

*Title:* **Bifunctional photoredox catalysts in asymmetric synthesis**

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The demand for chiral compounds, often as single enantiomers, has escalated sharply in recent years, driven particularly by the demands of the pharmaceutical industry, but also by other applications, including agricultural chemicals, flavors, fragrances, and materials. This widespread demand for chiral compounds has stimulated intensive research in asymmetric or enantioselective synthesis, a key process in modern chemistry. On the other hand, photocatalysis, an environmentally friendly and sustainable form of energy for triggering chemical transformations, has emerged as one of the best strategies for the synthesis of organic compounds.

When enantiopure products are desired, it is difficult to control product formation since excited states have short lifetimes and it makes challenging to control electron transfer process which leads the catalyst to not dictate the stereochemistry of the products so that the transformations taken into account provide achiral or racemic compounds. Additionally, merging the photoredox catalyst with a chiral catalyst is difficult because of the high reactivity and low activation barriers of radical intermediates. In spite of this awkwardness, asymmetric photocatalytic transformations nowadays have been successfully accomplished by using a dual-catalyst approach using a combination of a photocatalyst and a chiral organocatalyst and also with only one catalyst, named a bifunctional catalyst, where the same molecule has a chromophore unit and a catalytic unit so that it combines chirality and photoredox properties. In such transformations, visible-light redox sensitizers are combined with asymmetric catalysts (either in a single molecule or in a dual catalysis system), such as chiral secondary amines, chiral N-heterocyclic carbenes, chiral Brønsted acids, chiral Lewis acids, or chiral thiourea under mild reaction conditions.

Overall, in asymmetric photoredox catalysis the photoactivated sensitizers (or the bifunctional catalyst with photoexcitation) initiate a SET from or to a closed-shell organic or metallic molecule to produce radical cations or radical anions whose reactivities are then exploited to synthesize the desired enantiopure product. To sum up, these advances allow it to forge a green, sustainable and economical chemistry without forgetting enantioselective properties.