What makes fireflies glow?

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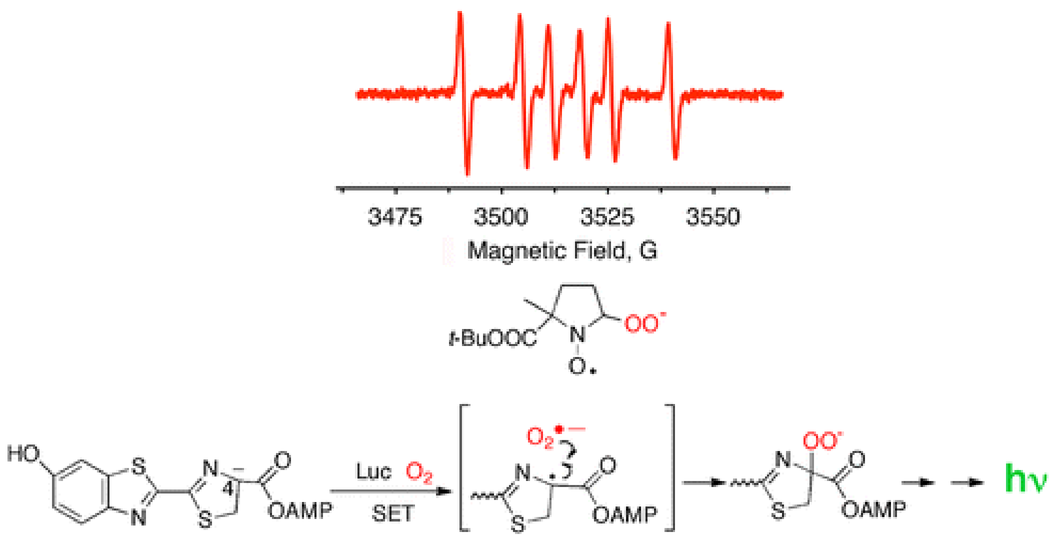

As fireflies are delighting children across the country with their nighttime displays, scientists are closing in on a better understanding of how the insects produce their enchanting glow. They report in the *Journal of the American Chemical Society* new evidence of how the beetles' chemistry works. Their findings could apply to the bioluminescence of other organisms, too.

About 60 years ago, scientists figured out in broad strokes the cascade of reactions that allows fireflies to produce light. It starts with a chemical called luciferin, which interacts with the energy-transporting molecule adenosine triphosphate, or ATP. The product of that reaction then combines with oxygen, and this in turn releases light. Intermediate steps, however, have not been fully fleshed out. Bruce R. Branchini and colleagues wanted to explore potential mechanisms.

The researchers experimented with the enzyme luciferase, which boosts the initial reaction between luciferin and ATP, under varying conditions. In contrast to the commonly accepted model, the resulting data suggest that the transfer of a single electron to oxygen occurs during one of the final steps to spur light production. Other studies of bioluminescence have pointed to the same mechanism, raising the possibility that it could be a unifying feature of the natural phenomenon.

More information: "Experimental Support for a Single Electron-Transfer Oxidation Mechanism in Firefly Bioluminescence" *J. Am. Chem. Soc.*, 2015, 137 (24), pp 7592–7595. DOI: 10.1021/jacs.5b03820

Abstract
Firefly luciferase produces light by converting substrate beetle luciferin into the corresponding adenylate that it subsequently oxidizes to oxyluciferin, the emitter of bioluminescence. We have confirmed the generally held notions that the oxidation step is initiated by formation of a carbanion intermediate and that a hydroperoxide (anion) is involved. Additionally, structural evidence is presented that accounts for the delivery of oxygen to the substrate reaction site. Herein, we report key convincing spectroscopic evidence of the participation of superoxide anion in a related chemical model reaction that supports a single electron-transfer pathway for the critical oxidative process. This mechanism may be a common feature of bioluminescence processes in which light is produced by an enzyme in the absence of cofactors.

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