X-ray Absorption Spectroscopy in Organic Chemistry

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X-ray absorption spectroscopy (XAS) is a powerful technique for elucidating the electronic states and local structures of target atoms. A key advantage of XAS lies in its applicability across diverse environments, including organic solvents, which makes it highly attractive for probing organic compounds and reaction intermediates. Despite this potential, the use of solution-state XAS in organic chemistry has remained limited.

Our group has explored XAS as a tool to deepen the mechanistic understanding of organic reactions. To this end, we have developed both *in situ* and *ex situ* solution cells, as well as reaction apparatuses compatible with organic solvents, thereby enabling solution-state XAS experiments under realistic conditions.[1–3] In this seminar, I will introduce our recent developments and applications of solution-state XAS to organic chemistry. In particular, I will focus on the characterization of reaction intermediates in a Lewis acid–mediated Suzuki–Miyaura cross-coupling reaction.[1] Through solution-state XAS, we identified a stable triflate-bridged Pd/Zn binuclear resting-state complex. Complementary theoretical calculations revealed that highly reactive cationic Pd species are gradually released from this complex, thus achieving a balance between reactivity and thermal stability. Furthermore, I will discuss the structural analysis of densely fluorinated cubanes—specifically hexafluorodihalocubanes—that exhibit exceptionally short carbon–halogen bonds.[3] By combining solution-state XAS with single-crystal X-ray diffraction, we were able to disentangle solvent effects and packing forces that influence carbon–halogen bond lengths, highlighting the unique insights afforded by solution-state XAS.

References

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