

## X-RAY SPECTROSCOPY STUDIES OF TI-BASED METAL ORGANIC FRAMEWORKS

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Some Ti-based metal organic frameworks (MOFs) have demonstrated photocatalytic properties. MIL125-NH<sub>2</sub> is a well-studied Ti-based MOF consisting of titanium-oxo clusters connected via amino terephthalic acid linkers. This structure possesses a stable, long-lived charge separated excited state in which, upon photoexcitation, an electron migrates from a linker to the metal cluster. The band structure of this framework can be modified through the replacement of Ti metal sites with d block transition metals via a direct synthesis pathway. However, further research is required on the underlying electronic structure and excited state behavior of the modified framework. Fundamental steady state and time resolved X-ray spectroscopy experiments have been carried out in order to determine the effects of heterometal doping concentration on the charge separation lifetime and the electronic environment of MIL125-NH<sub>2</sub>. Fe K-edge X-ray transient absorption (XTA) measurements have been conducted, which show that doped MIL125-NH<sub>2</sub> has a long-lived excited state lifetime component of over 20 microseconds, due to iron trap sites on the metal ring. The long-lived charge separation excited state is seen even in higher doping levels, as the framework inhibits charge recombination. Ti K- $\beta$  resonant x-ray emission spectroscopy (RXES) measurements show a shift in pre-edge resonant features towards lower emission energy, with the inclusion of iron heterometals. Localized d transitions on the Ti seem to be less intense with the addition of Fe into the MOF structure.

