INL/CON-23-72539-Revision-0

Impact of trivalent f-element complexation and chemical environment on the radiation-induced chemical reactivity of TODGA and HOPO ligands

May 2023

Changing the World's Energy Future

Gregory Peter Holmbeck

Idaho National Laboratory

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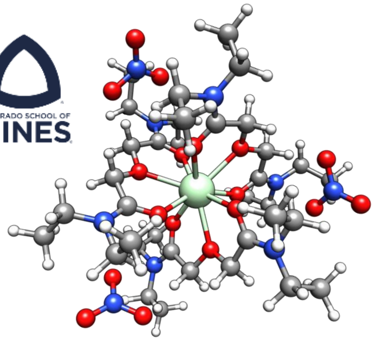
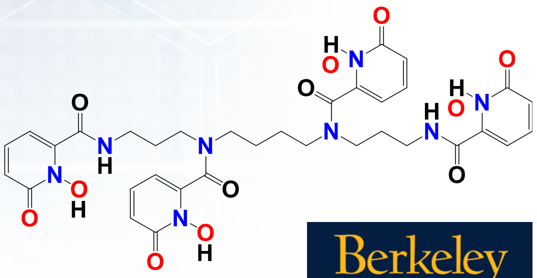
Chemistry Research



Impact of trivalent *f*-element complexation and chemical environment on the radiation-induced chemical reactivity of TODGA and HOPO ligands



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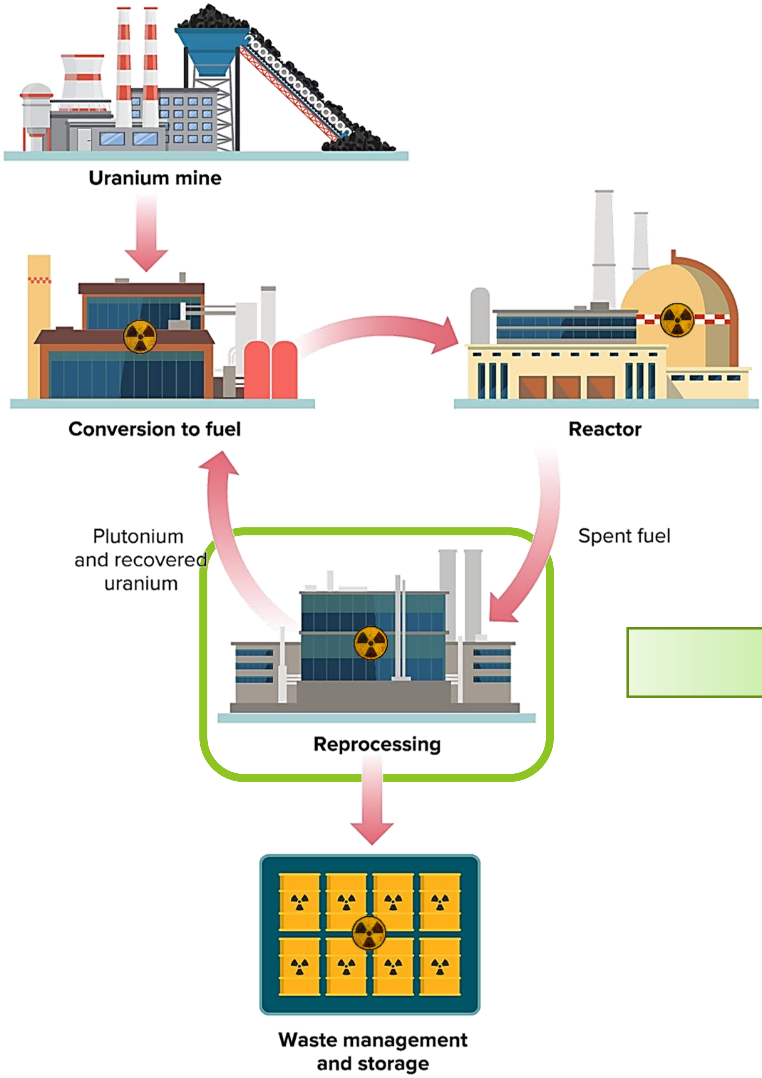
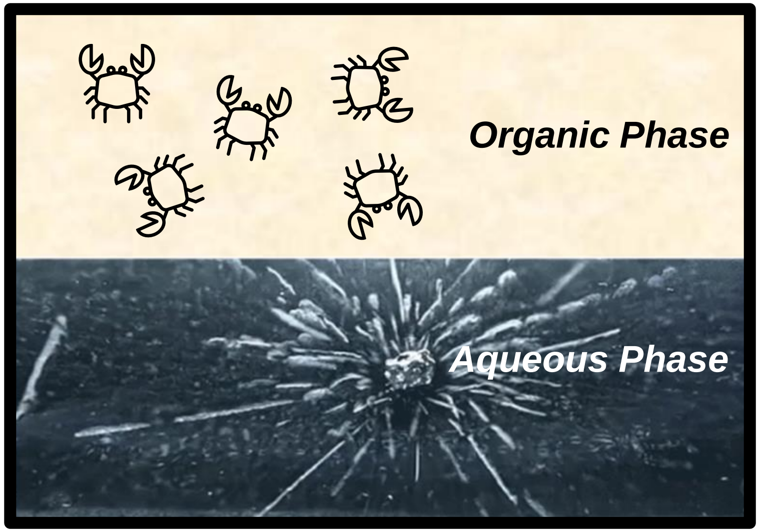
Reprocessing used nuclear fuel



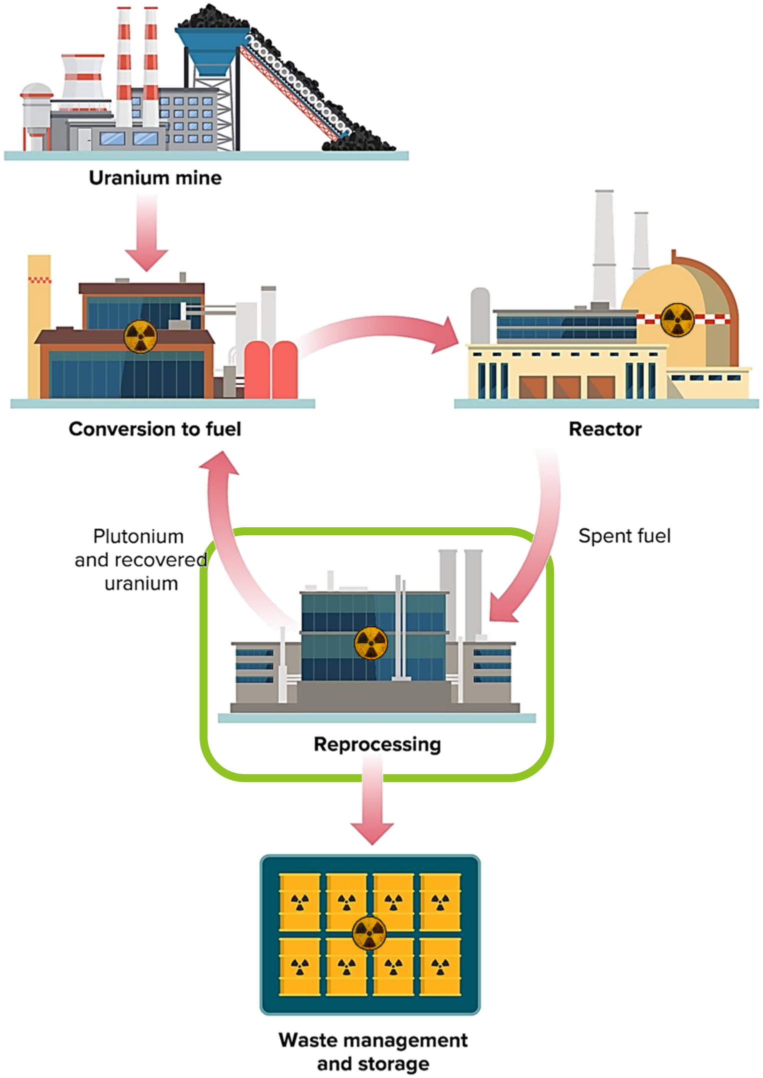
Solvent Extraction Reprocessing

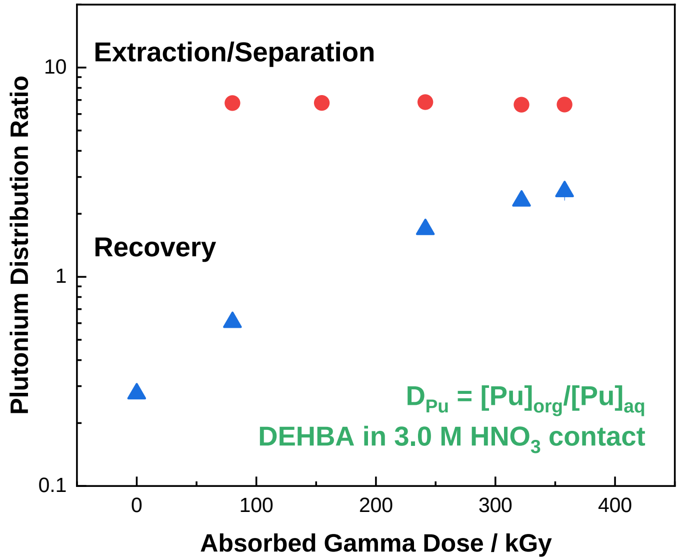
Ligands/organic diluent:HNO_3/H_2O
(± additives)

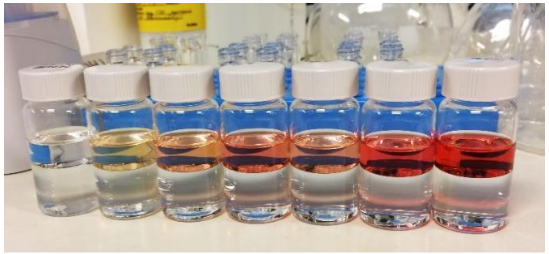


- Strategies and Considerations for the Back End of the Fuel Cycle, Nuclear Technology Development and Economics, NEA No. 7469, **2021**.
- Bruffey *et al.*, Innovative Separations R&D Needs for Advanced Fuel Cycles Workshop, August 30-September 1, 2021. Report for the US Department of Energy, Office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

Reprocessing radiation chemistry







Increasing Gamma Dose

- Horne, Zarzana, Grimes, Rae, Ceder *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, Mezyk, Mincher, Zarzana, Rae, Tillotson, Schmitt, Ball, Ceder, Charbonnel, Guilbaud, Saint-Louis, and Berthon, *Rad. Phys. Chem.*, **2020**, *170*, 108608.

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

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

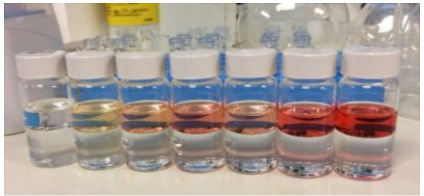
$HNO_3 \rightsquigarrow HNO_3^* \longrightarrow HNO_2 + O$

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

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

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**.

Impact of *f*-element complexation on ligand radiolysis

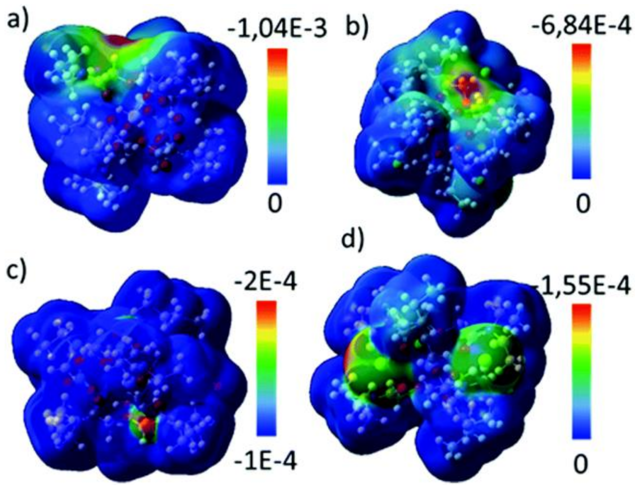
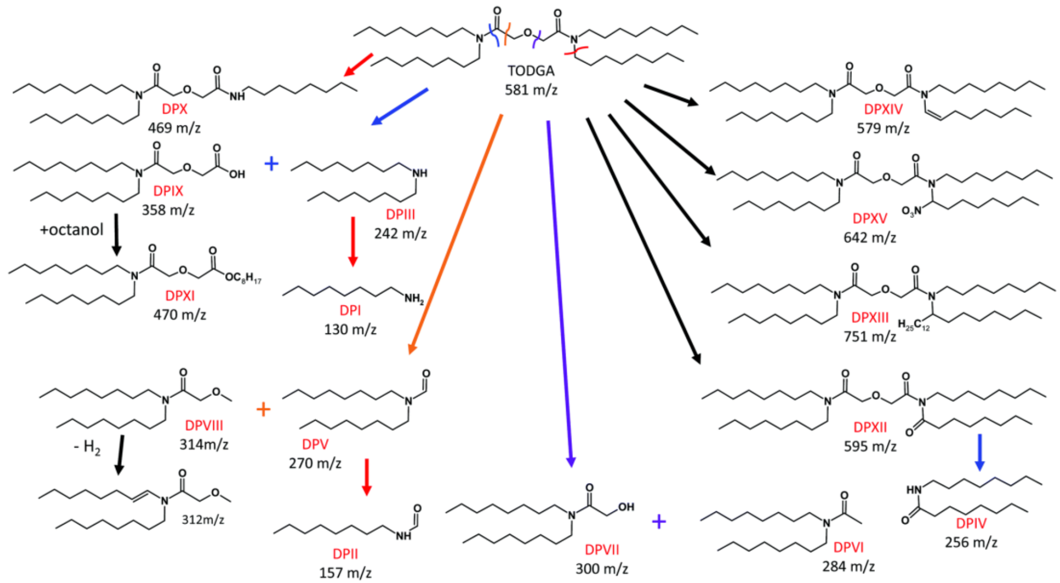


Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** $[Nd(TEDGA)_3](NO_3)_3$, **(b)** $[Nd(TEDGA)_3]Cl_3$, **(c)** $[Am(TEDGA)_3](NO_3)_3$, and **(d)** $[Am(TEDGA)_3]Cl_3$.



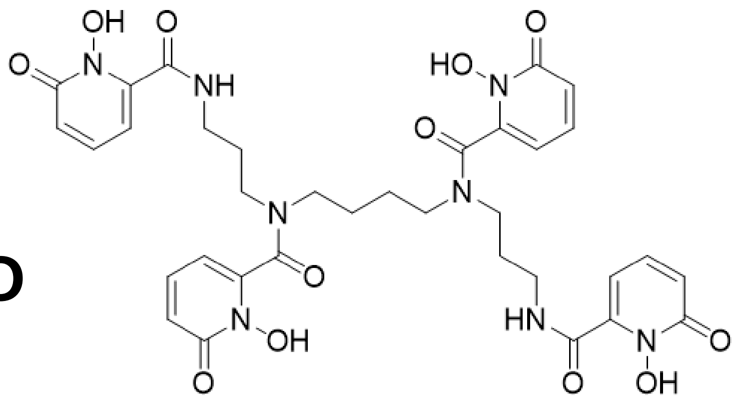
"…in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products."
Kimberlin *et al.*, *PCCP,* **2022**, *24*, 9213.

- 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-Louis, Guillaumont, Cames, Guilbaud, and Berthon, *PCCP*, **2022**, *24*, 9213.

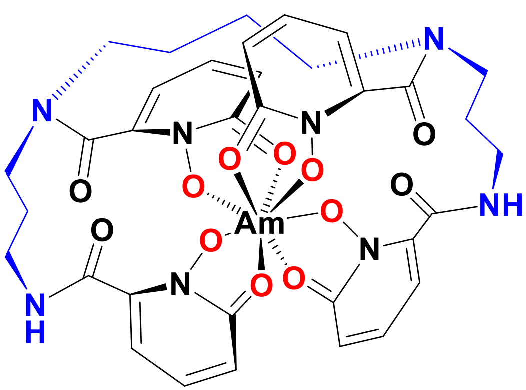
HOPO and TODGA ligands

(A)

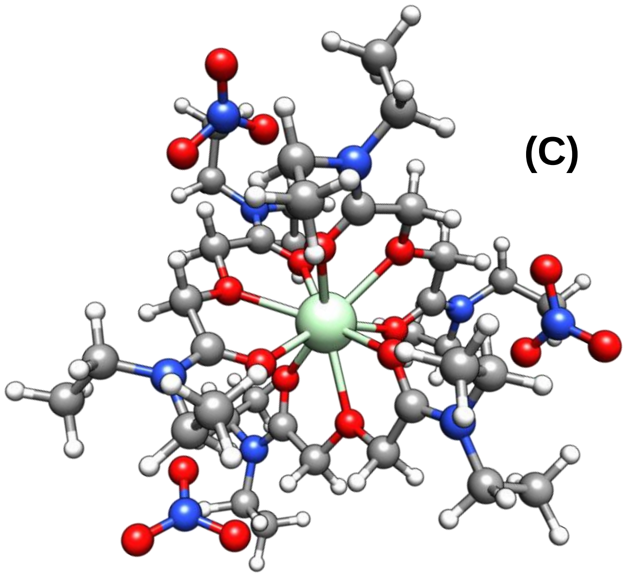
HOPO



(B)



(C)

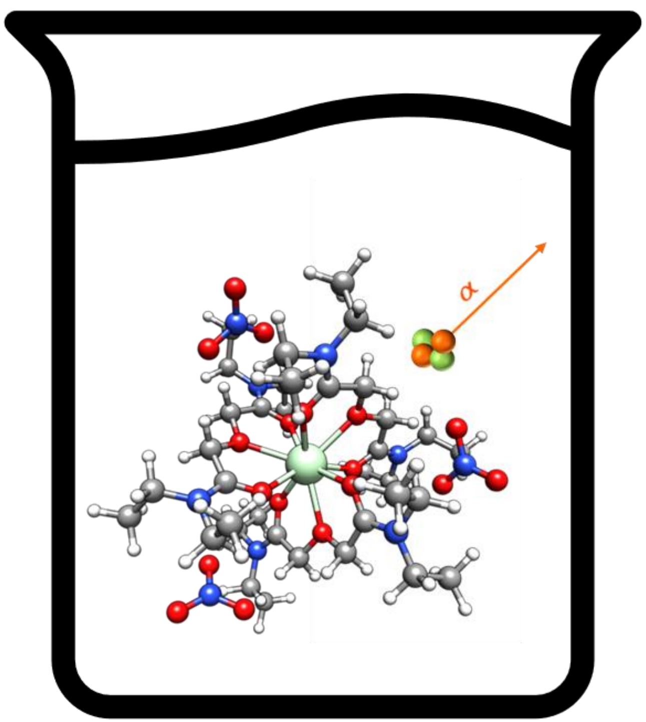


TODGA

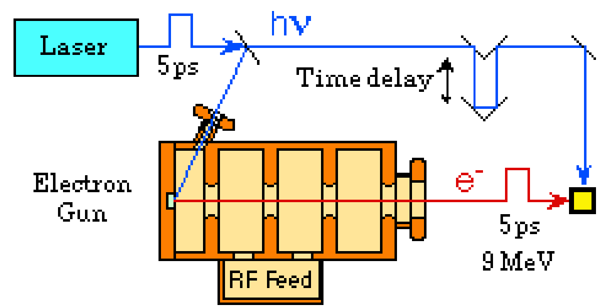
- Sasaki, Sugo, Suzuki, and Tachimori, *Solv. Extr. Ion Exch.* **2001**, *19*, 91.
- Deblonde, Ricano, and Abergel, *Nat. Commun.* **2019**, *10 (1)*, 2438.
- Wang, Deblonde, and Abergel, *ACS Omega* **2020**, *5 (22)*, 12996.
- Wang, Zhang, and Abergel, *Sep. Purif. Technol.* **2021**, *259*, 118178.

Ligand irradiations

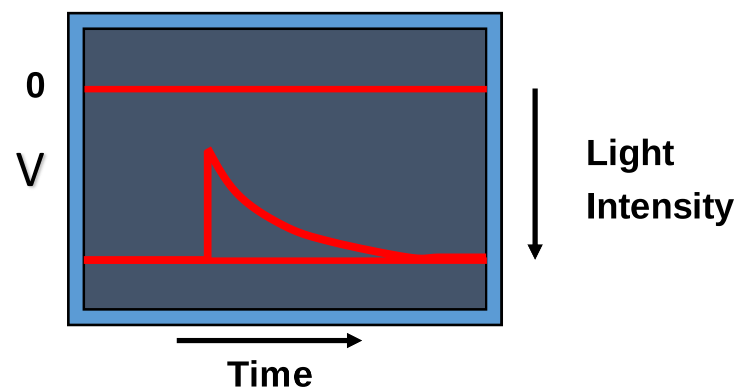
Alpha self-radiolysis



Electron pulse

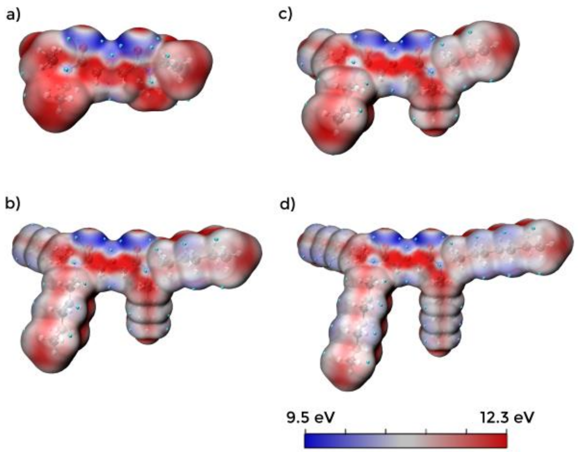


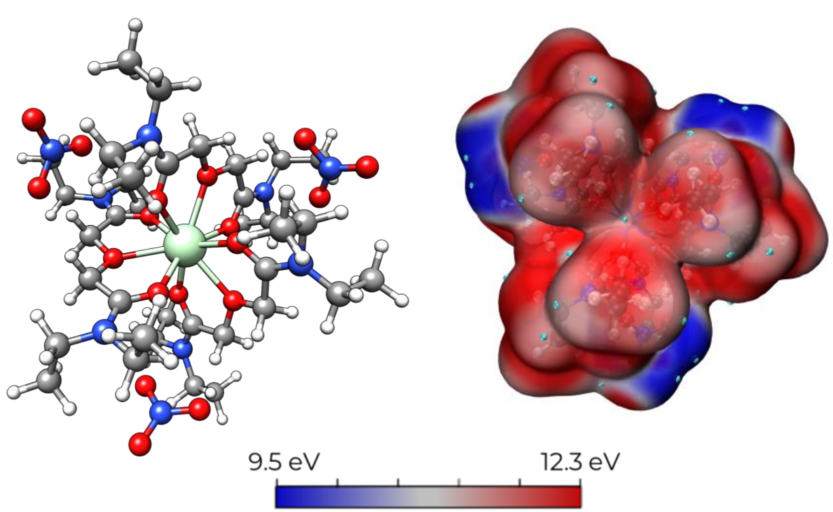
Transients are detected by optical absorption changes.

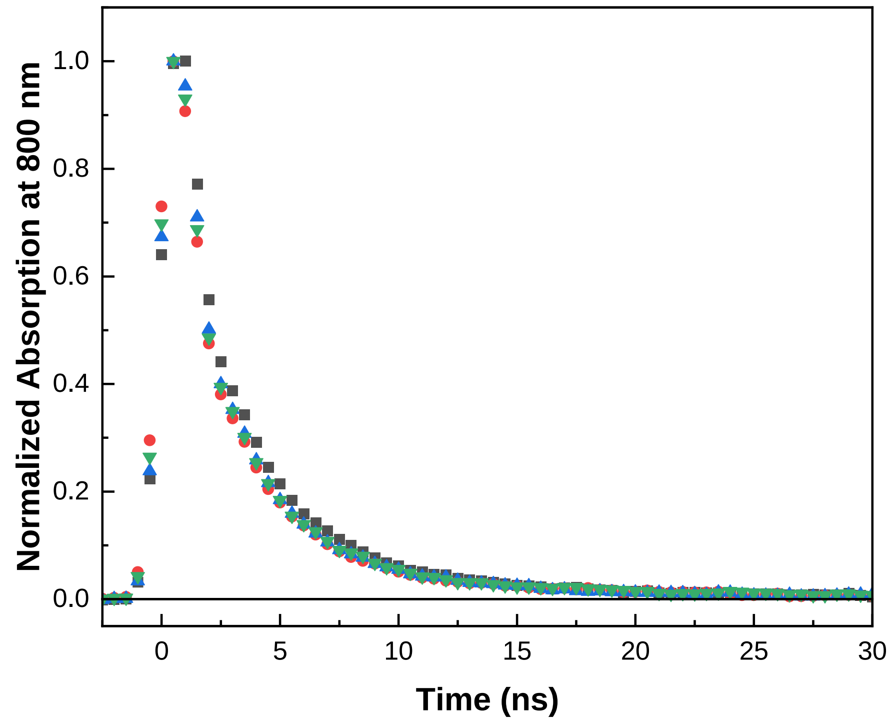


- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php
- Wang, Mezyk, McLachlan, Grimes, Zalupski, O'Bryan, Cook, Abergel, and Horne, *J. Phys. Chem. B* **2023**, Accepted.
- Horne, Celis Barros, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *PCCP* **2023**, *Under Review*.

TODGA irradiation



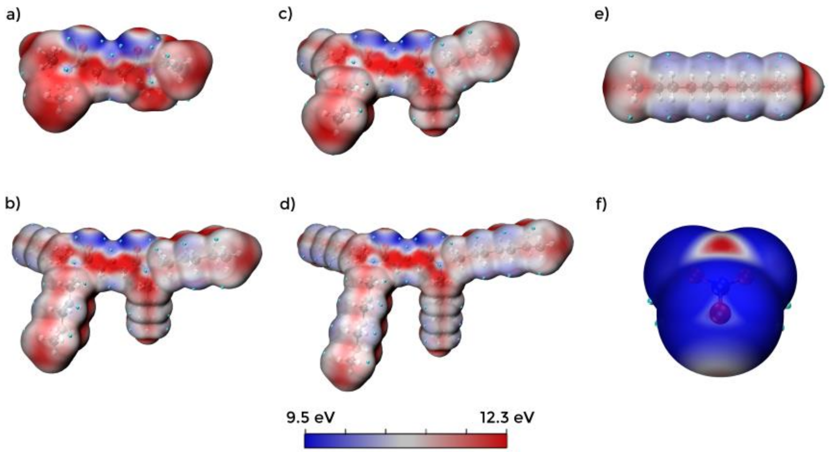


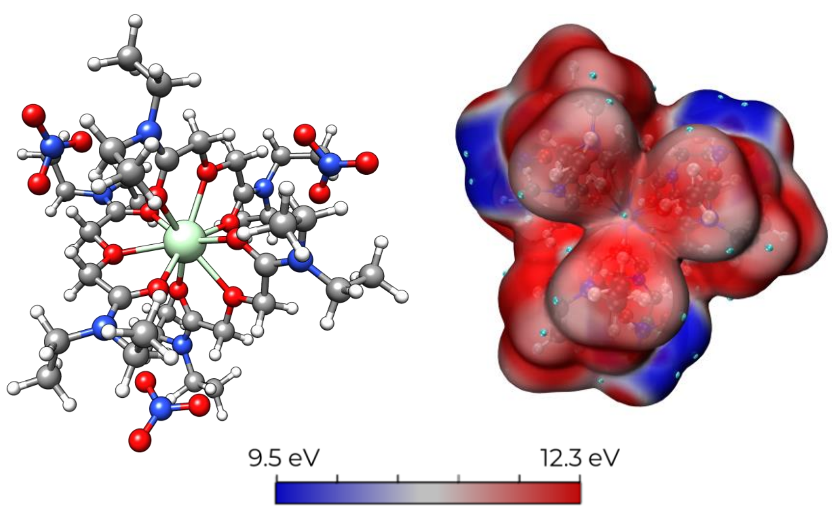


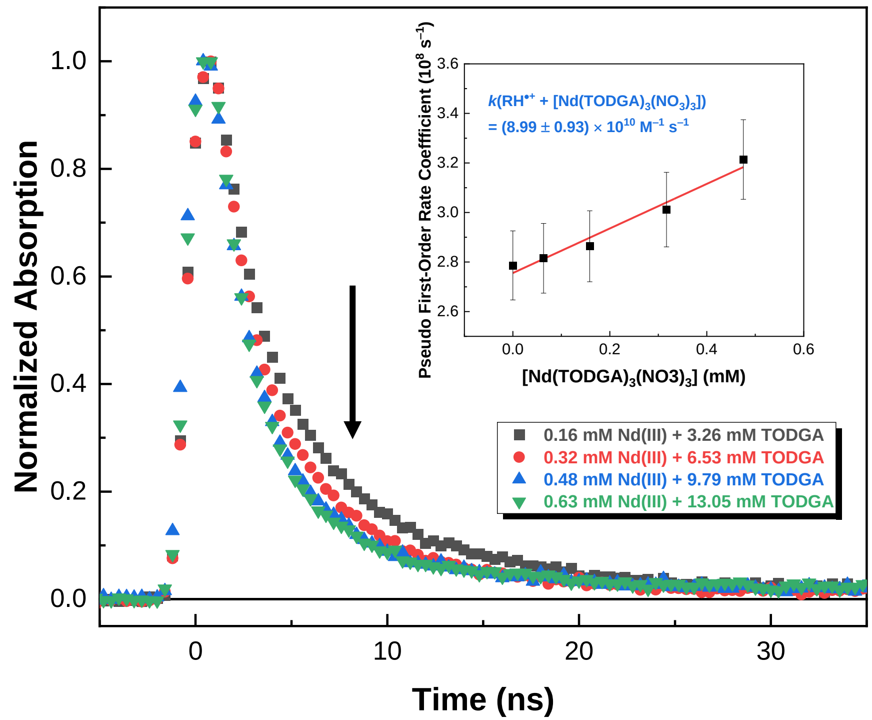
- **Experiment:** Kinetic traces for electron pulse irradiated solutions of 10 mM TODGA in 0.5 M DCM/*n*-dodecane without (■) and with pre-equilibration with either water (●), 1.0 M $NaNO_3$ (▲), or 1.0 M HNO_3 (▼).

- Horne, Celis Barros, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *PCCP* **2023**, Under Review.

[Nd(TODGA)$_3$(NO$_3$)$_3$] complex irradiation



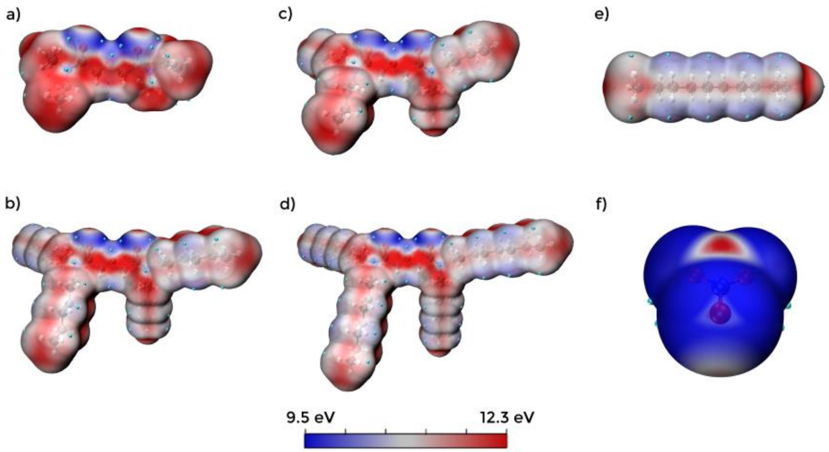


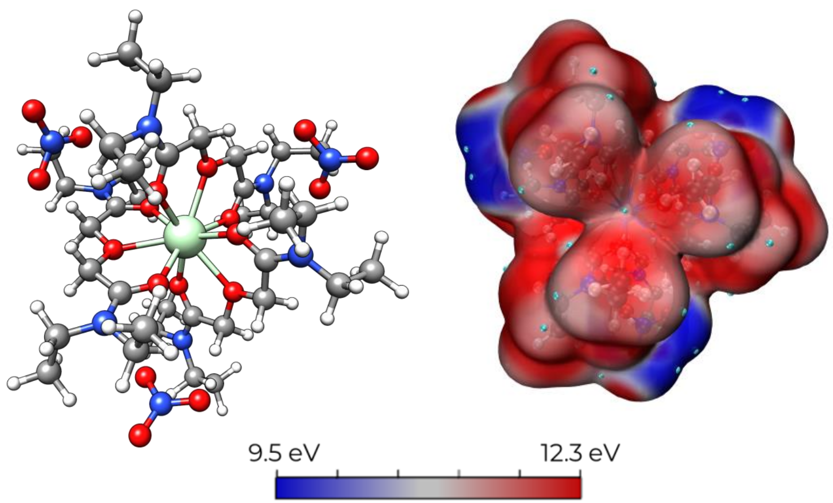


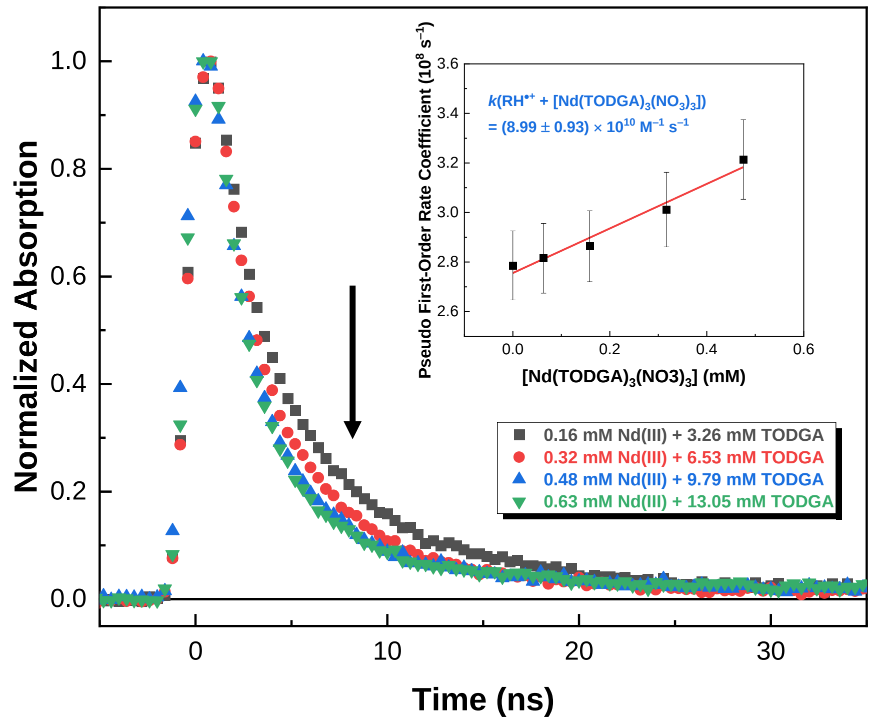
- **Experiment:** Kinetic traces for electron pulse irradiated solutions of TODGA in the presence of Nd(III) in 0.5 M DCM/dodecane: 0.16 (■), 0.32 (●), 0.48 (▲), and 0.63 (▼) mM Nd(III).

- Horne, Celis Barros, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *PCCP* **2023**, Under Review.

$[Ln(TODGA)_3(NO_3)_3]$ complex irradiation



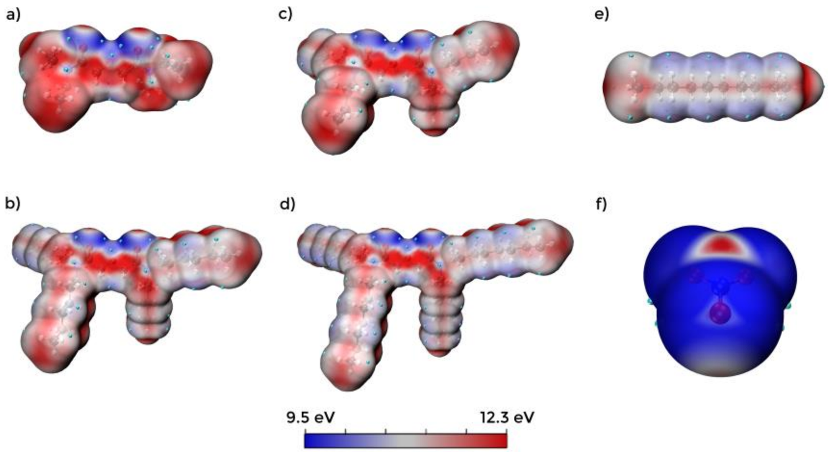


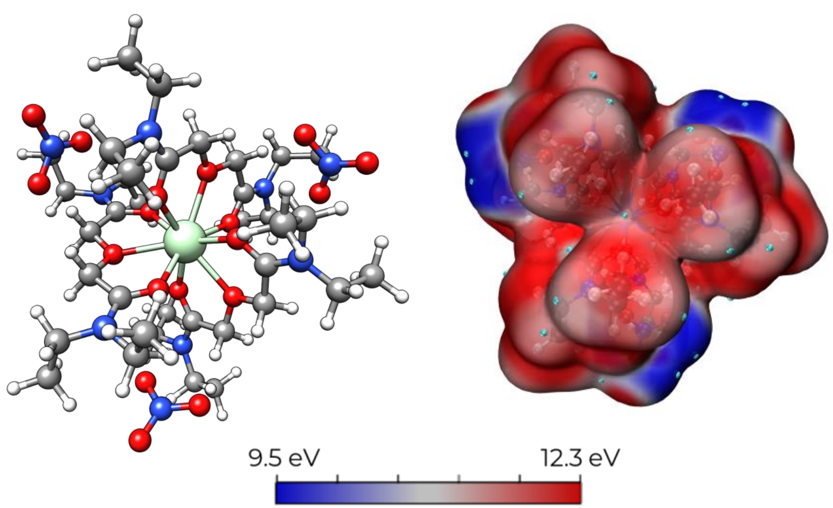


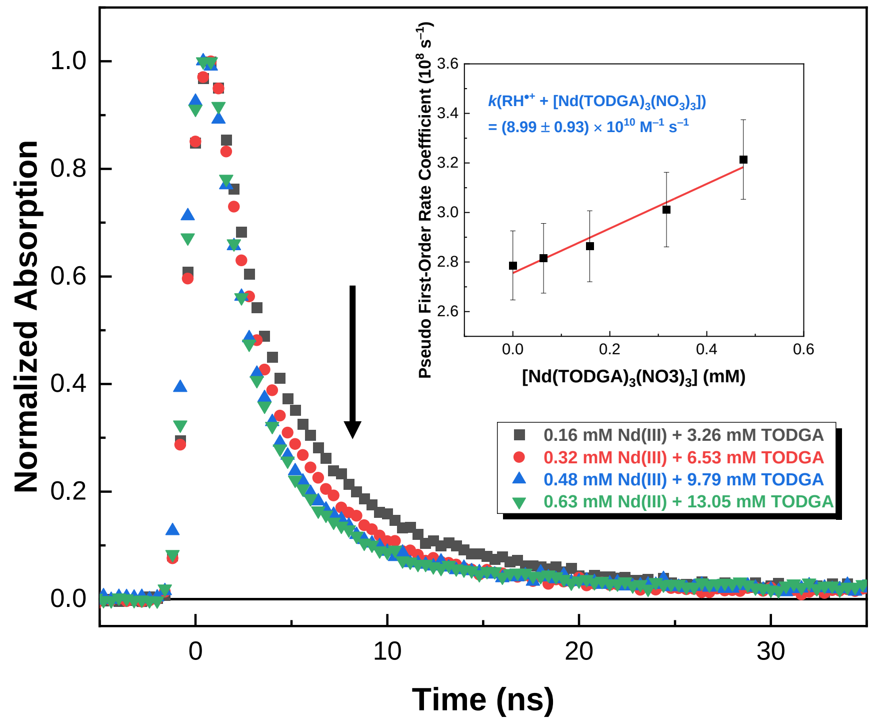
Ligand	Second-Order Rate Coefficient (k, $\times 10^{10}$ M^{-1} s^{-1})			
	Non-Complexed Ligand	Nd(III) Complex	Gd(III) Complex	Yb(III) Complex
TODGA	0.97 ± 0.60	8.99 ± 0.93	2.88 ± 0.40	1.53 ± 0.34

- Zarzana, Groenewold, Mincher, Mezyk, Wilden, Schmidt, Modolo, Wishart, and Cook, *Solv. Extr. Ion Exch.* **2015**, *33 (5)*, 431.
- Horne, Celis Barros, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *PCCP* **2023**, Under Review.

$[Ln(TODGA)_3(NO_3)_3]$ complex irradiation



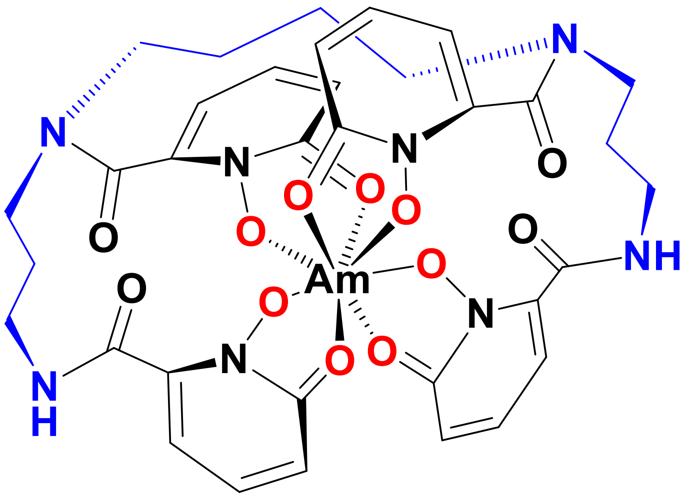


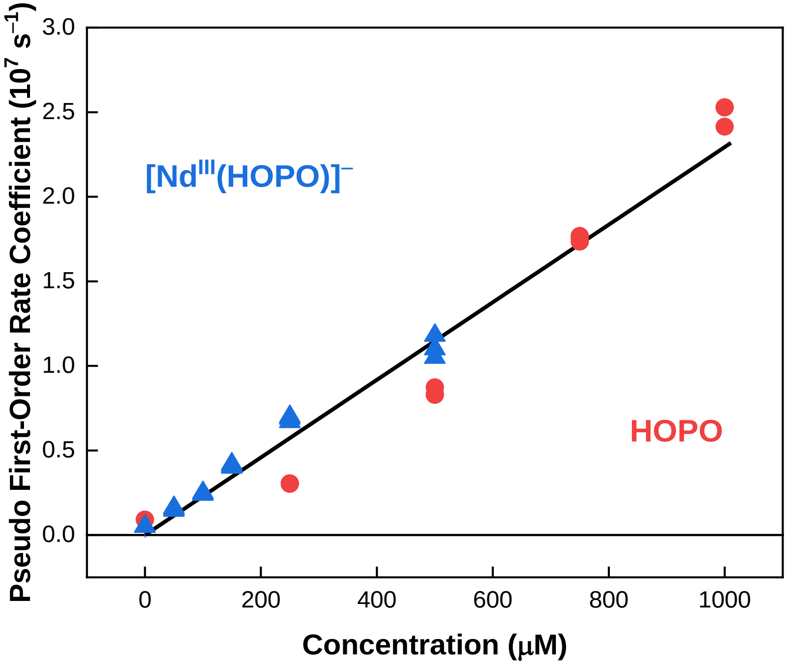


- **Computations:** average local ionization energy analysis highlights the sites of the molecule susceptible to a radical or electrophilic attack.

- Horne, Celis Barros, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *PCCP* **2023**, _Under Review_.

[Nd(HOPO)]⁻ complex irradiation

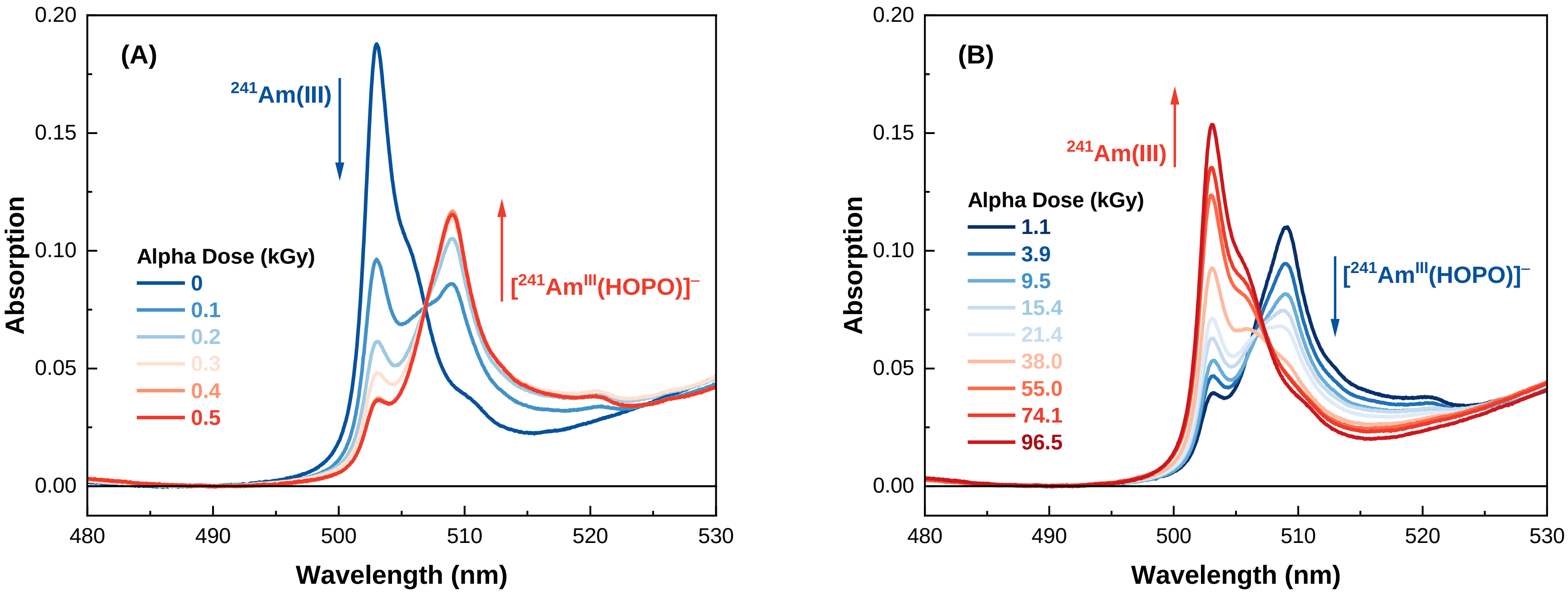




- **Experiment:** Second-order determination of the rate coefficient for the e_{aq}^- reaction with HOPO and its [Nd (HOPO)]⁻ complex. Solid lines are weighted linear fits with slopes corresponding to the second-order rate coefficient:
  - **$k(e_{aq}^- + \text{HOPO}) = (2.39 \pm 0.06) \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$**
  - **$k(e_{aq}^- + [\text{Nd}^{\text{III}}(\text{HOPO})]^-) = (2.20 \pm 0.06) \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$**

- Wang, Mezyk, McLachlan, Grimes, Zalupski, O'Bryan, Cook, Abergel, and Horne, *J. Phys. Chem. B* **2023**, Accepted.

$[Am(HOPO)]^-$ complex irradiation



- **Experiment:** Changes in the absorption spectrum of 0.5 mM $^{241}Am(III)$ in aqueous 0.1 M HCl solution with the addition of 0.5 mM HOPO as a function of absorbed alpha dose. Color gradient (**blue** to **red**) indicates increasing absorbed alpha dose: 0 to 0.5 kGy **(A)** and 1.1 to 96.5 kGy **(B)**.

- Wang, Mezyk, McLachlan, Grimes, Zalupski, O'Bryan, Cook, Abergel, and Horne, *J. Phys. Chem. B* **2023**, Accepted.

Conclusions

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- Understanding radiation chemistry is essential for innovating nuclear energy technologies.

- Metal ion complexation can have significant effects on the fundamental radiation chemistry of separations ligands, owing to ***steric effects***, ***electron distribution differences***, and the ***facilitation of inner vs. outer sphere mechanisms***.

- Wang, Mezyk, McLachlan, Grimes, Zalupski, O'Bryan, Cook, Abergel, and Horne, *J. Phys. Chem. B* **2023**, Accepted.
- Horne, Celis Barros, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *PCCP* **2023**, *Under Review*.

Proposed path forward for innovative separations

- Steady-state irradiation studies are essential for evaluating the longevity of ligands and the efficacy of their degradation products.
- An organic phase radiolysis model is needed to complement predictive capabilities available for the aqueous phase.
- Direct dissolution approaches will need to be thoroughly evaluated as the aqueous phase plays a key role in the radiation chemistry of the entire solvent system.

- 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**.

Acknowledgements

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Material Recovery & Waste Form Development

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COLORADO SCHOOL OF MINES

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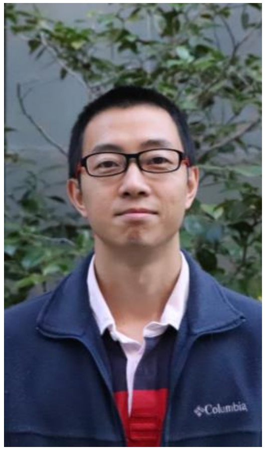




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