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Photocatalysis beyond conventional precious metal complexes

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Abstract

Precious metals, e.g. Ru and Ir, are expensive, scarce and non-renewable resources. As oppose to many renewable resources, these cannot be deliberately produced wherever one wishes. The mining of these metal ores is limited to their natural abundance which is restricted to only a few places of the world. In addition to their high price, the metals - which the modern world technology is dependent on - are associated with the risk of a potential supply cutoff related to any momentary global geopolitical instabilities. Many modern-day chemical methods, among them photoredox catalysis, has become dependent on Ru and Ir. The price, scarcity and instability of the supply chain calls for a state-of-the-art update of the research field's toolbox.

The two factors substitutability and recycling rate of the relative supply risk index (RSR) have been investigated within the context of Ru and Ir as applied to photoredox catalysis. Specifically, earth abundant Fe as an alternative and heterogenization of Ir were studied as potential elements of the future toolbox of photoredox catalysis.

A protocol for an oxidative fragmentation of ethers and acetals to ketones and esters was developed using a simple Fe(III) photocatalyst. Fe and its complexes generally have much lower excited state life-times than those of Ru and Ir, and a high value is often assumed to be required for any reactions to occur. However, the results disclosed here question that assumption.

A similar transformation was also developed that addressed the shortcoming of pre-synthesis of acetals by enabling an *in situ* formation from aldehydes. Furthermore, this visible light promoted reaction proceeded without any added photocatalyst.

Lastly, the reaction scope of a heterogenized Ir catalyst was investigated. The reusable catalytic material could be applied to a range of different classes of photoredox reactions and in addition catalyzed the reactions faster than the corresponding homogeneous catalyst.

In summary, the results show that the go-to catalysts in photoredox catalysis are not essential. Inexpensive and short excited state life-time Fe(III) photocatalysts and heterogenized constructs constitute, conceptually, two attractive alternatives worthy of further research.

Keywords: Iron photocatalysis, Heterogenization