Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for: Impact of Lanthanide Ion Complexation and Temperature on the Chemical Reactivity of N,N,N′,N′-tetraoctyl diglycolamide (TODGA) with the Dodecane Radical Cation

Gregory P. Horne,[a]* Cristian Celis Barros,[b] Jacy K. Conrad,[a] Travis S. Grimes,[a] Jeffery R. McLachlan,[a,c] Brian M. Rotermund,[b] Andrew R. Cook,[d] and Stephen P. Mezyk[e]*

[a] *Center for Radiation Chemistry Research, Idaho National Laboratory, Idaho Falls, ID, P.O. Box 1625, 83415, USA.*

[b] *Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, USA.*

[c] *Department of Chemistry, Florida International University, Miami, Florida 33199, USA.*

[d] *Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973, USA.*

[e] *Department of Chemistry and Biochemistry, California State University Long Beach, 1250 Bellflower Boulevard, Long Beach California, 90840-9507, USA.*

*Corresponding authors. E-mail: gregory.horne@inl.gov and stephen.mezyk@csulb.edu.

Gd(III) and Yb(III) TODGA Complex Reaction Kinetic Data

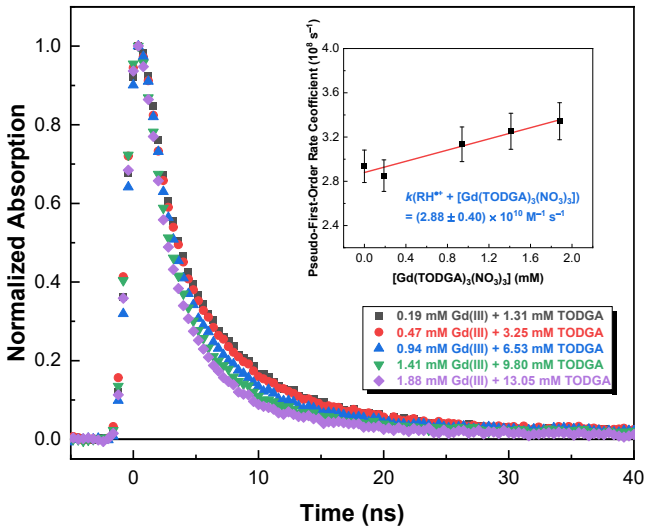

Figure S1. Normalized kinetic traces at 800 nm for electron pulse irradiated solutions of TODGA in the presence and absence of Gd(III) in aerated 0.5 M DCM/*n*-dodecane at 23 ± 1 °C: 0.19 (■), 0.47 (●), 0.94 (□), 1.41 (❑), and 1.88 (◆) mM Gd(III) ions. *Inset:* Second-order determination of the rate coefficient for the reaction of $[Gd^{III}(TODGA)_3(NO_3)_3]$ with $RH^{\bullet+}$. Individual data points are the faster pseudo-first-order component of the double-exponential fit to the data shown in the main figure. The weighted linear fit corresponds to a second-order reaction rate coefficient of $k([Gd^{III}(TODGA)_3(NO_3)_3] + RH^{\bullet+}) = (2.88 \pm 0.40) \times 10^{10}$ M^{-1} s^{-1}.

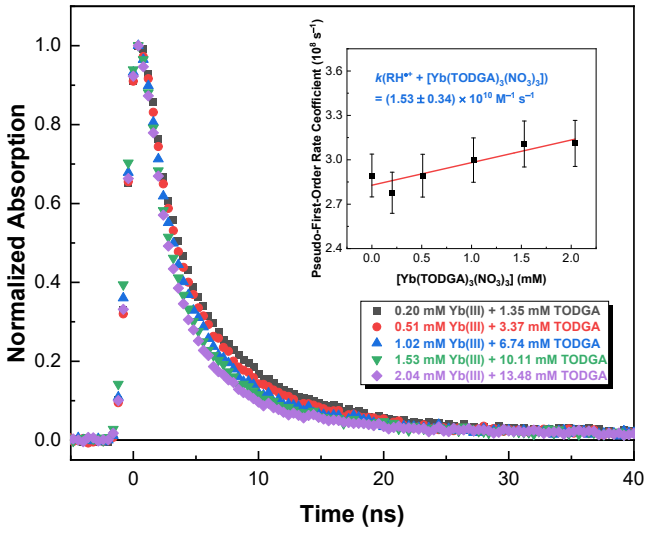

Figure S2. Normalized kinetic traces at 800 nm for electron pulse irradiated solutions of TODGA in the presence and absence of Yb(III) in aerated 0.5 M DCM/*n*-dodecane at 23 ± 1 °C: 0.20 (■), 0.51 (●), 1.02 (□), 1.53 (❑), and 2.04 (◆) mM Yb(III) ions. *Inset:* Second-order determination of the rate coefficient for the reaction of $[Yb^{III}(TODGA)_3(NO_3)_3]$ with $RH^{\bullet+}$. Individual data points are the faster pseudo-first-order component of the double-exponential fit to the data shown in the main figure. The weighted linear fit corresponds to a second-order reaction rate coefficient of $k([Yb^{III}(TODGA)_3(NO_3^-)_3] + RH^{\bullet+}) = (1.53 \pm 0.34) \times 10^{10}$ M^{-1} s^{-1}.

Geometry Optimized Molecular Structure for $[Ln^{III}(TODGA)]^{3+}$ Complex

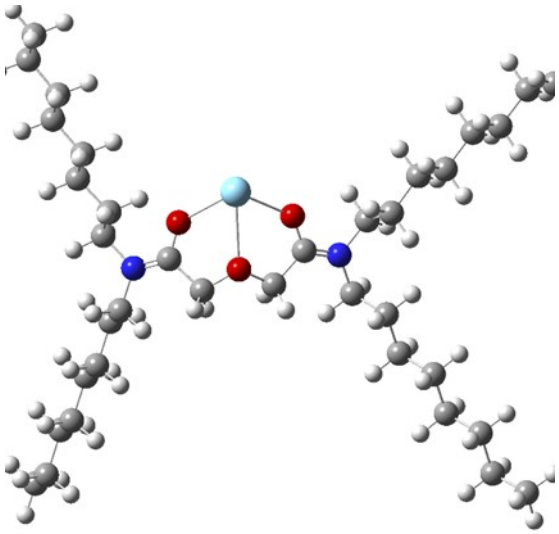

Figure S3. Calculated structure for a single TODGA molecule bound to a Ln(III) ion center with no NO_3^- counter anions, $[Ln^{III}(TODGA)]^{3+}$. With this simplified complex, both hole transfer and proton transfer from dodecane radical cation are predicted by calculations to become exceedingly unfavorable, ΔG ~ +1.86 and +5.26 eV, respectively.

Geometry Optimized Bond Lengths for $[Ln^{III}(TEDGA)_3(NO_3)_3]$ Complexes

Table S1. Optimized bond lengths (Å) for the calculated Nd(III), Gd(III), and Yb(III) ion complexes. The average values have also been included at the bottom of the table showing the expected decrease in the Ln–O bond lengths.

Bond	Bond length (Å)		
	$[Nd^{III}(TEDGA)_3(NO_3)_3]$	$[Gd^{III}(TEDGA)_3(NO_3)_3]$	$[Yb^{III}(TEDGA)_3(NO_3)_3]$
$O_{C=O1}$ (1)	2.4325	2.3992	2.3791
$O_{C=O2}$ (1)	2.4534	2.3863	2.3728
O_{ether} (1)	2.5527	2.5036	2.4921
$O_{C=O1}$ (2)	2.4287	2.3929	2.3709
$O_{C=O2}$ (2)	2.4506	2.3865	2.3764
O_{ether} (2)	2.5526	2.5183	2.4865
$O_{C=O1}$ (3)	2.4348	2.3958	2.3706
$O_{C=O2}$ (3)	2.4446	2.3847	2.3719
O_{ether} (3)	2.5671	2.4986	2.5059
$O_{C=O\ avg}$	2.4408	2.3909	2.3736
$O_{ether\ avg}$	2.5574	2.5068	2.4948

ALIE Calculations for Non-Complexed Diglycolamide Molecules and NO_3^- Anions.

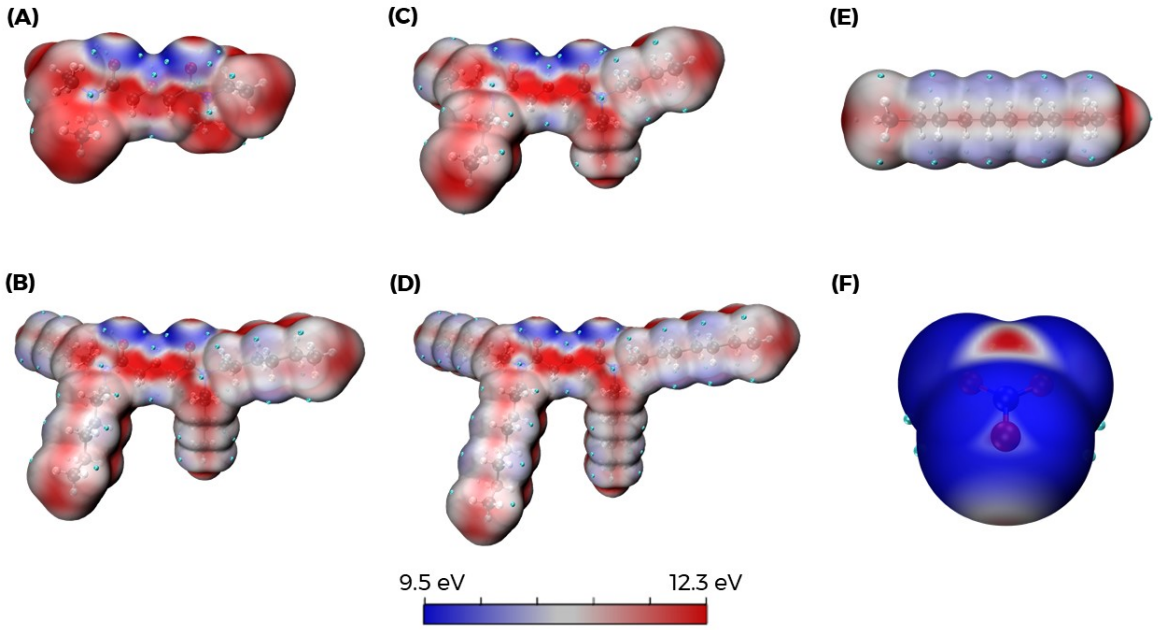

Figure S4. ALIE surfaces of non-complexed diglycolamide molecules with tetra ethyl (**A**), butyl (**B**), hexyl (**C**), octyl (**D**), and decane (**E**) chains, in addition to a non-complexed NO_3^- anion (F). The lowest ALIE regions are shown in blue, which indicate the least bound electron density on the molecular surface (0.0005 a.u.). Cyan dots on the surface indicate the ALIE local minima, $\bar{I}_{S,min}(\mathrm{r})$.