Electronic Supporting Information (ESI) for

Trapped in the Coordination Sphere: Nitrate Ion Transfer Driven by the Cerium(III/IV) Redox Couple

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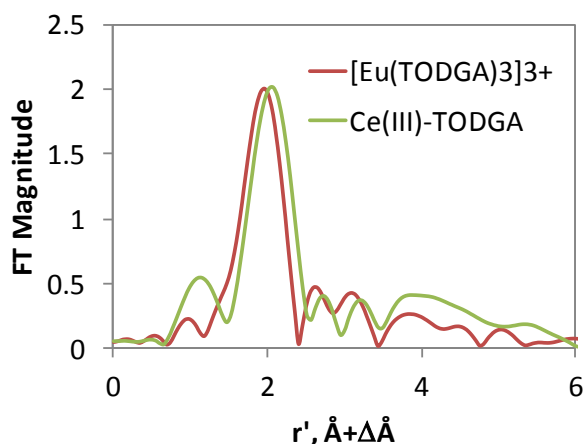
Figure S1. Comparison of EXAFS collected from the Ce(III)-TODGA organic phase prepared in this study, with the previously reported EXAFS of $[Eu(TODGA)_3]^{3+}$.[1] Note that, besides the shifted peak positions that are due to the lanthanide contraction, the relative intensities and relative positions of the major and minor oscillations are very similar. Another important feature to note in these FT data is the single intense peak for the Ce-O and Eu-O interactions. Whereas single-crystal X-ray diffraction data for molecular structures of various M(III) complexes with short-chain-diglycolamides (other than TODGA for which no X-ray crystallography data are available) reveal that the M-O(carbonyl) distances are shorter than the M-O(ether) distances (the average distance difference between the amidic and etheric O atoms is approx. 0.1 Å, see structure precedent cited in ref. 1), the EXAFS interatomic distance resolution (approx. 0.15 Å as determined by $\Delta r \geq \pi/(2\Delta k)^2$) is insufficient to disentangle the carbonyl and ether oxygen interactions. The result is a single, unresolved M(III)-O shell. In contrast, the M(III)-C(carbonyl) and M(III)-C(ether) distances are resolvable (the average distance difference is approx. 0.2 Å). As a result, the primary data are conservatively modeled with a single shell of O atoms with a single (large) Debye-Waller factor and two C shells.
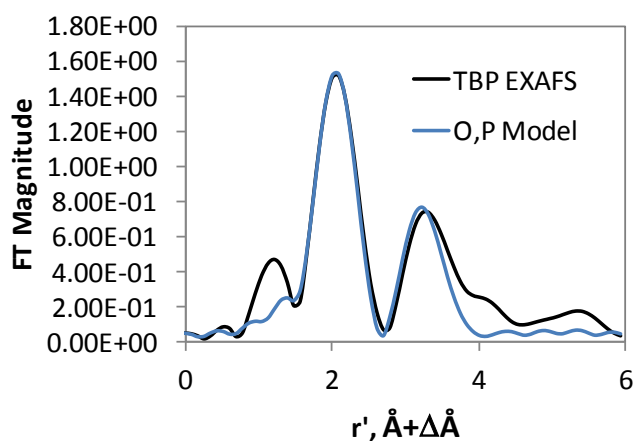
Figure S2. FT EXAFS of the Ce(III)-TBP solution and the 2-shell (O, P) model used to fit it. All parameters were floated during the fitting procedure. The metrics for this model are shown in the following table. Nine-oxygen coordination of cerium(III) is a common structural motif for a cation of its size.[3-9]

Shell	CN	r, Å	σ^2, Å^2	E_0, eV
O	9(1)	2.539(7)	0.010(1)	-0.3
P	9(1.5)	3.663(9)	0.017(3)	9.6
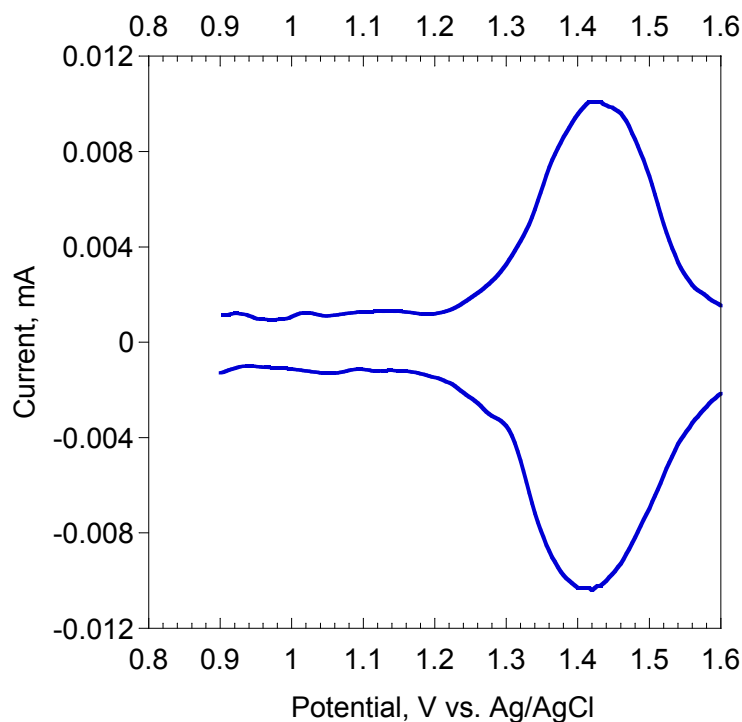
Figure S3. Conventional (two-phase) DPV for an aqueous solution of 0.1 M Ce(NO$_3$)$_3$·6H$_2$O in 5 M HNO$_3$ with a Grafoil® working electrode. Two separate scans are shown: (1) the positive current response (top) was obtained for the scan from the initial electrode potential of +0.90 V to the final electrode potential of +1.60 V, whereas (2) the negative current response (bottom) was obtained for the scan from the initial electrode potential of +1.60 V to the final electrode potential of +0.90 V.

References
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