TRIPLET-TRIPLET ANNIHILATION POLYMERIZATION (TTAP) FOR HIGH-RESOLUTION 3D PRINTING

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Two-photon polymerization (TPP) is currently the dominant approach to 3D printing with very high spatial resolution, down to ~ 100 nm, but suffers from very limited volumetric write speeds compared to conventional stereolithography (SLA) approaches and requires a specialized high intensity pulsed laser source. Here, we demonstrate a new method of photosensitized 3D printing initiated through triplet-triplet-annihilation (TTA) energy upconversion that achieves sub-micron resolution with an LED light source, requiring six orders of magnitude less intense light than TPP. TTA limits polymerization to the focal point of light, and resolution can be modulated from 0.6 μm to over 4 μm thanks to a micromirror array, which also offers the potential for parallelization and high throughput printing. We demonstrate a unique 3D printing mechanism capable of fabricating sub-micron features, and present a model for the system combining established kinetics for TTA and photopolymerization, which provides insight into the mechanism and guides the choice of printing parameters.