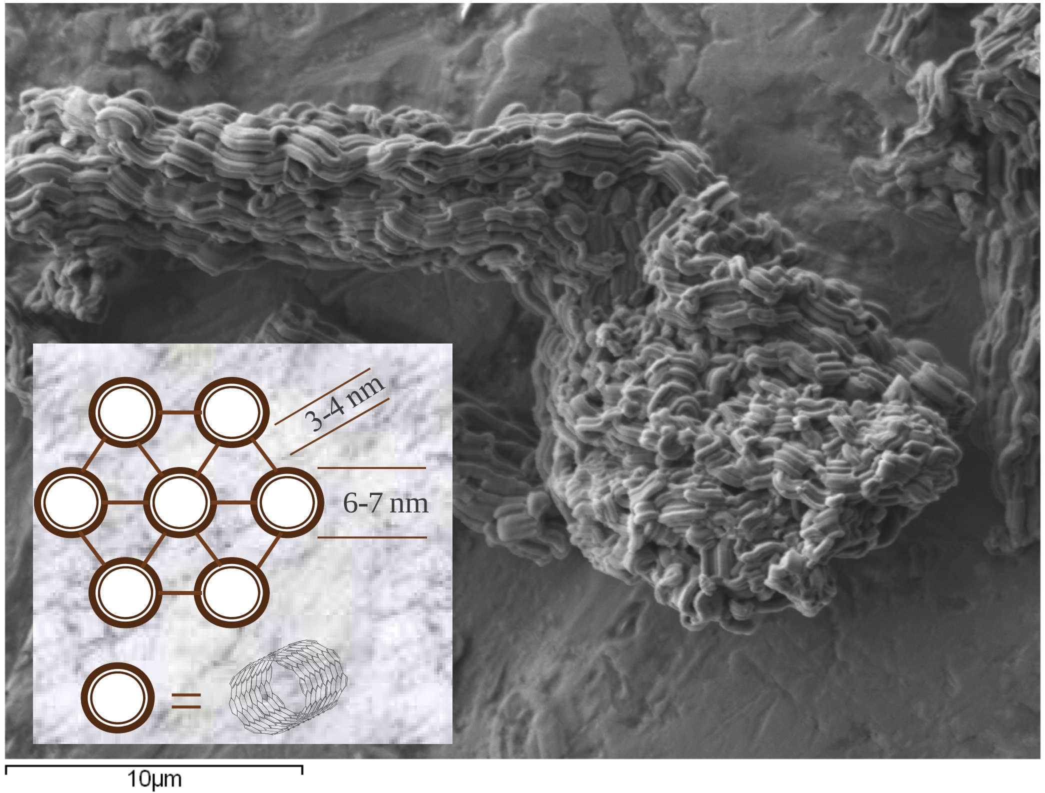


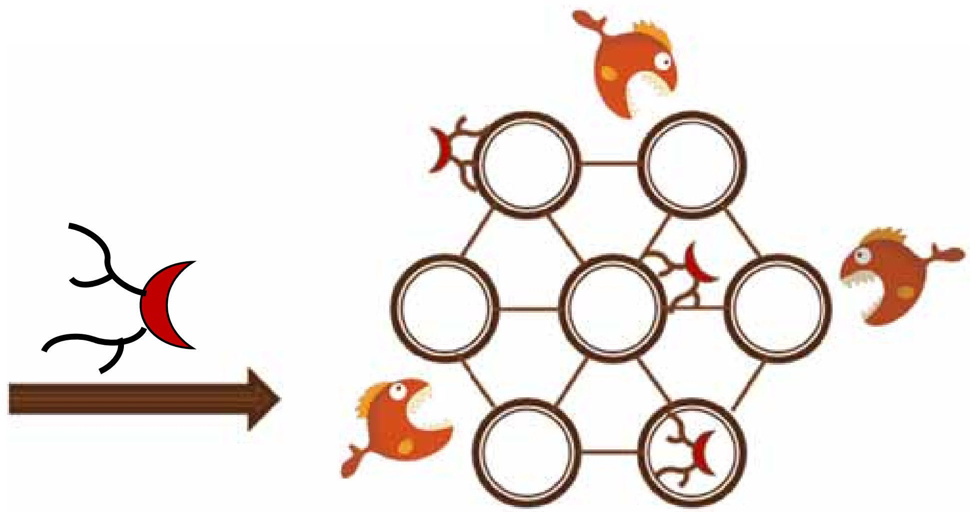
- Impacts of γ radiolysis on the liquid-liquid distribution of americium vary drastically depending on the chemical composition of the non-aqueous environment

Ravi, J.; Selvan, B.R.; Venkatesan, K.A.; Antony, M.P.; Srinivasan, T.G.; Vasudeva Rao, P.R. J. Radioanal. Nucl. Chem. **2014,** 299, 879-885. (DGA data)

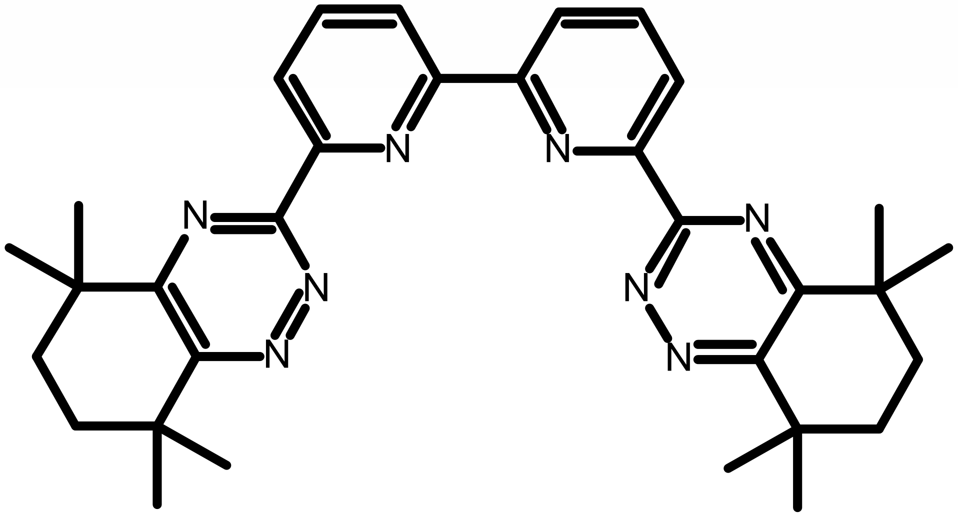
Can we protect molecules via encapsulation?

Research efforts seek to explore “shielding” properties of mesoporous carbon nanostructures, which will be utilized as encapsulating hosts for the metal ion complexing reagents. The hybrid materials are tested for their ability to alleviate the damaging influence of free radicals produced when the energy of radioactive decay is deposited in matter. Shortly, the project seeks antioxidizing benefits of such hybrid capsules.





Radioprotection concept demonstration for:



1) Verify $CyMe_4BTBP$

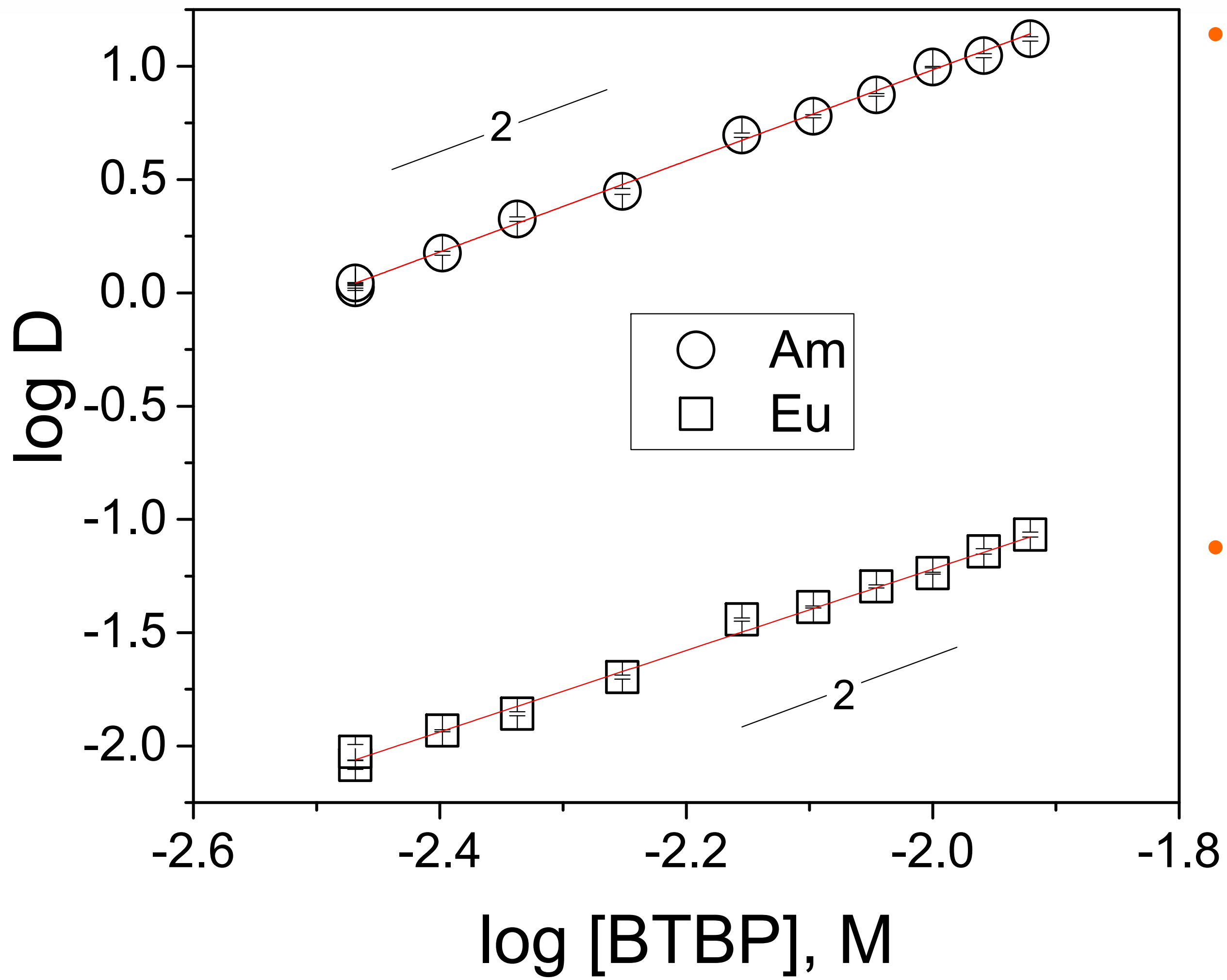
2) Prepare hybrid material

3) Verify hybrid maintains the metal ion coordination functionality

4) Develop a suitable platform to be used to study the radioprotection concept

5) Irradiate “unprotected” reagent in conventional SX system and “protected” reagent in mesoporous carbon framework

1) Verify $CyMe_4BTBP$



- SX conditions:

  Org: BTBP in *n*-octanol

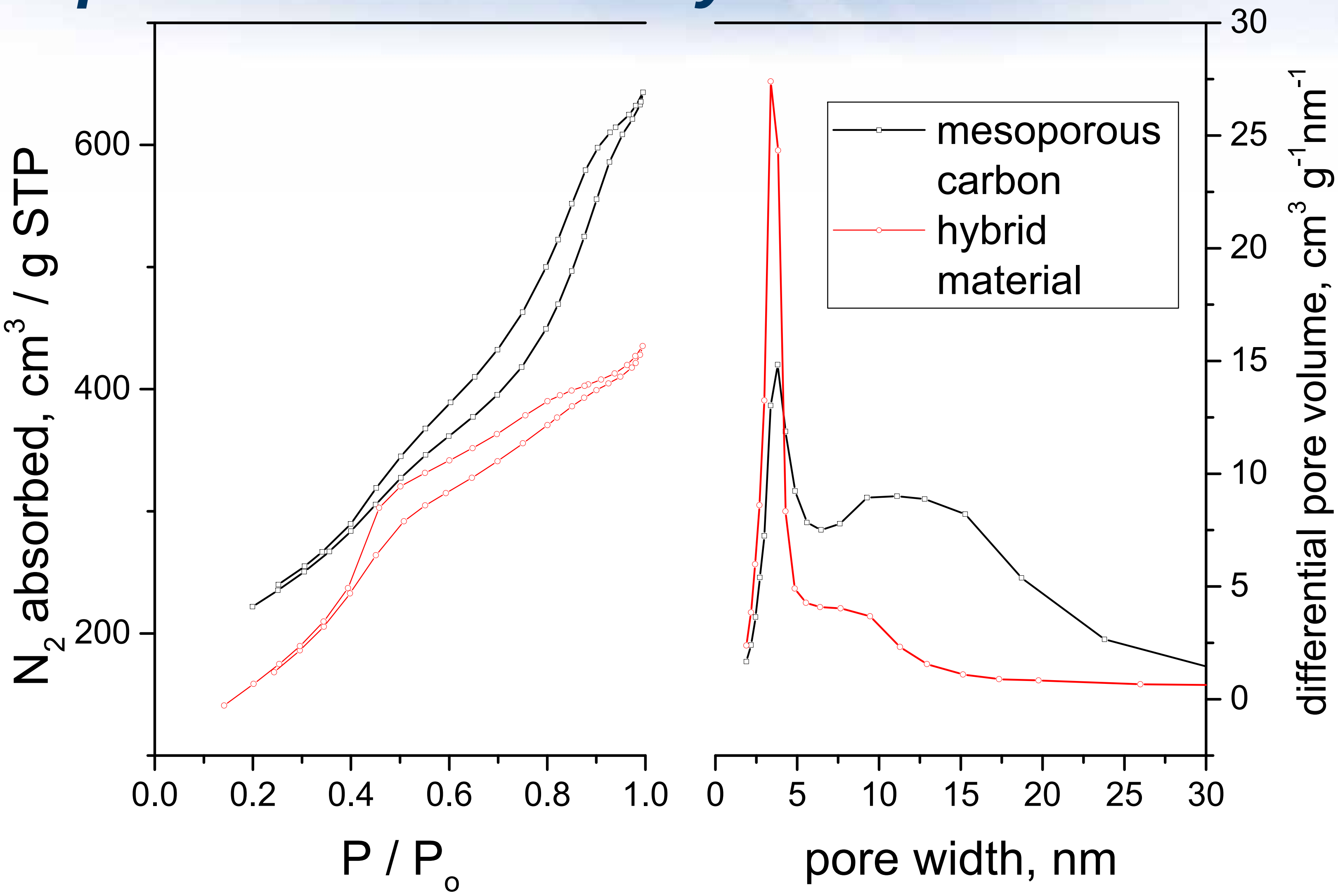
  Aq: 1 M HNO_3

  3 x pre-equilibration

  180 min contact

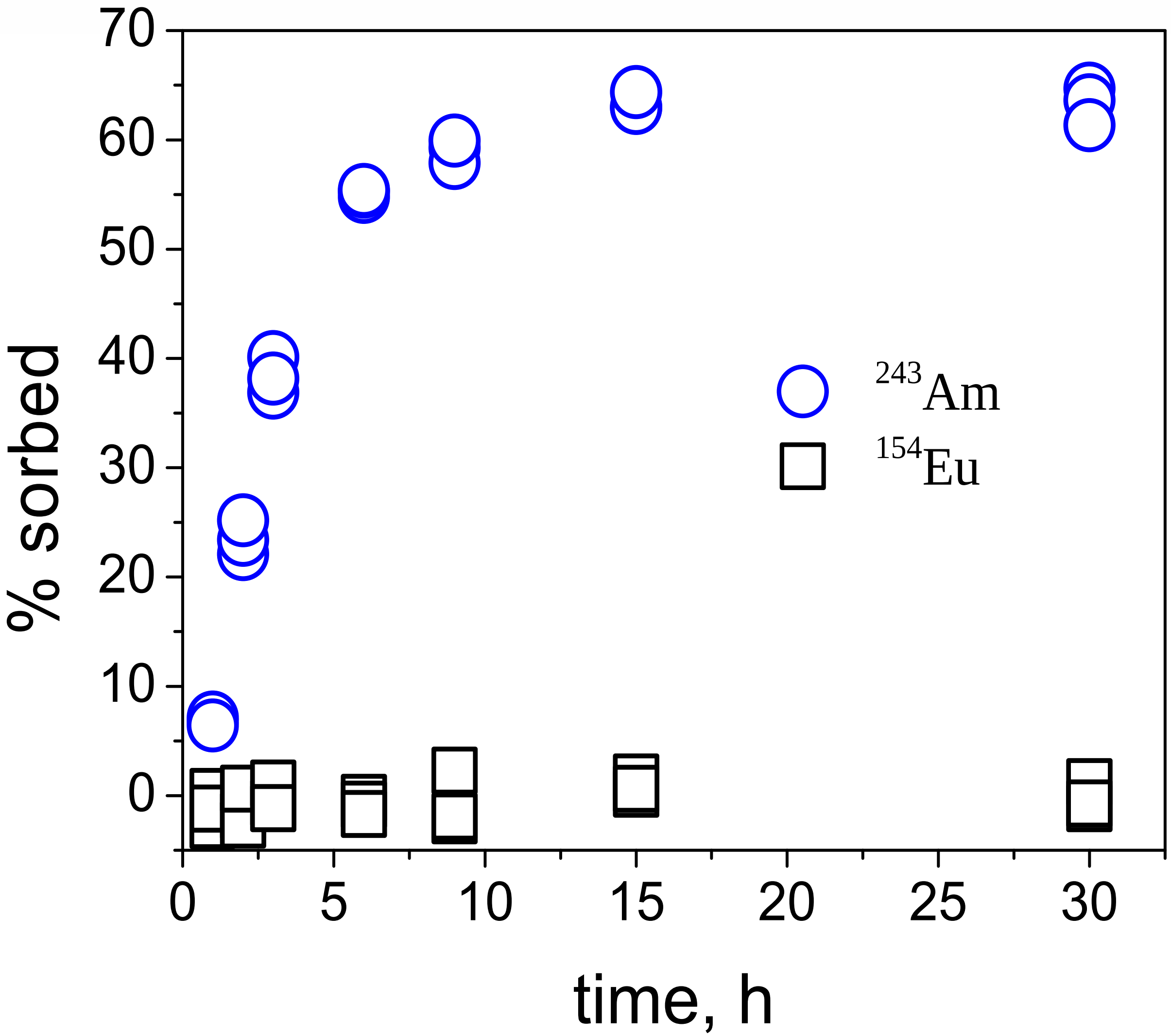
- Expected SX behavior for $CyMe_4BTBP$ was observed based on collected distribution ratios, ligand dependency slopes, and trivalent actinide / trivalent lanthanide differentiation.

2) Prepare CMK / BTBP hybrid



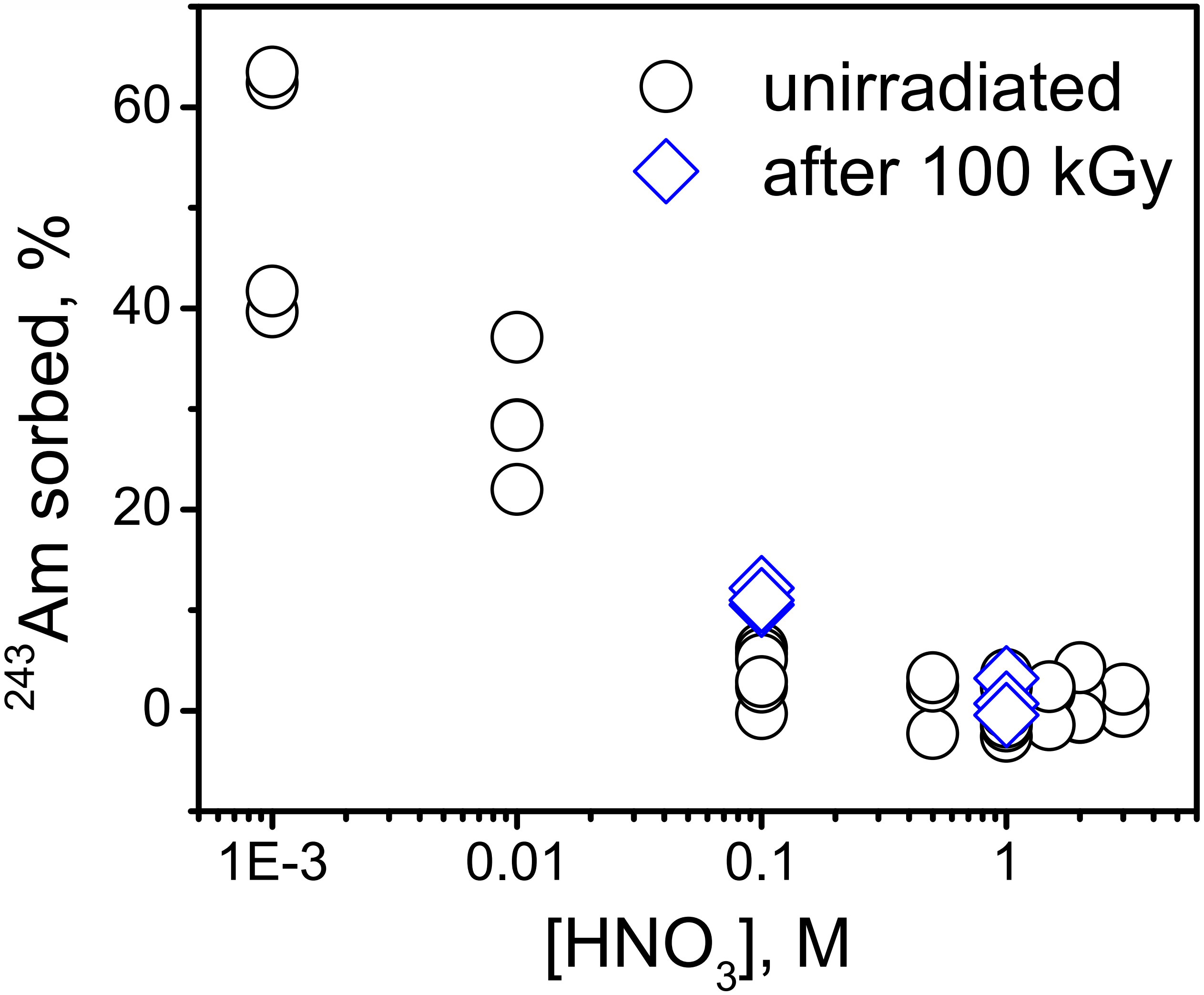
- Due to high hydrophobicity of carbon materials various molecular entities may adsorb within their porous framework
- N_2 adsorption isotherm (BET analysis) reveals that pore size distribution maxima has shifted, indicating that BTBP adsorbed inside the mesopores of CMK-3

3) Verify hybrid maintains functionality



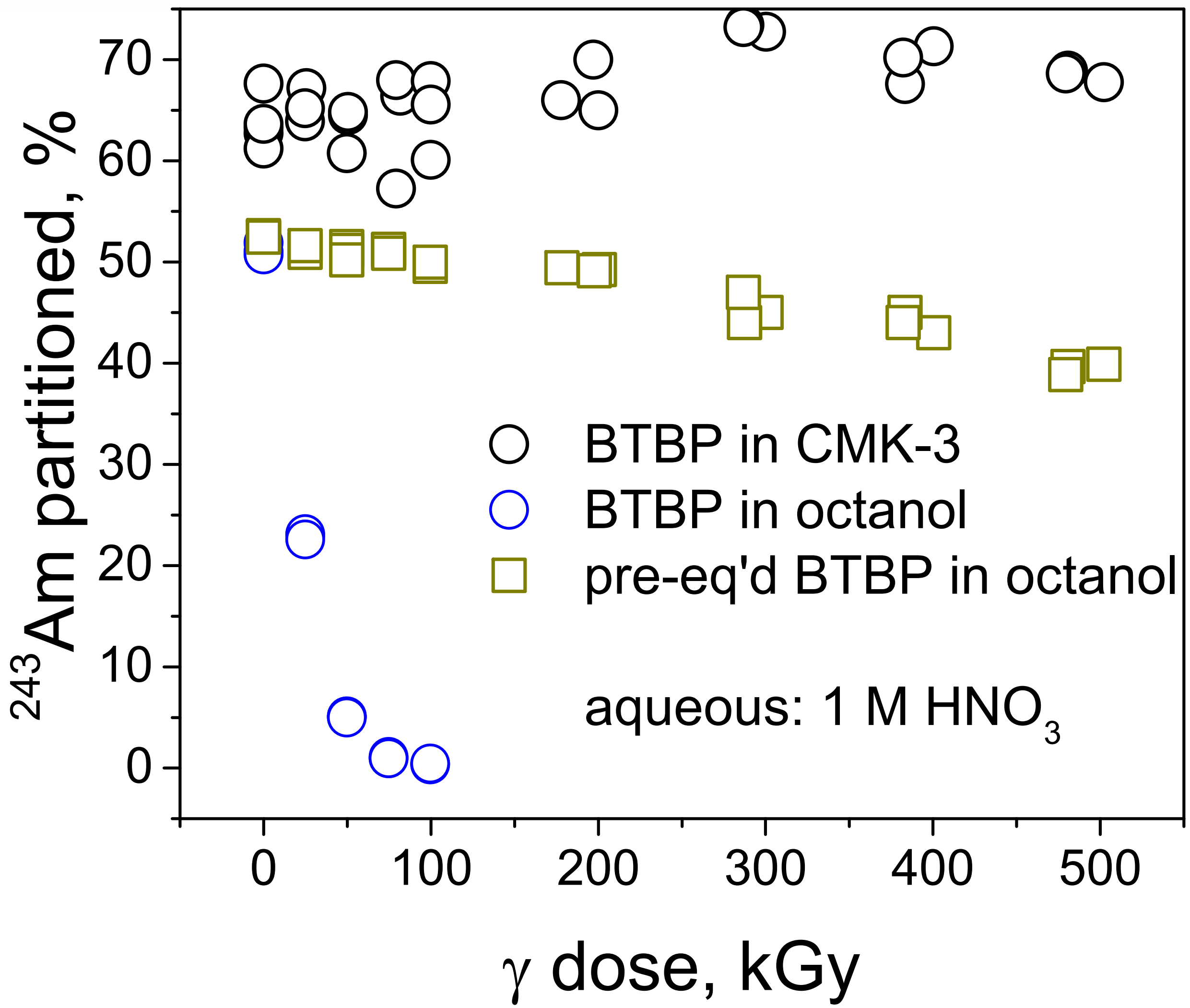
- Expected trivalent actinide / trivalent lanthanide differentiation is maintained after adsorption of nitrogen heterocycle inside the mesoporous framework
- Challenging complexation kinetics are magnified due to steric constraints of immobilized ligand

4) Develop a suitable platform for demonstration



- Mesoporous carbons tested (CMK-3) adsorb trivalent *f*-elements at mildly acidic conditions
- Contact time, and coinciding oxidation of CMK-3 surfaces, does not alter adsorption efficiency
- γ-radiation appears to slightly influence adsorption from 0.1 M HNO_3

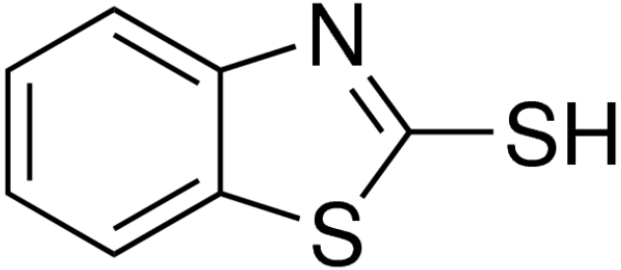
5) Impact of γ dose on Am^{3+} distribution – comparison of the "protected" and traditional SX systems

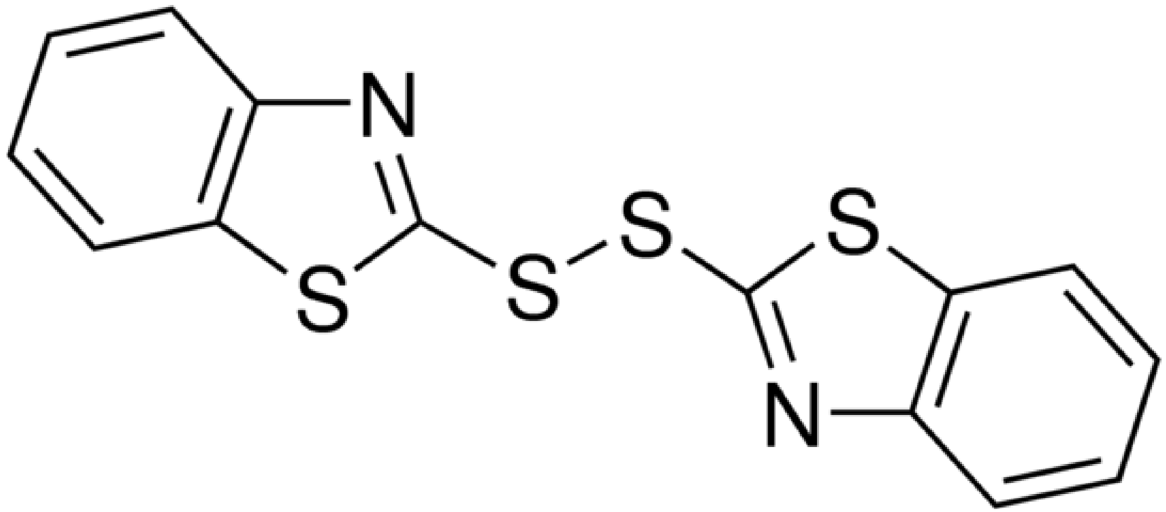


- Liquid-liquid (3.4 mM BTBP in octanol), and solid-liquid (15 % w/w BTBP encapsulated in CMK-3) systems received up to 500 kGy dose in a ^{60}Co γ irradiator
- Smaller effects of radiolytic damage were observed for this liquid-liquid system, relative to HDEHP
- Additional determinations are needed to reduce the uncertainty limits for the hybrid system

Ongoing work

- hybrid materials based on sulfur-functionalized reagents have been prepared to monitor whether the disulfide bridge mediated oxidation is slower when shielded by mesoporous carbon





- In-situ free radical production will enable delivery of Gy dose quantities to carefully monitor the degradation of mercaptobenzothiazole

Acknowledgements

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- Thank you for your attention.