

Long-Lived Terphenyl Radical Anion Super-Reductant for Photocatalysis Formed *via* Blue-to-UV Upconversion with Fully Resolved Mechanism

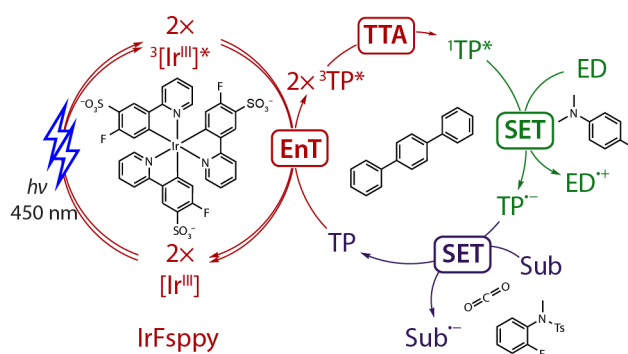
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The mechanistic elucidation of photoredox catalytic cycles is challenging but very important in order to design new reaction pathways. The rapidly advancing field of radical ion-mediated photocatalysis highlights the significant potential for synergy between mechanistic and synthetic approaches. The underlying reaction mechanisms are often highly complex, in part because they typically involve the sequential absorption of two photons per catalytic turnover, and partly due to the chemical instability and extremely short lifetimes of excited organic radicals.

We present a way to address these challenges through a fully elucidated photocatalytic mechanism for the biphotonic, visible-light generation of an organic *p*-terphenyl radical anion that, in its microsecond-lived ground state, exhibits a reduction potential of -2.5 V vs SCE which is comparable to those of previously reported excited organic radical anions with picosecond lifetimes. Our results establish blue-to-ultraviolet upconversion as a robust strategy for generating long-lived super-reductants *via* a consistent, controllable mechanism that enables the activation of small inert substrate molecules, including CO_2 .

This study forms a direct link between detailed mechanistic studies, where all elementary steps are observed, and synthetic applications, thereby illustrating the innovation potential enabled by mechanism-driven discovery of new photoreactivity.



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