

# Oxidation State Change of Cerium-based UiO-66 Architecture

Ying-Pin Chen<sup>1</sup>, Tieyan Chang<sup>2</sup>, Yu-Sheng Chen<sup>3</sup>

<sup>1</sup>ChemMatCARS <sup>2</sup>The University of Chicago, <sup>3</sup>University of Chicago

*schrodinger219@gmail.com*

Over the past decade, the UiO-66 series, constructed from  $M_6O_4(OH)_4$  nodes ( $M = \text{Zr, Hf, Th, Ti, Ce}$ ) and ditopic carboxylate linkers have aroused attention because of their great stability and diverse applications in the field of metal-organic frameworks (MOFs). Researchers discovered that not all the M-UiO-66s possess similar stimulus-responsive behaviors. The process of photo-excitation via Ligand-to-metal charge transfer (LMCT) is favorable only in the Ce-based UiO-66 crystal. Computational scientists proposed that LMCT is promoted from the empty 4f orbitals of  $\text{Ce}^{4+}$ .

However, single-crystal X-ray diffraction and Thermogravimetric Analysis (TGA) data revealed that a significant number of missing ligands is present in our Ce-UiO-66 crystals, suggesting that the Ce<sub>6</sub> node is likely composed of  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$ , instead of pure  $\text{Ce}^{4+}$ . This result indicates that the performance of photo catalysis using Ce-UiO-66 will be unreliable if the oxidation state of Ce-UiO-66 is incomplete. In this work, we present a method to confirm the oxidation state using single-crystal X-ray diffraction. As a consequence, single-crystal data demonstrated that the Ce-Ce bond length of the Ce<sub>6</sub> cluster is shrinking with air exposure time. This finding provides a facile way to rapidly judge the oxidation state of Ce-UiO-66 prior to catalysis use.