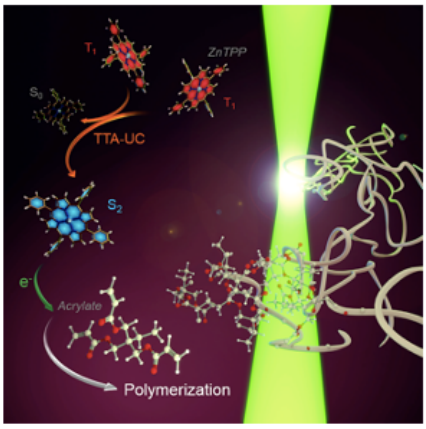
Visible-Light-Initiated Free-Radical Polymerization by Homomolecular Triplet-Triplet Annihilation



The upper S_2 excited state of ZnTPP is oxidatively quenched by the acrylates, resulting in the formation of an acrylate radical anion that engages in radical chain polymerization chemistry.

Awwad et al., *Chem* **2020**, *6*, 1–15.
November 5, 2020
https://doi.org/10.1016/j.chempr.2020.08.019
Work was performed at North Carolina State University

Scientific Achievement

A new visible-light photoactivation mechanism based on sensitized triplet fusion between two excited ZnTPP chromophores achieves free-radical polymerization from acrylate monomers without additives

Significance and Impact

Harvested the energy from two separately absorbed photons to initiate free-radical polymerization via excited state electron transfer from the upper excited states (S_2) of ZnTPP.

Research Details

- Ultrafast dynamic electron transfer from the ZnTPP S_2 excited state demonstrated using fluorescence upconversion spectroscopy.
- Radical products detected by EPR spectroscopy.
- Well-defined macro- and micron-sized polymer gels readily produced.

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Free-radical polymerization represents a key synthetic route enabling the production of myriad polymer, materials, and hydrogel composites generating billions of pounds of these macromolecules annually. Photoinitiation represents a major mode of activation in route to these materials but requires the input of high-energy UV light accompanied by numerous challenges. Translating this process to visible light mandates numerous additives and co-initiators to facilitate radical generation. We address these concerns by introducing a new photoactivation mechanism leveraging low-energy visible photons to drive free-radical polymerization in acrylates without additives. Homomolecular triplet-triplet annihilation in ZnTPP initiates radical chain polymerization in pure monomer solutions resulting in the formation of well-defined macro- and microscopic polymer gel objects. Given the range of excited-state potentials, triplet fusion likely applies to most free-radical polymerizations.