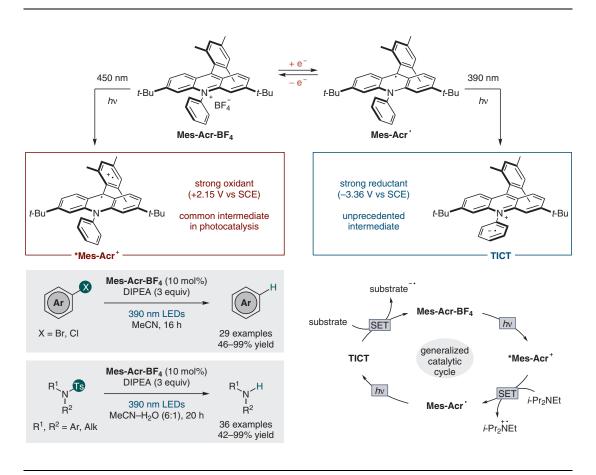
I. A. MACKENZIE, L. WANG, N. P. R. ONUSKA, O. F. WILLIAMS, K. BEGAM, A. M. MORAN, B. D. DUNIETZ, D. A. NICEWICZ* (UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL, USA)

Discovery and Characterization of an Acridine Radical Photoreductant *Nature* **2020**, *580*, 76–80.

Photoexcitation of an Acridine Radical Generates a Strong Organic Single-Electron Reductant



Significance: Nicewicz and co-workers report the characterization and utilization of an acridine radical derived from the common photoredox-catalyst **Mes-Acr-BF**₄. The stable radical was investigated experimentally and computationally in terms of its photochemical and redox properties. Upon irradiation, two distinct excited states are populated: a doublet state (D₁) and a twisted intramolecular charge-transfer state (TICT) in which the *N*-phenyl ring is twisted to allow charge transfer to the central acridine unit. The reduction potential of this compound was found to be as high as -3.36 V (vs. saturated calomel electrode), which is comparable to that of main-group alkali metals.

Comment: The described **Mes-Acr** radical could be generated in situ from **Mes-Acr-BF**⁴ through the use of *N*,*N*-diisopropylethylamine as a single-electron reductant. By applying this strategy, the photocatalytic cleavage of aromatic C–Cl and N–Ts bonds could be accomplished, the latter of which is usually performed by using strongly reducing alkali metals. The presented photocatalytic method is thus advantageous in terms of experimental convenience, functional-group tolerance, and atom economy. This work makes one question the inherent advantages associated with metals in organic chemistry, as well as the future limitations in reactivity for small-molecule organic catalysts.

Category

Organo- and Biocatalysis

Key words

photocatalysis

photoreduction

visible light

acridine radical

single-electron reduction