SILICATES AS AS LATENT RADICAL PRECURSORS:
VISIBLE-LIGHT PHOTOCATALYTIC OXIDATION OF HYPERVERALENT SILICON COMPOUNDS

Radical chemistry has witnessed an explosive growth over the last three decades.\(^1\) But the development of mild and sustainable preparative redox processes limiting the utilization of stoichiometric toxic metal complexes is still needed. Recently, visible-light photoredox catalysis has emerged as a valuable and a greener alternative to generate radicals by single electron transfer reactions from an appropriate photocatalyst - which can be a polypyridine complex of transition metal or an organic dye - that absorbs light in the visible region.

Since the pioneering studies of Kellogg, Pall and Deronzier, important contributions have been reported for synthetic purposes.\(^2\) In this context, we investigated various radical transformations\(^3\) involving photoreduction of ketoepoxides, ketoaziridines,\(^4\) \(^5\) \(^6\) \(^7\) and O-thiocarbamates\(^7\) and photooxidation of 1,3-dicarbonyl compounds.\(^8\) Then, we took advantage of the reactivity of the photogenerated radicals to create new carbon-carbon bonds and related mechanistic studies were performed. Many opportunities are now available to access all kinds of C-centered radicals, based whether on photooxidative or photoreductive processes. However, generation of unstabilized alkyl radicals is still a challenge. Recently, we reported the generation of unstabilized alkyl primary radicals by photooxidation of bis(catecholato)alkylsilicates.\(^9\) These radicals can be trapped by radical acceptors or engaged with (hetero)aryl halides or alkenyl halides as electrophiles in dual photoredox/nickel catalysis\(^10\) for the formation of C(sp\(^3\)) - C(sp\(^2\)) bonds.\(^11\) Usually, photoactive transition metal complexes based on ruthenium or iridium are used as photocatalysts but increasing efforts have been realized to develop processes involving organic photocatalysts.\(^12\) Our preliminary results obtained in this field have to be confirmed with other substrates and extended to other types of catalyses and challenging transformations.
References