

Substituent Effects on the Redox Property of Oxo-bridged Hexanuclear Cerium Complexes with *Ortho*- and *Para*-substituted Benzoate Ligands

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Oxo-bridged metal clusters are discrete models of metal oxides which are often utilized as catalysts and nano-scale materials. Since cerium oxide possesses unique redox, dioxygen uptake/release, and photo-responsive properties, the corresponding oxo-bridged cerium clusters have attracted a special interest; in fact, we previously found the unique photo-catalytic activity of oxo-bridged hexanuclear cerium(IV) complexes surrounded by carboxylate ligands for decarboxylative oxygenation of carboxylic acids.¹ We herein report on the substituent effect for the redox property of the oxo-bridged hexanuclear cerium(IV) clusters, $\text{Ce}_6\text{O}_4(\text{OH})_4(\text{OCOAr})_{12}$ (Ar = *ortho*- and *para*-substituted benzoate).

Treatment of $\text{Ce}(\text{O}^i\text{Bu})_4$ with two equiv. of *ortho*-dimethyl and *para*-substituted benzoic acids under inert atmosphere and subsequent addition of acetone gave the corresponding cerium(IV) clusters **1-6** in good yield (eq. 1). The tri-substituted benzoic acids were suitable for tuning the electron-donating/-withdrawing character due to the high solubility of the clusters as well as elimination of the solvent coordination to the cerium atoms. Effects of the substituents at the 4-position on their redox potentials are elucidated by the cyclic voltammetry, as shown in Figure 1. The redox potential for $[\text{Ce}(\text{IV})]_6/[\text{Ce}(\text{III})\text{Ce}(\text{IV})_5]$ was negatively shifted by introducing electron-donating substituents on the benzoate ligand from **1** (-0.33 V vs Fc^+/Fc) to **4** (-0.79 V vs Fc^+/Fc), while the effects for the electron-withdrawing substituents on the redox potential were small for complexes **5** and **6** having fluoride and chloride at the 4-position (-0.31 V for **5** and -0.38 V for **6** vs Fc^+/Fc). Characterization of the Ce(IV) clusters, redox properties, and chemical reduction using cobaltocene are disclosed in this presentation.

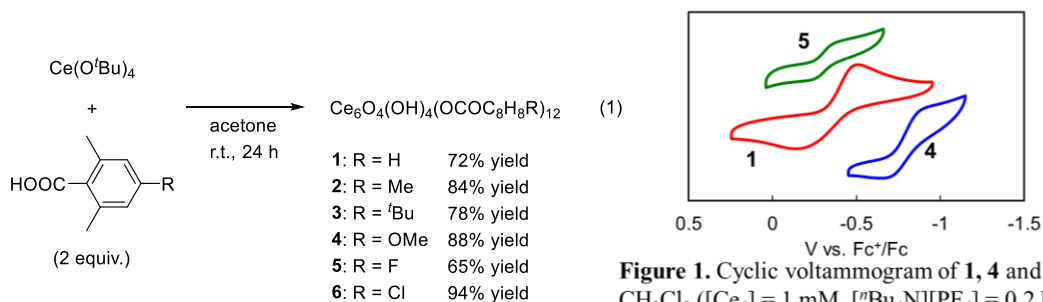


Figure 1. Cyclic voltammogram of **1**, **4** and **5** in CH_2Cl_2 ($[\text{Ce}_6] = 1 \text{ mM}$, $[\text{nBu}_4\text{N}][\text{PF}_6] = 0.2 \text{ M}$, scan rate = 100 mV/s for **1**, 10 mV/s for **4** and **5**).

1) Shirase, S.; Tamaki, S.; Shinohara, K.; Hirose, K.; Tsurugi, H.; Satoh, T.; Mashima, K. *J. Am. Chem. Soc.* **2020**, *142*, 5668-5675.