Photocatalytic Reactivity of Zwitterions

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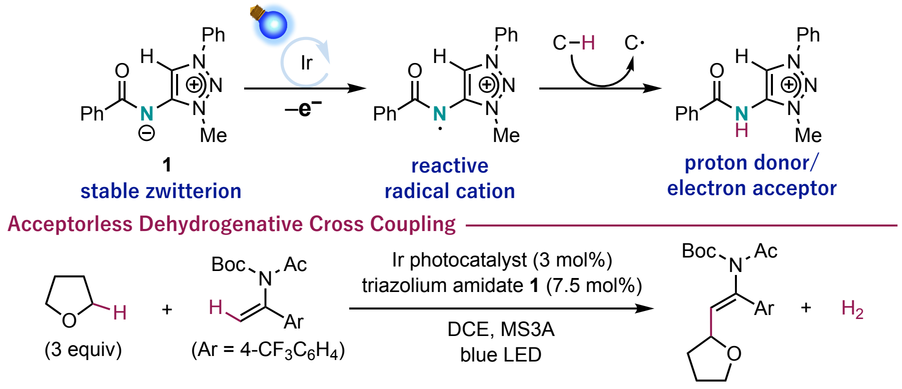
Zwitterions, which have both positive and negative charges in a single molecular framework, often exhibit unique properties such as large polarization, high crystallizability, and strong ionic interaction. These properties enable the application of zwitterions in a various field of chemical sciences. Another important aspect is their stability. Compared to typical cations and anions, zwitterions are generally easy to generate and often isolable owing to the stabilization by the inductive and resonance effects. From the viewpoint of synthetic chemistry, such stable species are usually unsuitable for the use as catalysts and reagents because they do not show notable reactivity. However, since highly polarized zwitterions efficiently undergo single electron transfer (SET) processes to generate the reactive radical ion species, zwitterions can be regarded as the easy-to-handle precursors of highly active intermediates. In light of this consideration and our research program on the design of ionic organic molecular catalysts,[1] we have been interested in the characteristic features of zwitterions, particularly in their potential reactivity exerted via photocatalytic activation.

One of our recent studies is the catalyst and reaction development by harnessing the reactivity of electron-deficient radical cations generated from the stable zwitterions through photocatalytic SET. For instance, we have devised a bench-stable, zwitterionic 1,2,3-triazolium amidate **1** and achieved catalytic hydrogen-atom transfer (HAT) reactions based on the generation of the amidyl radical via intermolecular SET with a photocatalyst. Furthermore, the discovery that the conjugate acid of the triazolium amidate, 1,2,3-triazolium amide, behaves as a one-electron acceptor and oxidatively regenerates photocatalysts with dehydrogenation has led to the development of acceptorless dehydrogenative cross-coupling (ADC) reactions.[2]



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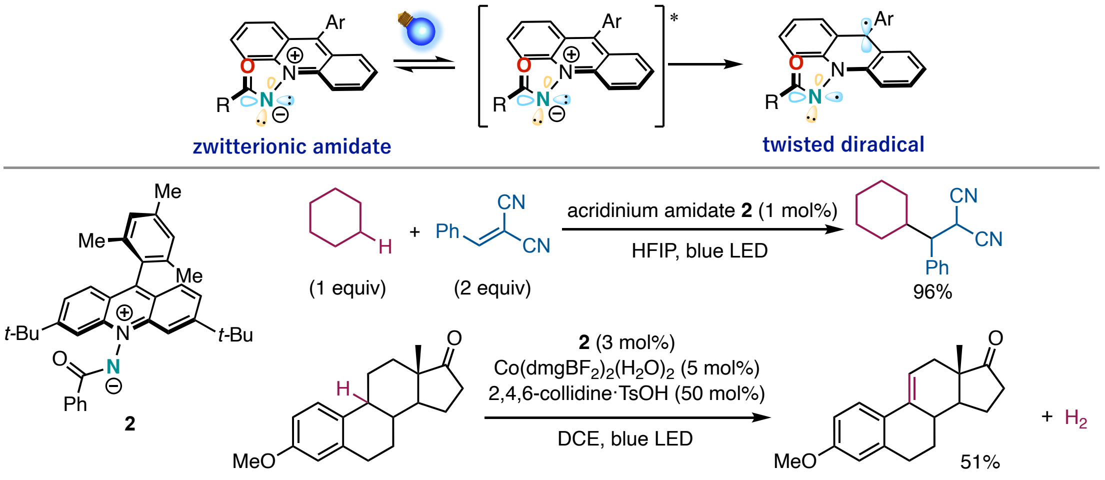
While triazolium amidate is effective for photoinduced HAT with a range of aliphatic C–H bonds, its intrinsic reactivity has yet to be fully elicited because the actual concentration of amidyl radicals generated in the intermolecular SET is extremely low. To overcome this problem, we have pursued an approach toward more efficient HAT directly triggered by the photoexcitation of zwitterions.

Photoinduced direct hydrogen atom transfer, termed d-HAT, has been regarded as an ideal strategy owing to its high catalyst economy and broad applicability.[3] The existing catalysts capable of undergoing d-HAT uniformly rely on molecular entities containing oxo groups (Z=O), such as aromatic ketones, xanthene dyes, and inorganic metal oxo complexes, thus being constrained to oxygen-centered radicals. This restriction poses inherent difficulty in enhancing the reactivity of the d-HAT catalysts owing to the limited possibility of structural modification around the oxo-groups. On the other hand, unlike oxo-containing molecules, their nitrogen analogs lack an ability to exert d-HAT catalysis, and no reliable strategy has been available to endow them with pertinent photocatalytic reactivity to promote HAT reactions. Under these circumstances, we have developed zwitterionic acridinium amidates as photoreactive amidyl radical precursors, which exert prominent reactivity as d-HAT catalysts. The key to our catalyst design was the perpendicular orientation of the acridinium 2p orbitals and lone pair in the 2p orbital of the amidate nitrogen. This enabled the generation of a twisted diradical consisting of reactive amidyl radicals and stable acridinyl radicals as HAT-active species via photoexcitation and intramolecular charge transfer.[4]



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