INL/CON-22-67196-Revision-0

Impact of f-element complexation on the radiolytic robustness of separations ligands

May 2022

Changing the World's Energy Future

Gregory P Horne

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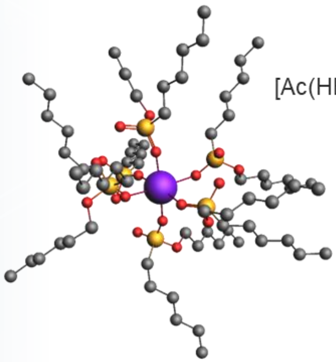
May 17th 2022

Gregory P. Horne
Center for Radiation Chemistry Research



Impact of *f*-element complexation on the radiolytic robustness of separations ligands

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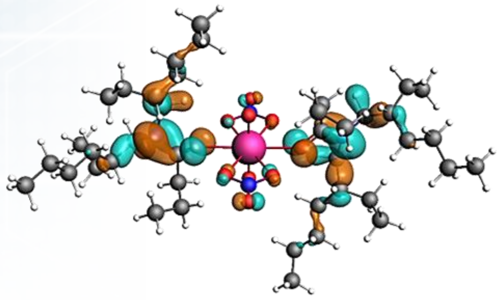


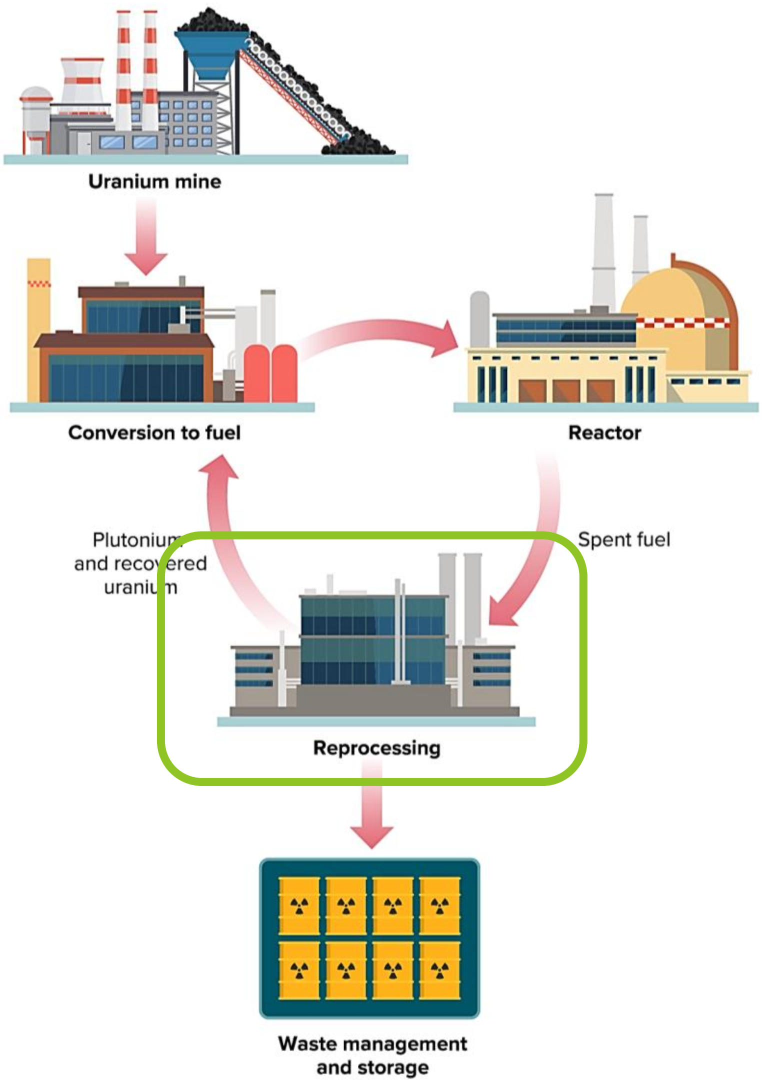
Los Alamos National Laboratory
2022 Actinide Separations Conference

NTRD Nuclear Technology Research & Development

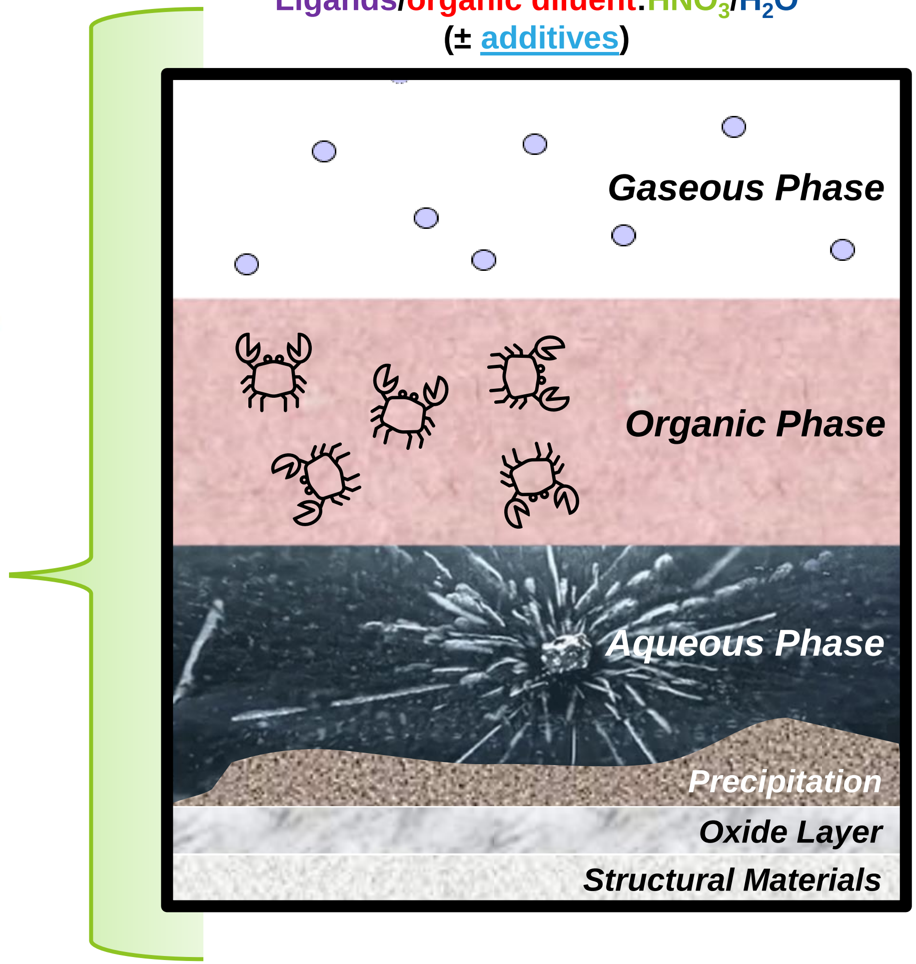
Material Recovery & Waste Form Development

INL Idaho National Laboratory

Reprocessing used nuclear fuel



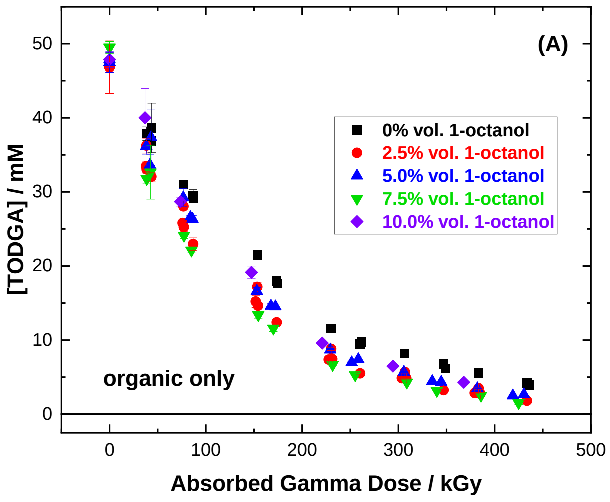
Solvent Extraction Reprocessing
Ligands/organic diluent:HNO_3/H_2O
(± additives)

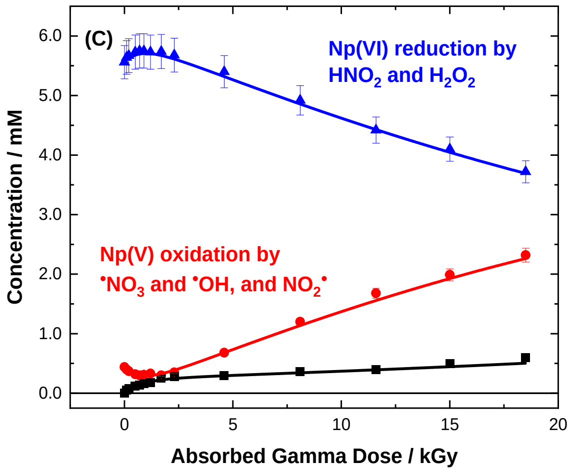


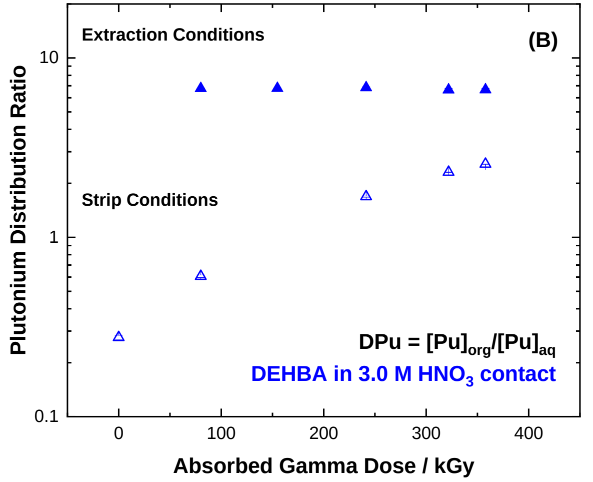
- Strategies and Considerations for the Back End of the Fuel Cycle, Nuclear Technology Development and Economics, NEA No. 7469, **2021**.
- Bruffey *et al.*, Innovative Separations R&D Needs for Advanced Fuel Cycles Workshop, August 30-September 1, 2021. Report for the US Department of Energy, Office of Nuclear Energy Workshop on Innovative Separations R&D Needs for Advanced Fuel Cycles, **2022**, under review.

Reprocessing radiation challenges

- **Destruction of active molecules**
- **Degradation product formation**
- **Metal ion redox chemistry**







- Horne, Zarzana, Rae, Cook, Mezyk *et al.*, *PCCP*, **2020**, *22*, 24978.
- Horne, Zarzana, Grimes, Rae, Ceder *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, Grimes, Mincher, and Mezyk, *J. Phys. Chem. B*, **2016**, *120 (49)*, 12643.

Reprocessing radiation chemistry

Water Radiolysis

$H_2O \rightsquigarrow e^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$

Indirect Radiation Effects

$HNO_3 + {}^\bullet OH \rightarrow {}^\bullet NO_3 + H_2O$

$NO_3^- + e^- \rightarrow NO_3^{\bullet 2-}$

$NO_3^{\bullet 2-} + H_2O \rightarrow {}^\bullet NO_2 + 2OH^-$

$NO_3^- + H^\bullet \rightarrow HNO_3^- \rightarrow {}^\bullet NO_2 + OH^-$

${}^\bullet NO_2 + {}^\bullet NO_2 \rightleftharpoons N_2O_4$

$N_2O_4 \rightarrow HNO_2 + HNO_3$

Direct Radiation Effects

$NO_3^- \rightsquigarrow NO_3^{-*} \rightarrow NO_2^- + O$

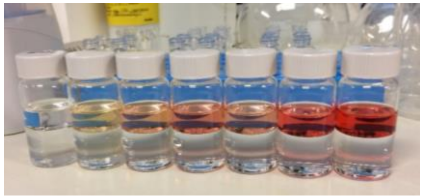
$HNO_3 \rightsquigarrow HNO_3^* \rightarrow HNO_2 + O$

$NO_3^- \rightsquigarrow {}^\bullet NO_3 + e^-$

$HNO_3 \rightsquigarrow {}^\bullet NO_3 + H^\bullet$

Alkane Radiolysis

$R\text{-}CH_3 \rightsquigarrow e^-, RH^{\bullet +}, RH^\bullet, {}^\bullet CH_3, H^\bullet, H_2$



- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

Reprocessing radiation chemistry

Water Radiolysis

Direct Radiation Effects

<u>Key Transient Species</u>

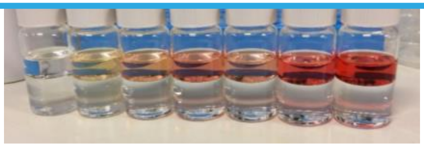
e_{aq}^{-}, $H^{\bullet}$, and **$^{\bullet}OH$** from **H_2O**

$^{\bullet}NO_3$ from **HNO_3**

$RH^{\bullet+}$ from ***n*-dodecane**

H_2

$N_2O_4 \rightarrow HNO_2 + HNO_3$



- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

Complexation effects

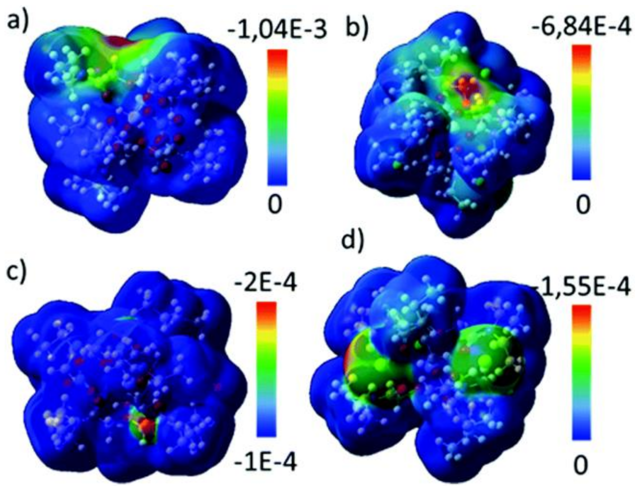
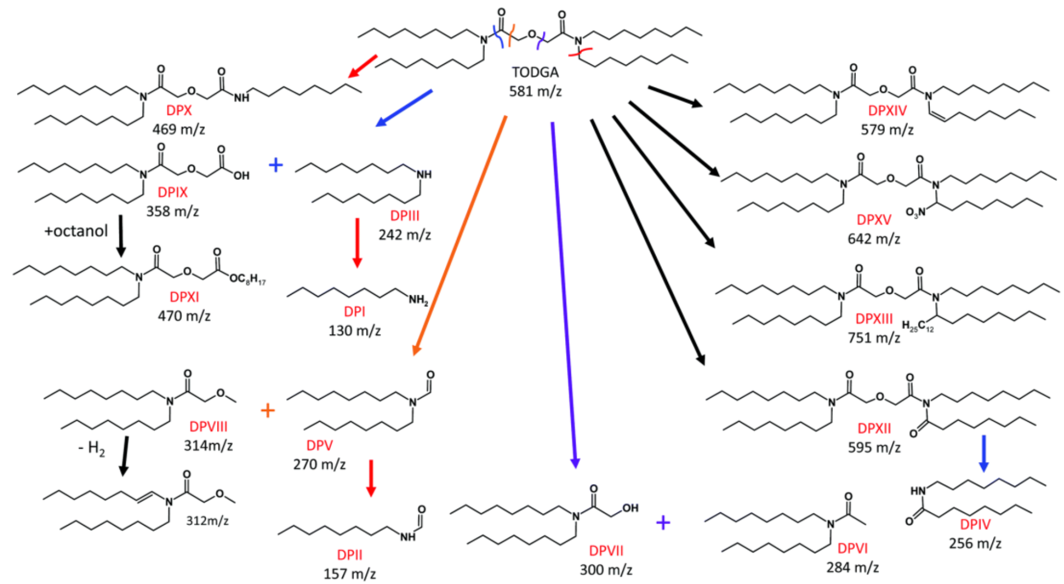
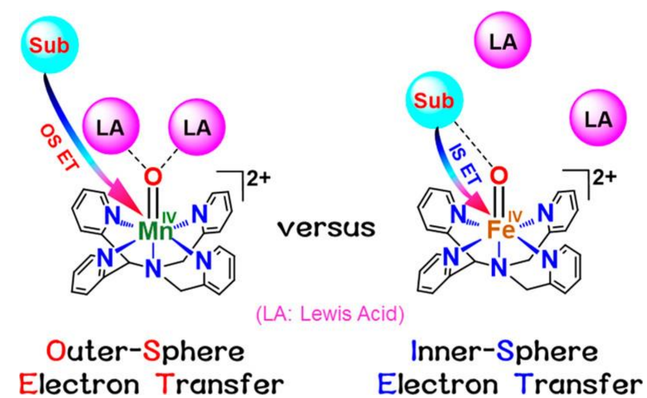


Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** $[Nd(TEDGA)_3](NO_3)_3$, **(b)** $[Nd(TEDGA)_3]Cl_3$, **(c)** $[Am(TEDGA)_3](NO_3)_3$, and **(d)** $[Am(TEDGA)_3]Cl_3$.



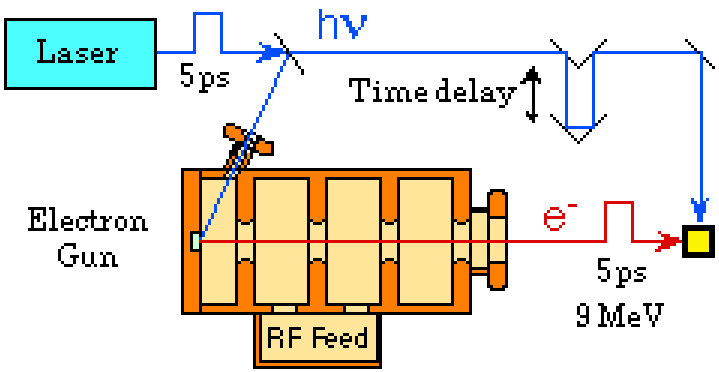
"…in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products." Kimberlin *et al.*, *PCCP,* **2022**.



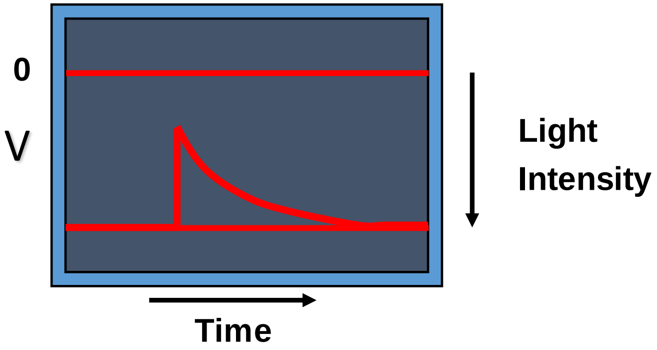
Sharma, Lee, Li, Nam, and Fukuzumi, *Inorg. Chem.*, **2019**, *58 (20)*, 13761.

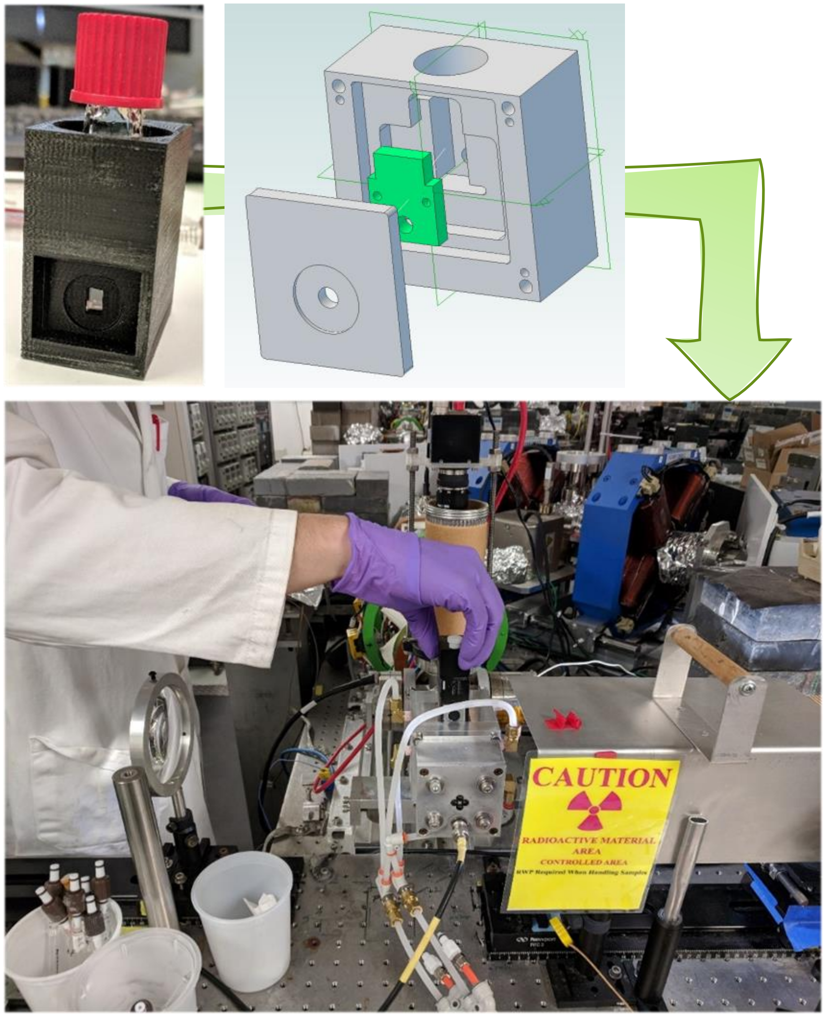
- Bhattacharyya and Kundu, Int. *J. Radiat. Phys. Chem.*, **1971**, *3*, 1.
- Kundu and Matuura, *Int. J. Radiat. Phys. Chem.*, **1975**, *7*, 565.
- Ilan and Czapski, *Biochimica et Biophysica Acta*, **1977**, *498*, 386.
- Buettner, Doherty, and Patterson, *Fed. Euro. Biochem. Soc.*, **1983**, *158 (1)*, 143.
- Kimberlin, Saint-Loius, Guillaumont, Cames, Guilbaid, and Berthon, PCCP, **2022**, *24*, 9213.

Electron pulse radiolysis



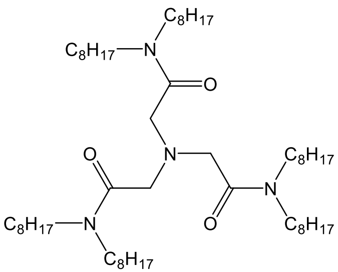
Transients are detected by optical absorption changes.

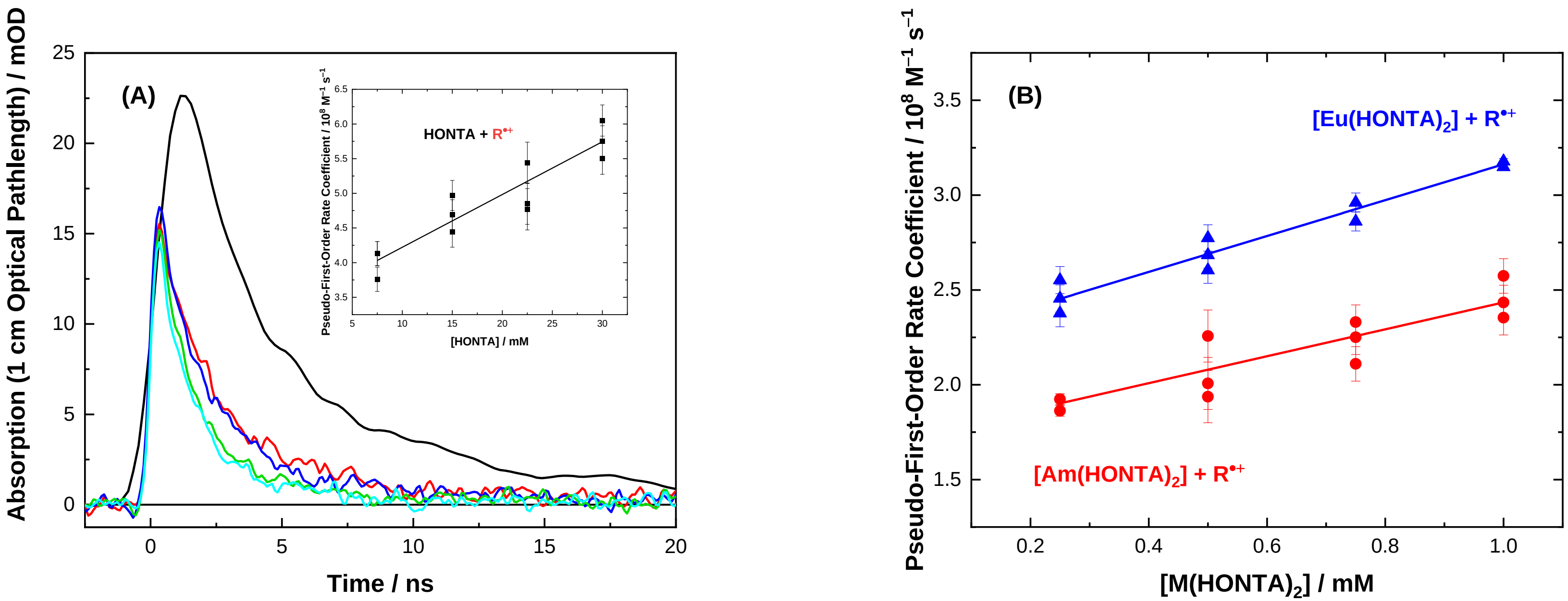




- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php

It all started with HONTA

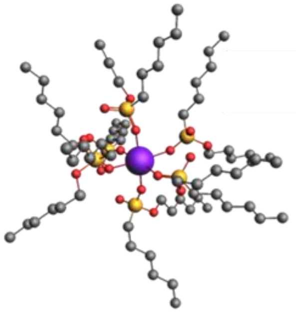


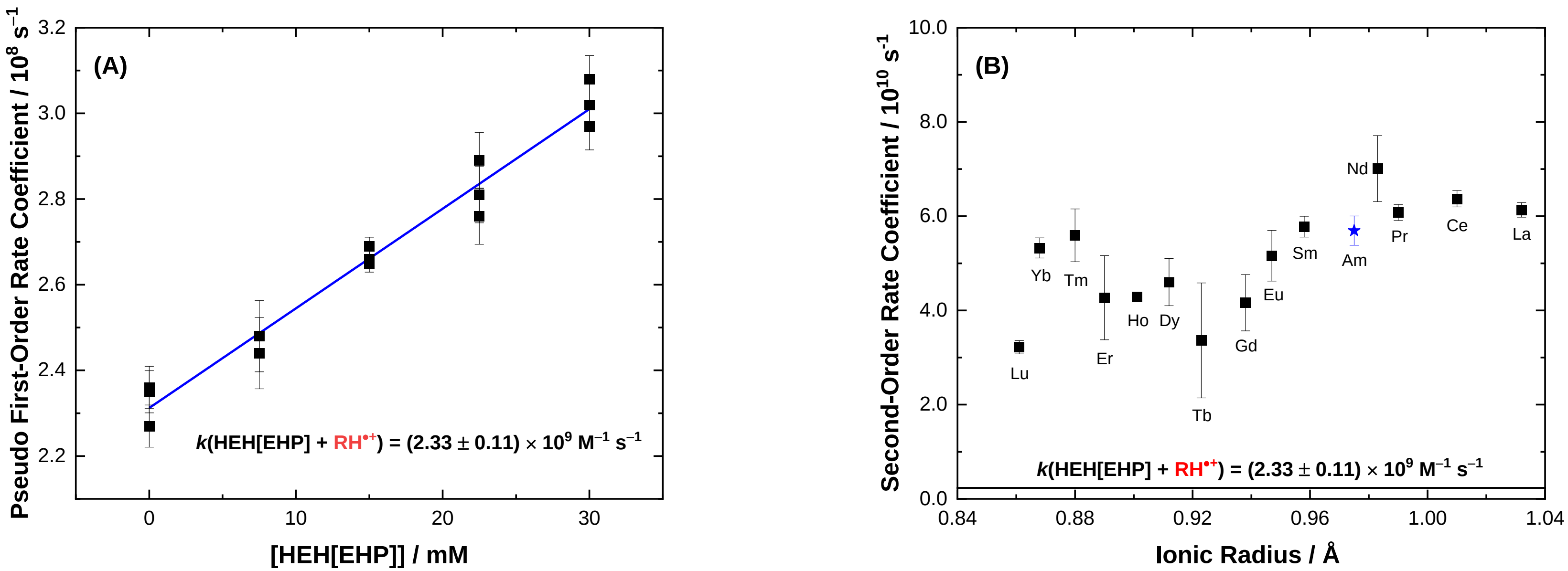


- Complexation of **HONTA** with either **Eu^{3+}** of **Am^{3+}** afforded an order of magnitude increase in rate coefficient (*k*):
  - *k*(**HONTA** + **$RH^{\bullet+}$**) = **(7.6 ± 0.8) × 10^9 M^{-1} s^{-1}.**
  - *k*(**$Am(HONTA)_2$** + **$RH^{\bullet+}$**) = **(7.1 ± 0.7) × 10^{10} M^{-1} s^{-1}.**
  - *k*(**$Eu(HONTA)_2$** + **$RH^{\bullet+}$**) = **(9.5 ± 0.5) × 10^{10} M^{-1} s^{-1}.**

- Toigawa, Peterman, Meeker, Grimes, Zalupski, Mezyk, Cook, Yamashita, Kumagai, Matsumura, Horne, *PCCP*, **2021**, *23*, 1343.

Then the HEH[EHP] saga



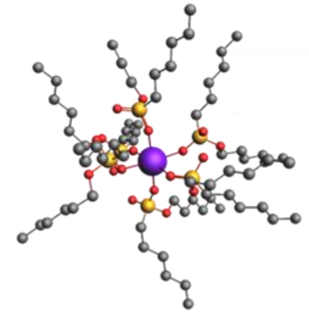


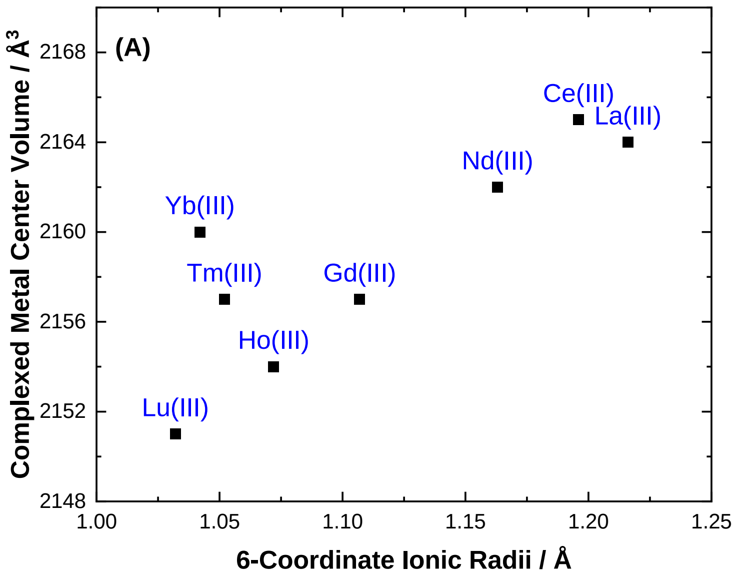
- **Methodology:** Δ[HEH[EHP]]/[M{(HEH[EHP])$_2$}$_3$] in 0.5 M DCM/*n*-dodecane; **RH•$^+$** decay measured at 800 nm over 200 ns using the *Brookhaven National Laboratory* (BNL) *Laser Electron Accelerator Facility* (LEAF).

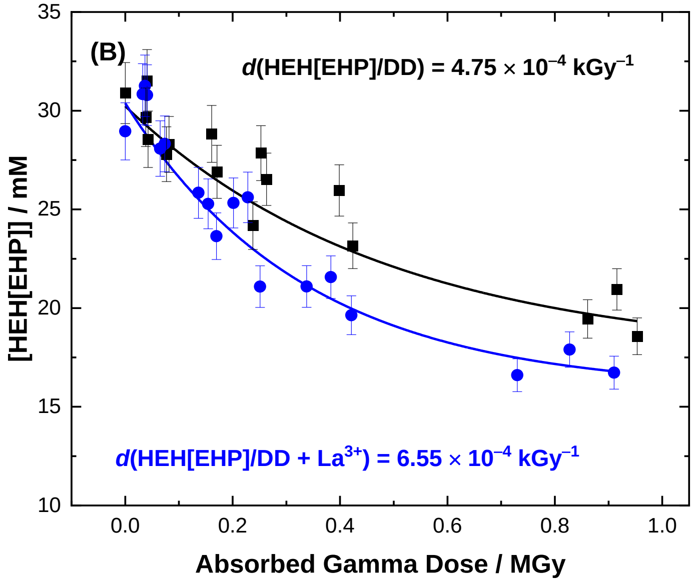
BROOKHAVEN NATIONAL LABORATORY

- Baxter, Cellis-Baros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *Dalton Trans.*, **2022**, *in preparation*.

Size Matters…







- **Computations:** Geometry optimization using ADF2020 (*GGA OPBE functional + ZORA/STO-TZP basis set for all atoms*); Wave functions using ORCA (*Hybrid PBE0 functional + DKH-def2-SVP/DKH-def2-TZVP/SARC-DKH-TZVP*); and QTAIM metrics obtained from DFT wave functions using the AIMALL software.

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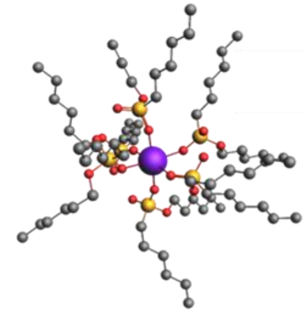
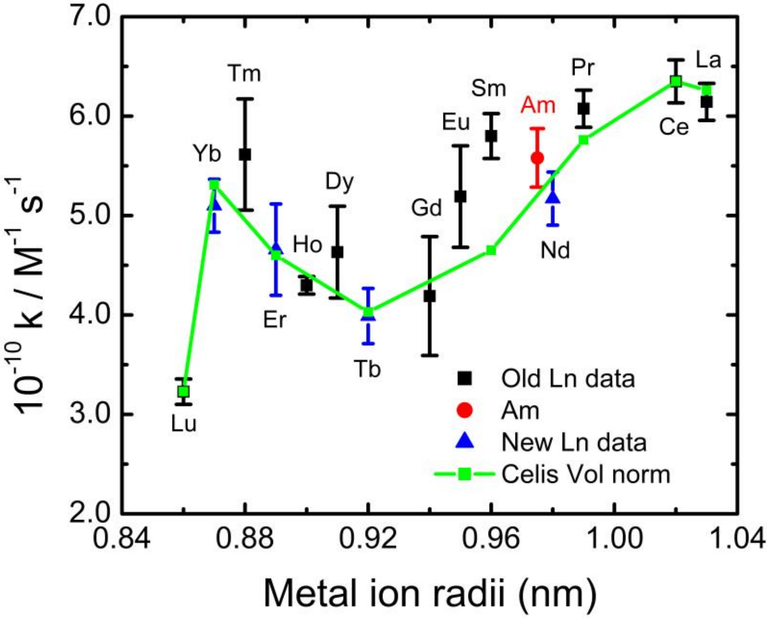
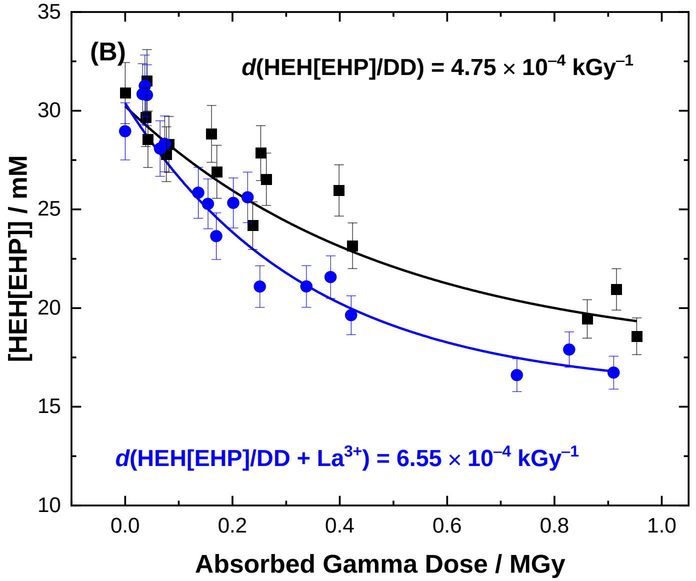
Size matters…







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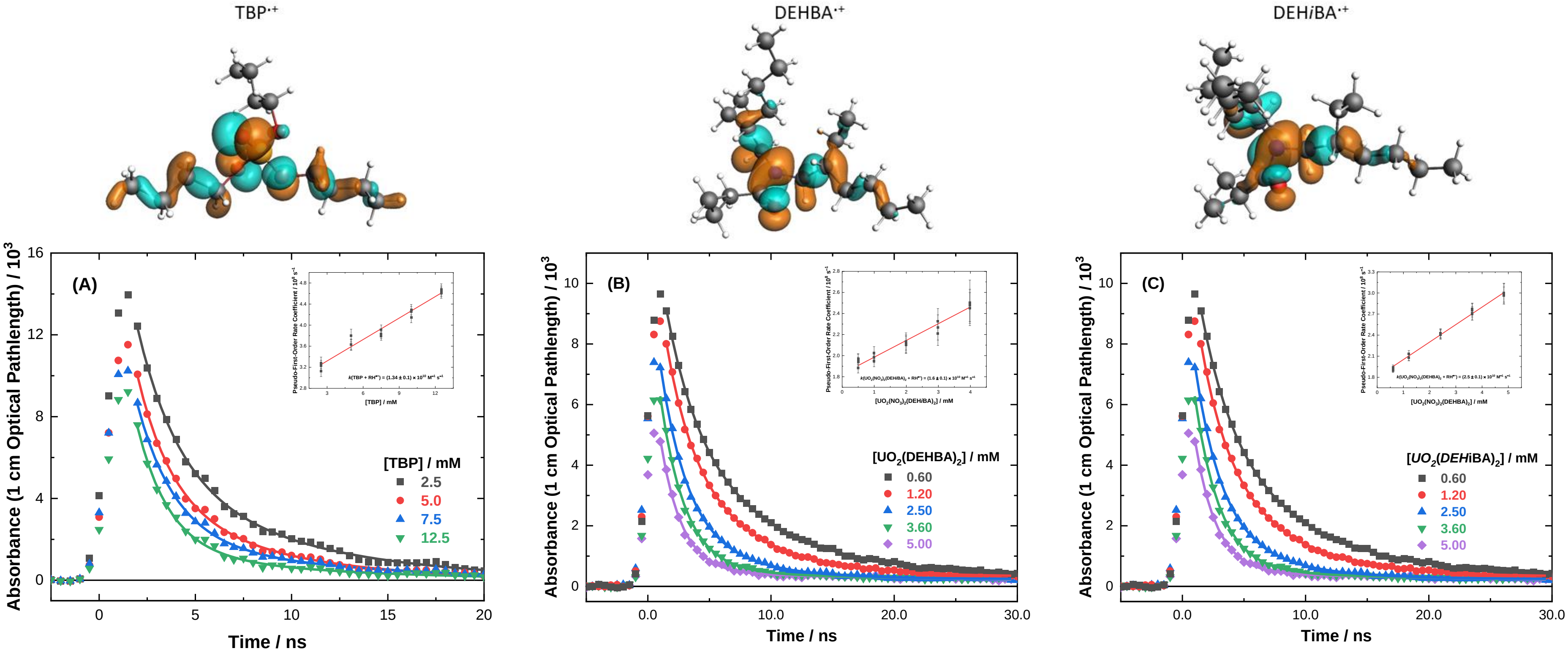
- Baxter, Cellis-Baros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *Dalton Trans.*, **2022**, *in preparation*.

Is there a ligand dependence?



- UO_2^{2+} complexation had negligible effect on the reaction of **TBP** with **RH•⁺**, k(**TBP** + **RH•⁺**) = **(1.3 ± 0.1) × 10¹⁰ M⁻¹ s⁻¹**.
- For **DEHBA** and **DEHiBA**, UO_2^{2+} complexation afforded a **2.6x** and **1.4x** increase in their respective rate coefficients, respectively.

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- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.

Is there a ligand dependence?

$[UO_2(NO_3)_2(TBP)_2]^{\cdot+}$ $[UO_2(NO_3)_2(DEHBA)_2]^{\cdot+}$ $[UO_2(NO_3)_2(DEH\textit{i}BA)_2]^{\cdot+}$

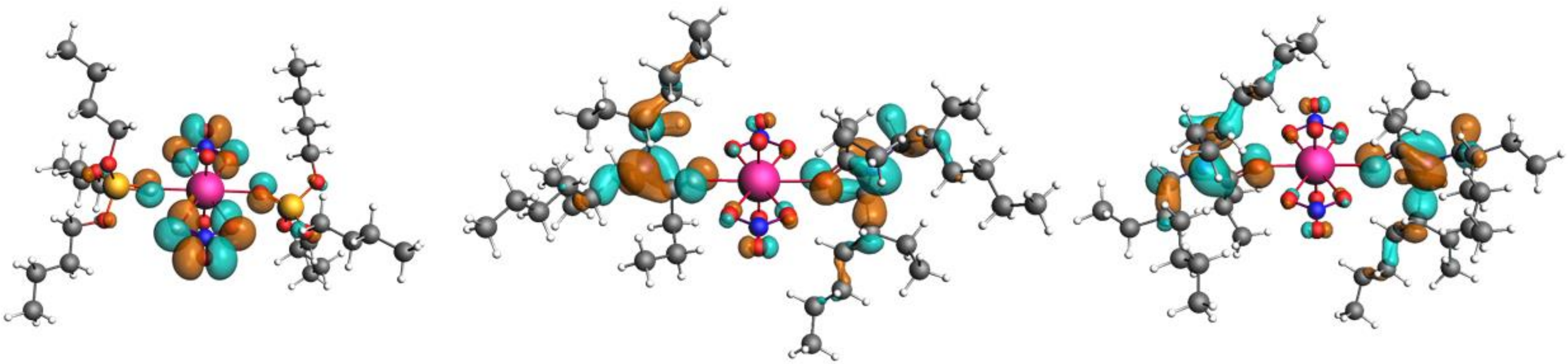

Table 1 Electronic structure calculation free energy (ΔG) values for the reaction of $RH^{\bullet+}$ with TBP, DEHBA, and DEHiBA for electron/hole transfer and proton transfer scenarios

Ligand	$\Delta G_{\text{electron/hole transfer}}$ (eV)	$\Delta G_{\text{proton transfer}}$ (eV)
TBP	0.16	−0.36
DEHBA	−0.88	−0.60
DEHiBA	−0.90	−0.57

Electron/Hole Transfer

$RH^{\bullet+} + \text{Ligand} \rightarrow RH + [\text{Ligand}]^{\bullet+}$

Proton Transfer

$RH^{\bullet+} + \text{Ligand} \rightarrow R^{\bullet} + [\text{Ligand(+H)}]^{+}$

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- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.
- Frisch, Trucks, Schlegel, Scuseria, Robb, *et al.*, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.
- ADF 2021.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

Conclusions

- Chemical kinetics were measured for the reaction of **RH•⁺** with *f*-element complexes with HONTA, HEH[EHP], TBP, DEHBA, and DEHiBA.
- Complexation has a profound effect on reaction kinetics, from changes in electron distribution to size.
- **Understanding the impact of complexation on the radiation-induced degradation mechanisms of reprocessing ligands is essential for accurate estimates of process viability.**

Berkeley
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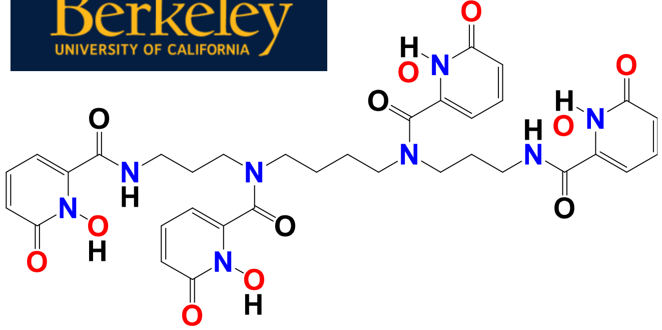

Radical	Rate coefficient (k, M^{-1} s^{-1})	
	HOPO	**Nd(HOPO)**
e_{aq}^{-} (10^{10})	3.17 ± 0.04	11.4 ± 0.1
$H^{•}$ (10^{9})	5.5 ± 0.2	5.5 ± 0.2
$^{•}OH$ (10^{10})	1.66 ± 0.06	1.05 ± 0.02
$^{•}NO_3$ (10^{9})	3.79 ± 0.10	2.61 ± 0.03

- Wanga, Abergel, McLacklan, Grimes, Pilgrim, O'Bryan, Cook, Mezyk and Horne, *Rad. Phys. Chem.*, **2022**, *in preparation*.

Acknowledgements

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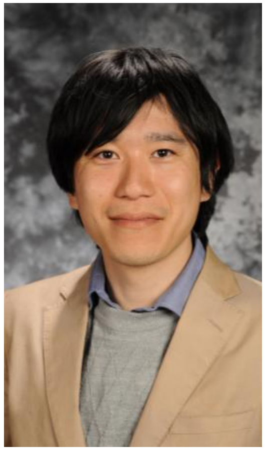

Material Recovery & Waste Form Development

NTRD Nuclear Technology Research & Development

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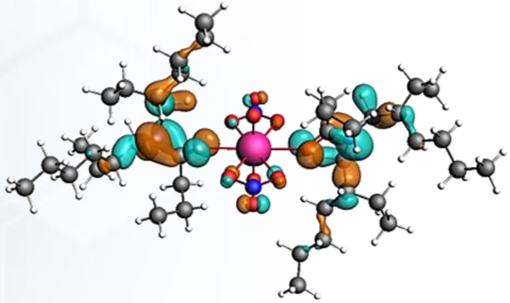
BROOKHAVEN NATIONAL LABORATORY

FLORIDA STATE UNIVERSITY

JAEA



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