# MICRO-722
# **3D printing with Light**

## **3D printing by UpConversion particles**

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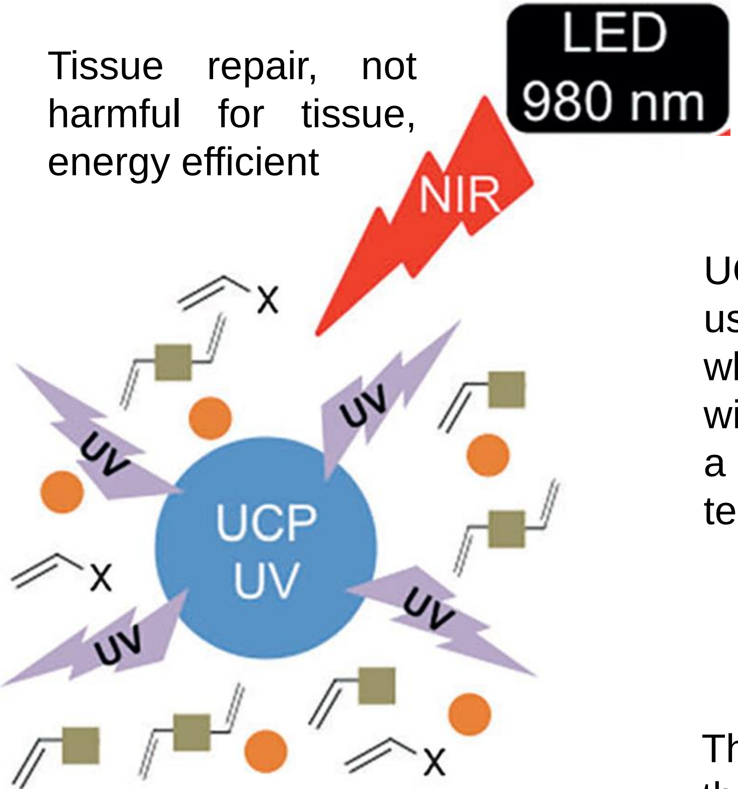
# UpConversion Particles

Upconversion particles can be used in 3D printing to enable deep photopolymerization and volumetric printing at a focal point using a low power continuous wave excitation. In photon upconversion, two or more incident photons of relatively low energy are absorbed and converted into one emitted photon with higher energy.

Tissue repair, not harmful for tissue, energy efficient




A higher upconversion threshold can lead to more efficient energy transfer and better control over the upconversion process. (designing versatile UCP, the concentration of particles)

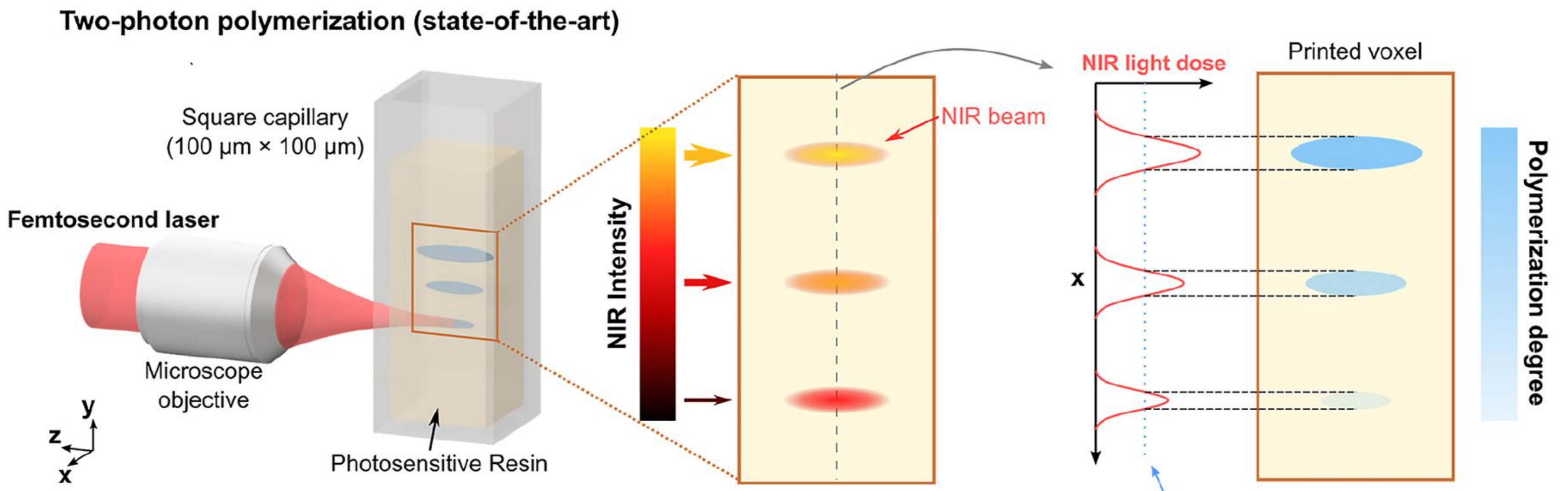
UCNPs are typically fabricated using a co-precipitation method, where lanthanide ions are mixed with a precipitating agent to form a solid and then annealed at high temperatures.

The UCNPs emission peaks at 345 and 361 nm under the excitation of 980-nm (NIR).

The specific emission bands of the UCNPs had a good overlap with the absorption band of the lithium-base photoiniator.

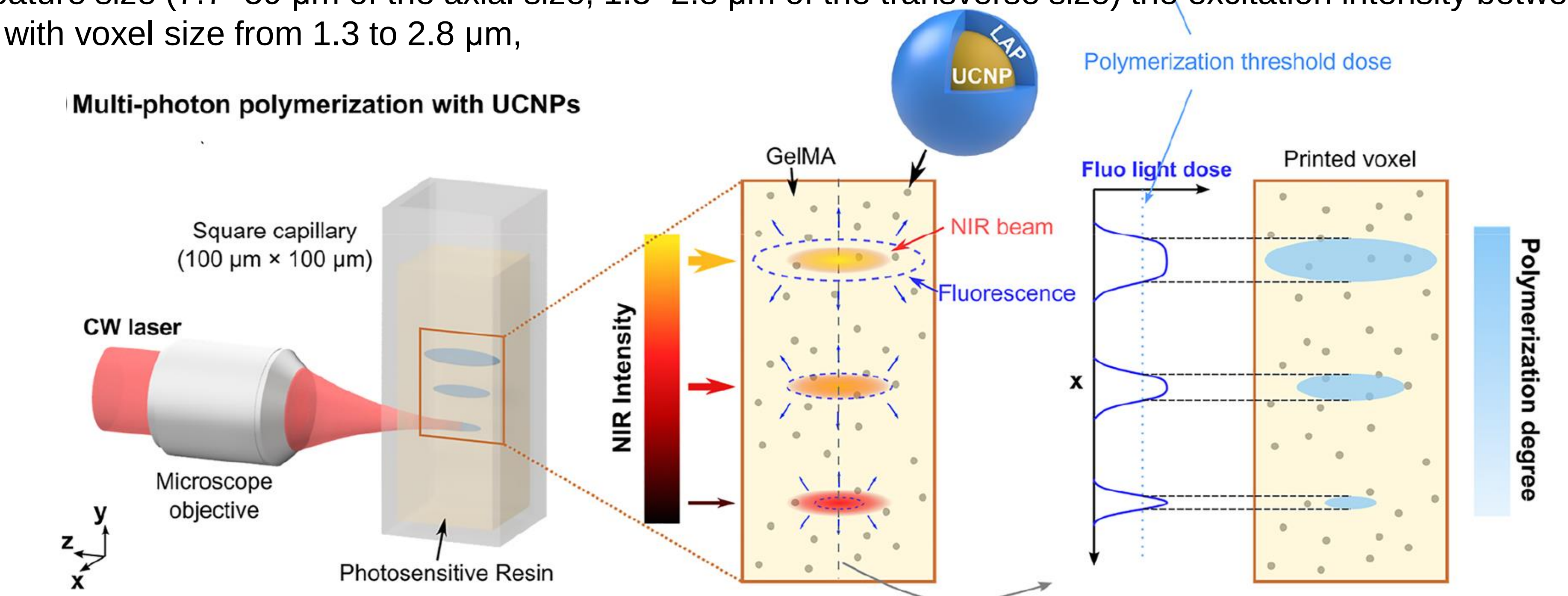
Wang, K. et. al. (2020). *Photochemistry and Photobiology*, *96*(4), 741-749.

# Multi-photon polymerization using upconversion nanoparticles for tunable feature-size printing




The printed voxel size can be tuned by adjusting the NIR intensity which produces under or over-polymerized parts.

The feature size (7.7–59 µm of the axial size, 1.3–2.8 µm of the transverse size) the excitation intensity between $7.7 \times 10^4$ and $1.1 \times 10^6$ W/cm$^2$ along with voxel size from 1.3 to 2.8 µm,

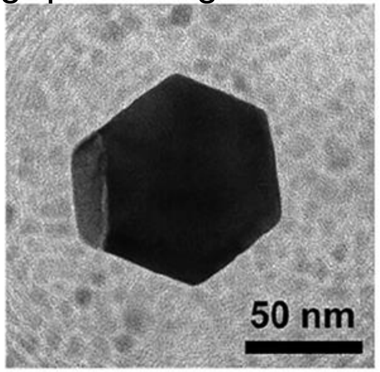



By upconversion nanoparticles (UCNPs), the beam size of the upconverted fluorescence depends on the NIR intensity which enables printing voxels of different sizes with the same degree of polymerization.

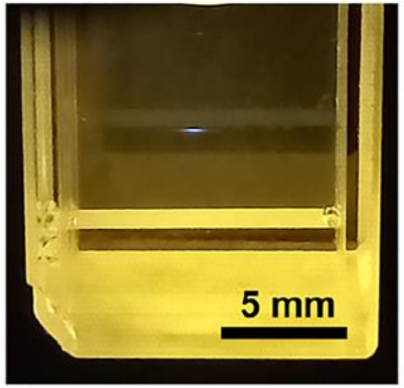
The power-dependent nonlinearity

# Multi-photon polymerization using upconversion nanoparticles for tunable feature-size printing

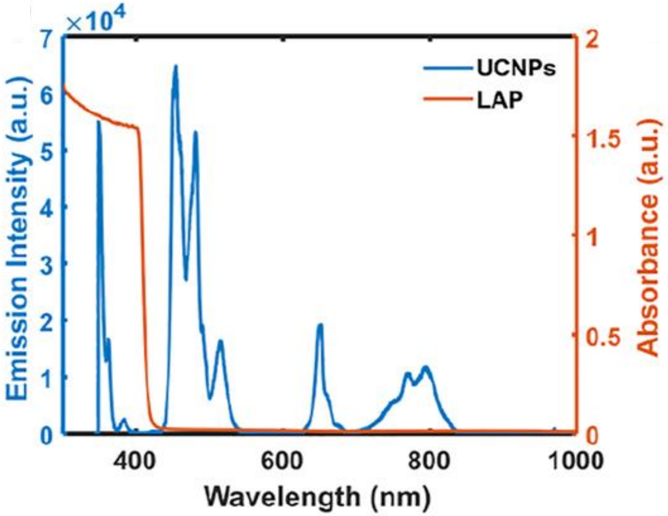
The core/shell $NaYF_4$: $Yb^{3+}$,$Tm^{3+}$/$NaYF_4$ ~60 nm: hexagonal; shell ~3 nm for eliminating quenching factor.



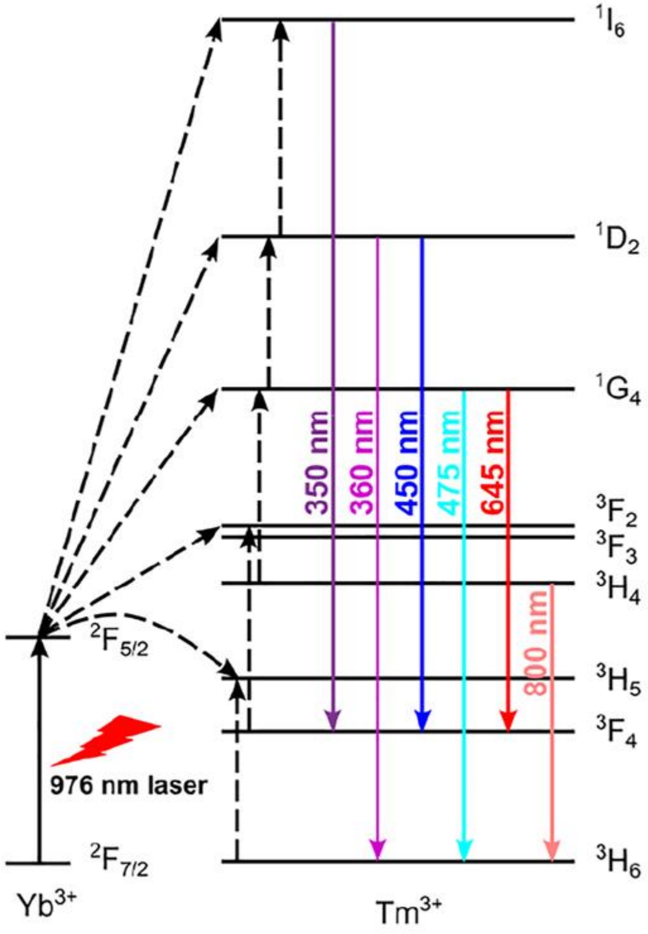

976-nm light beam



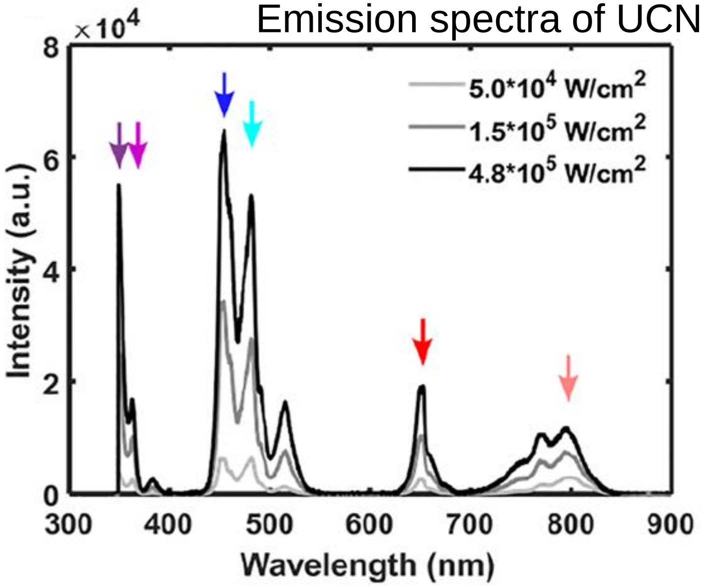

Photopolymerization is initiated with the absorption band of 350 nm.

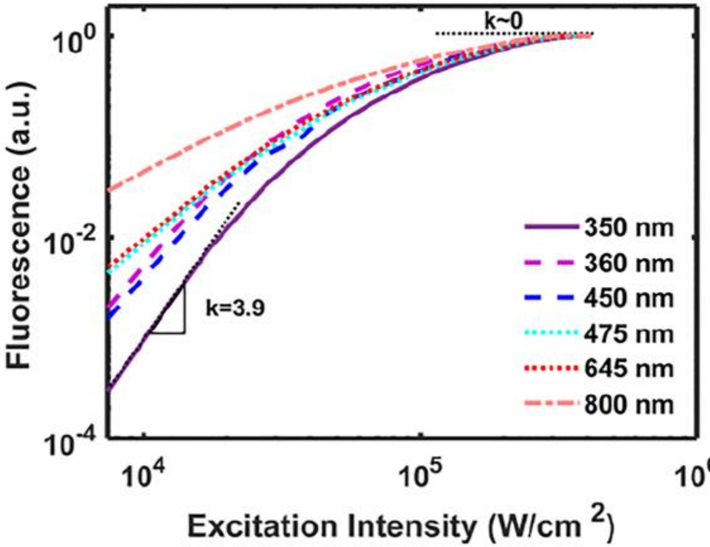



The $Yb^{3+}$ ion acts as the sensitizer that absorbs a NIR photon and transfers it to $Tm^{3+}$



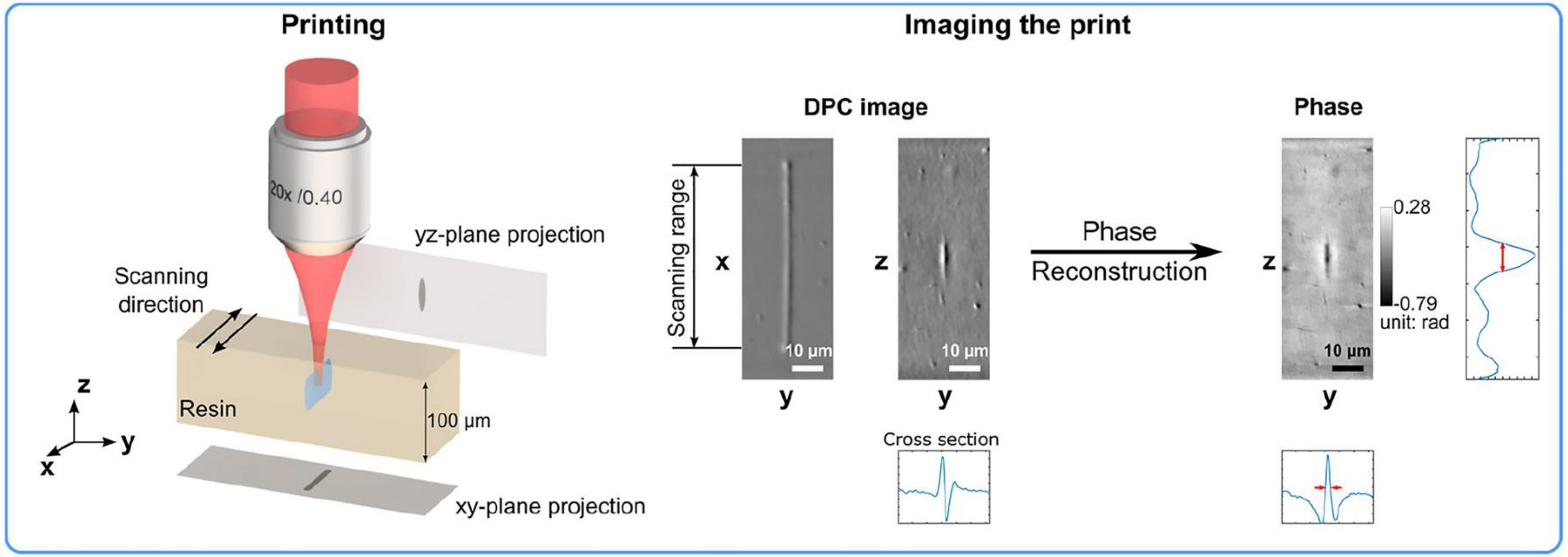

Emission spectra of UCNPs at different excitation intensities.



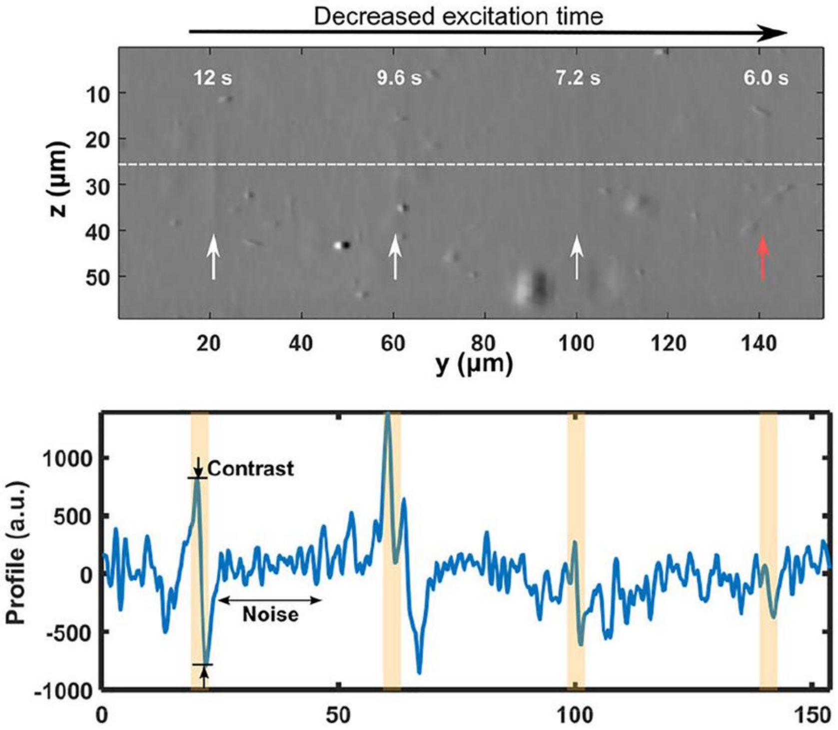



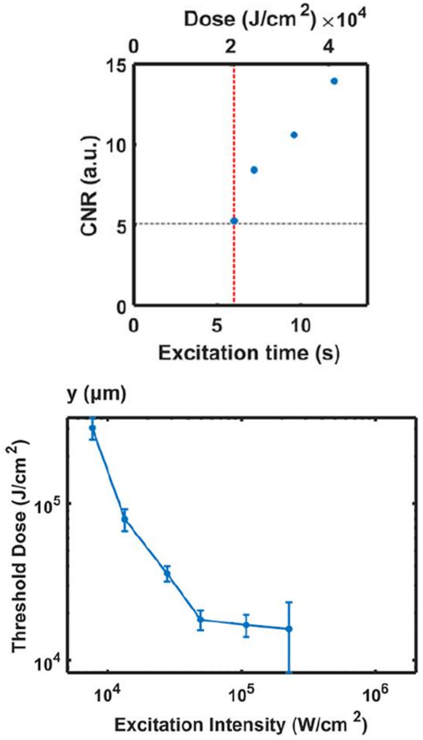
# Multi-photon polymerization using upconversion nanoparticles for tunable feature-size printing

The polymerization threshold dose (loop number for each excitation intensity and time) is defined as the dose for which the CNR is equal to 5 (almost invisible voxel).

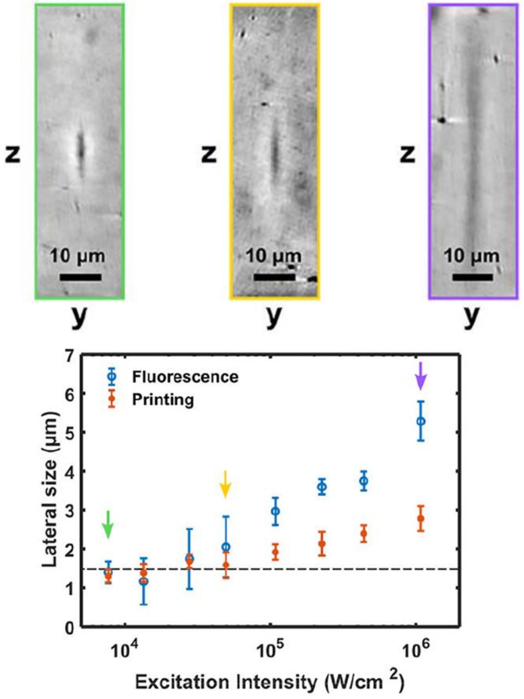



NIR threshold dose NIR intensity of 1.1 × $10^5$ W/$cm^2$.

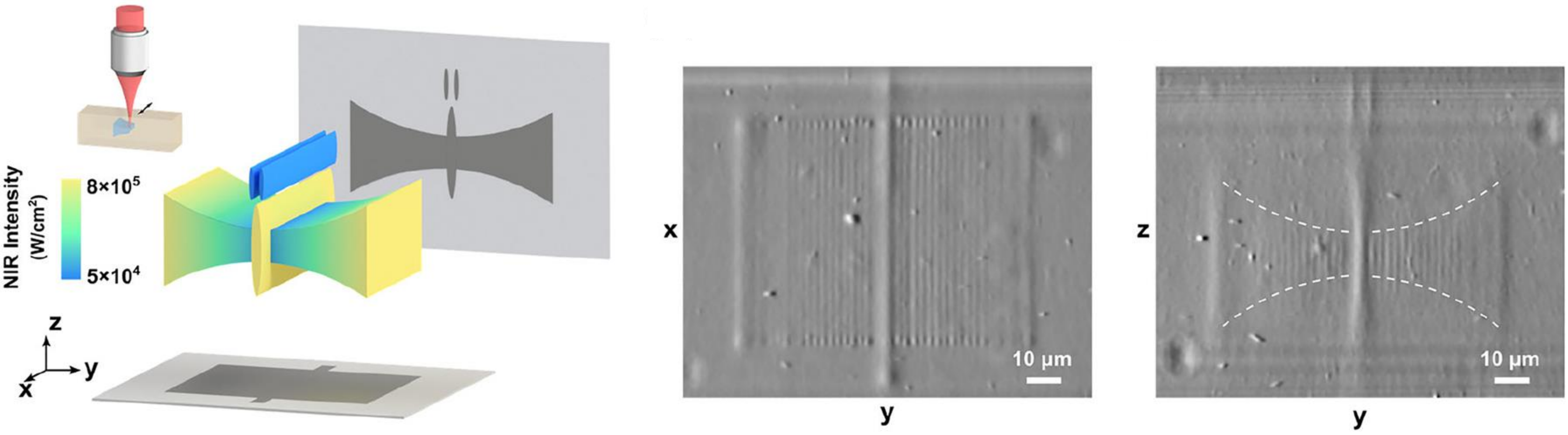



Voxel size



# Multi-photon polymerization using upconversion nanoparticles for tunable feature-size printing

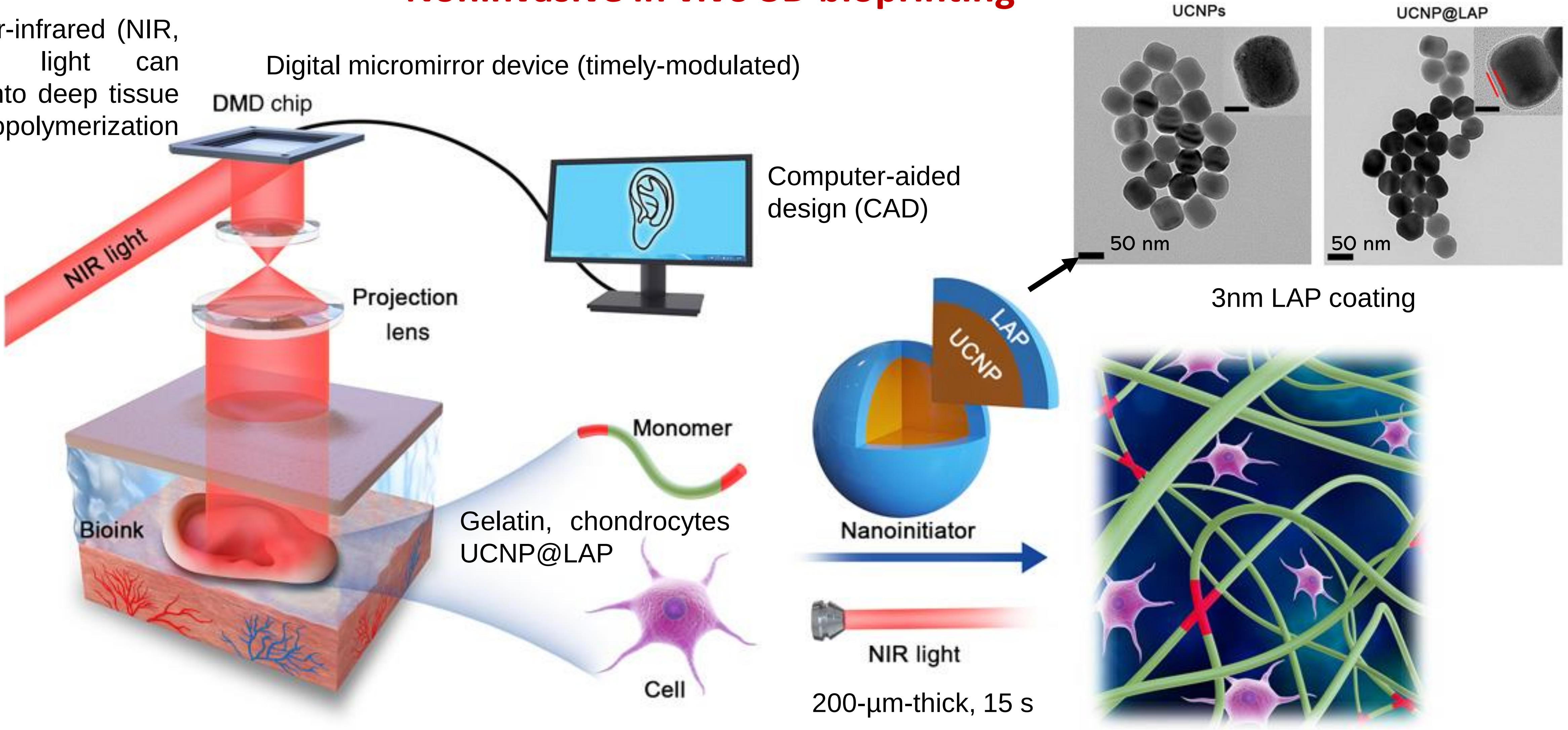



Fabricating butterfly-shaped nanoantenna thanks to nonlinearity offered by UCNP. Voxels printed at high intensities merge and form a smooth surface.

By calibrating the nonlinearity and the polymerization dynamics, other upconverting processes may also be applied to tunable feature-size printing with better efficiency or higher resolution.

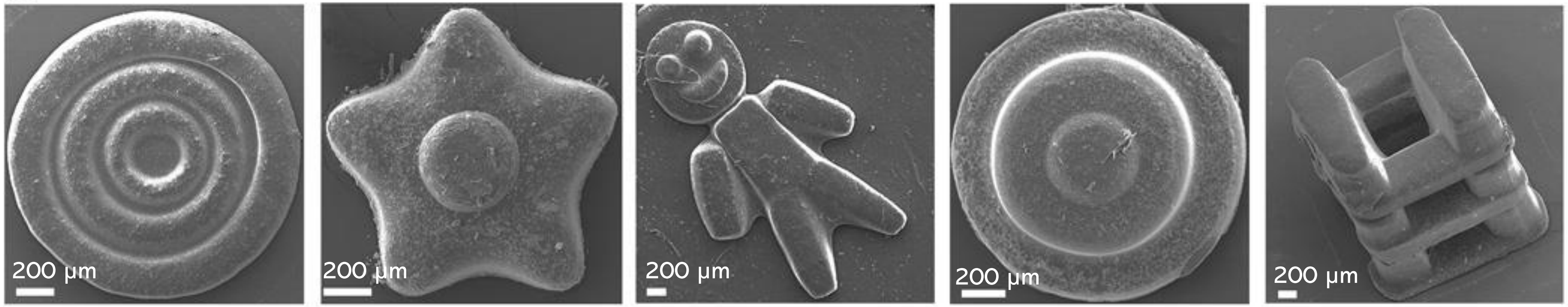
# Noninvasive in vivo 3D bioprinting

Digital, near-infrared (NIR, 980 nm) light can penetrate into deep tissue by photopolymerization (DNP).

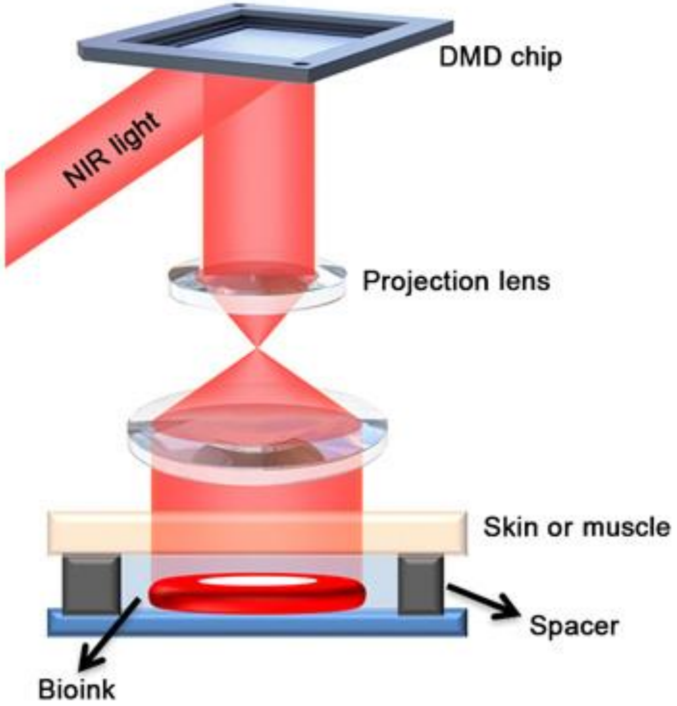


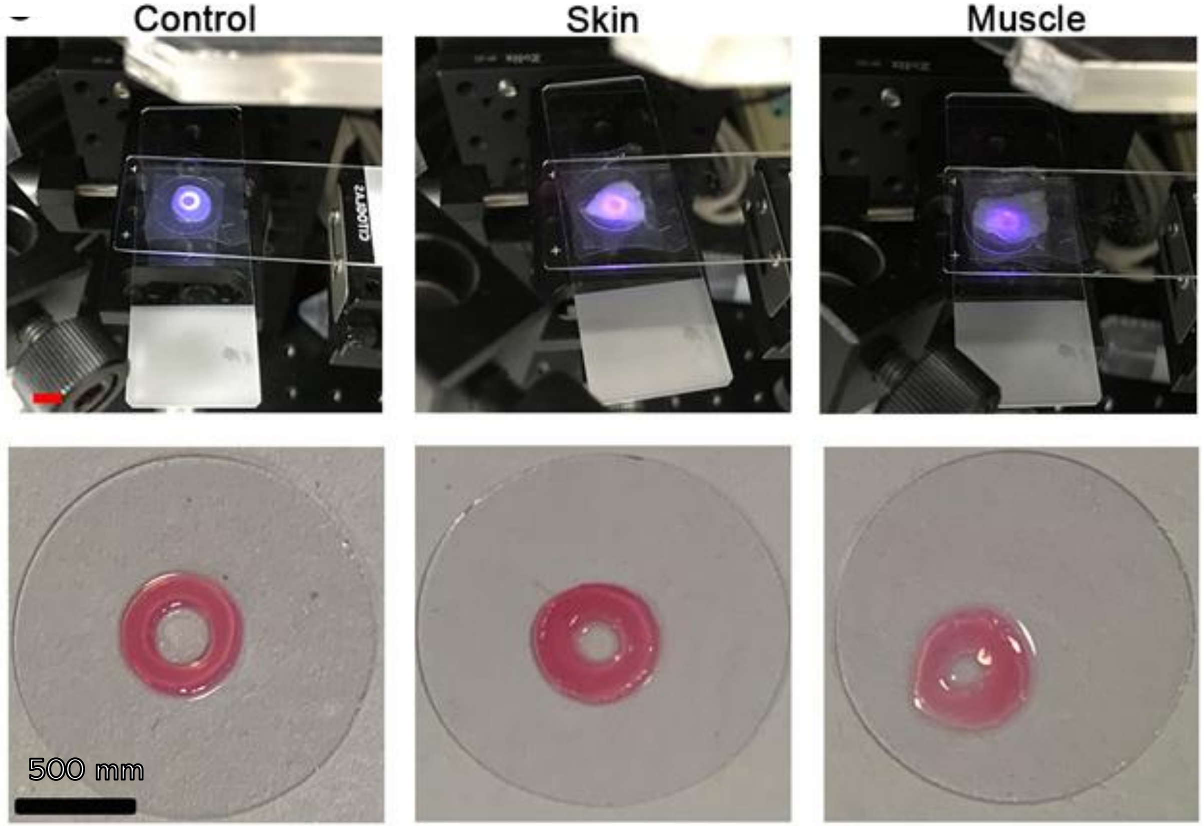

Digital light processing (DLP), without surgery implantation, personalized ear-like tissue constructs with chondrification and a muscle tissue repairable cell-laden conformal scaffold were obtained subcutaneously with high cell viability of post-printing and superior printing speed *via* noninvasive method.

# Noninvasive in vivo 3D bioprinting

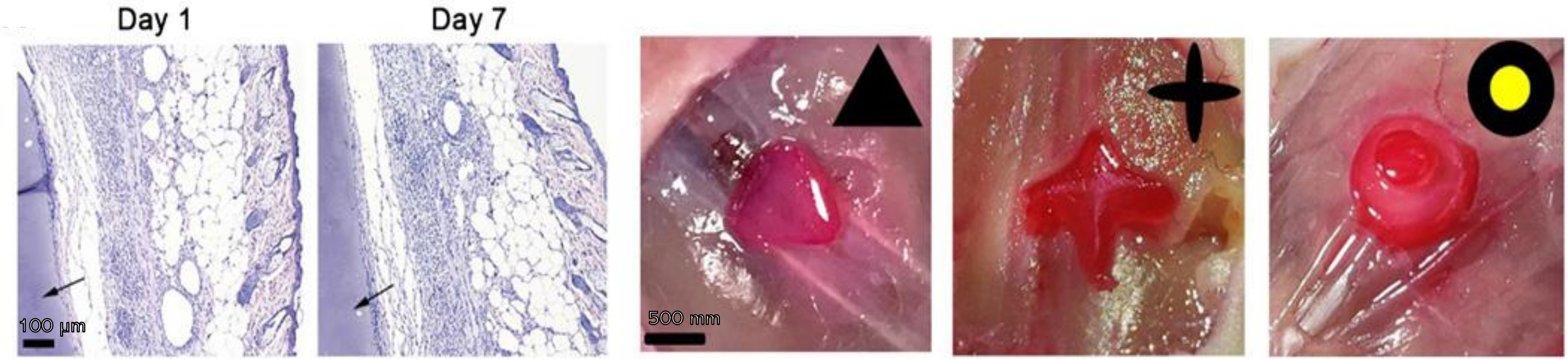



Three-ring | Flower-like | Danboard | Round cake-like | Truss



# Noninvasive in vivo 3D bioprinting




1 or 7 days after printing, the surrounding tissues have complete tissue structures without significant inflammation.

In vivo condition that often has lower oxygen concentration might facilitate the DNP-based process for bioprinting.

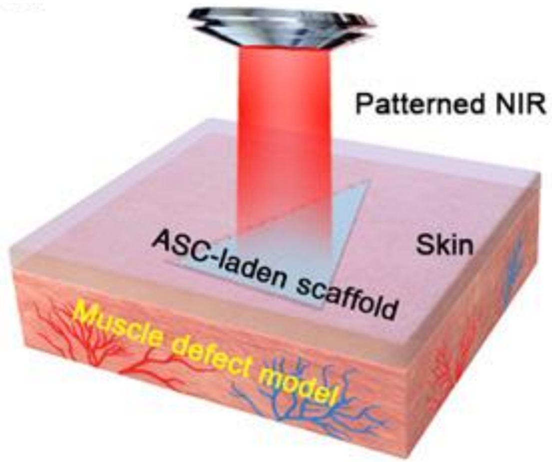
The flexibility of the DNP is validated by printing different structures.

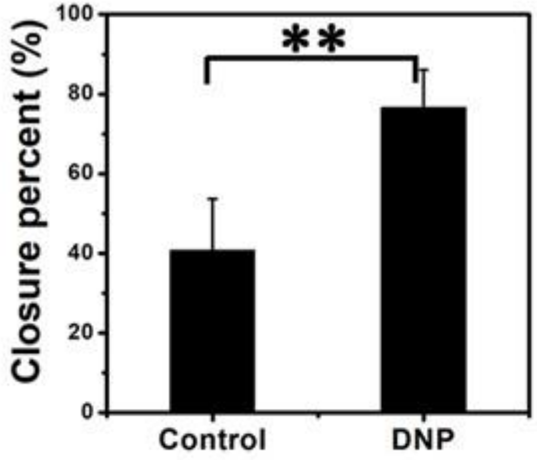
# Noninvasive in vivo 3D bioprinting

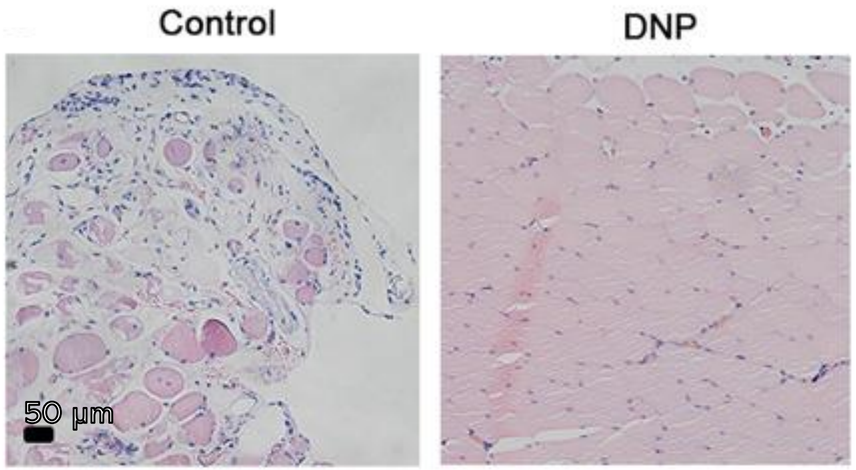
Auricle defect often needs the implantation of artificial auricle in vivo. While the implantation process would cause iatrogenic injury a noninvasive process is needed.

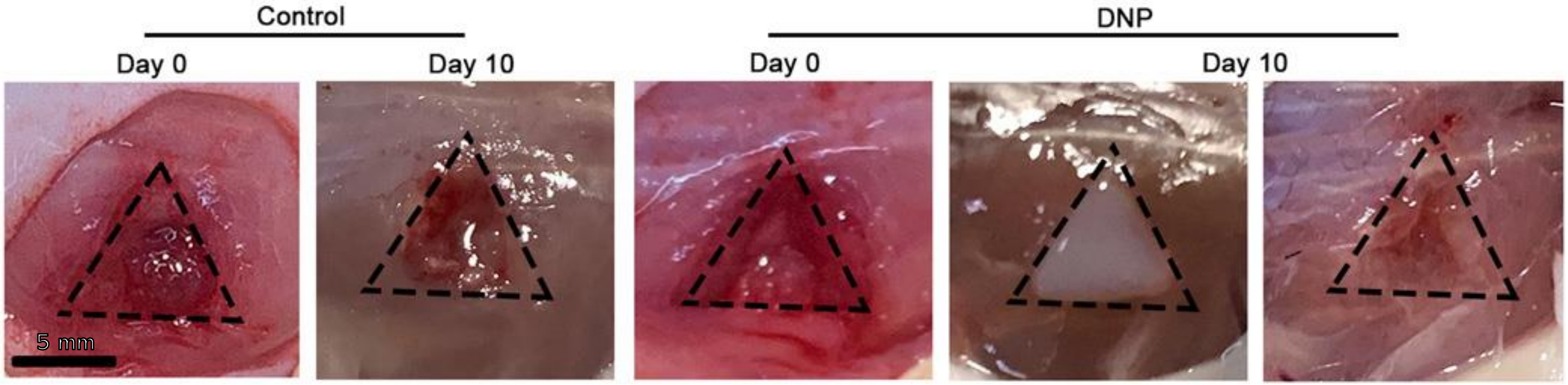
# Noninvasive in vivo 3D bioprinting

Closed injury treatment is promoted by noninvasively printing adipose-derived stem cells (ASCs).



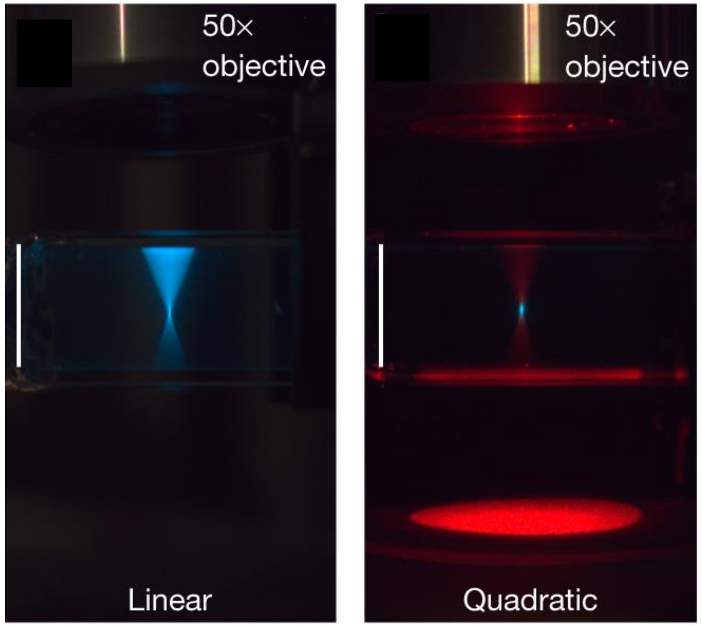



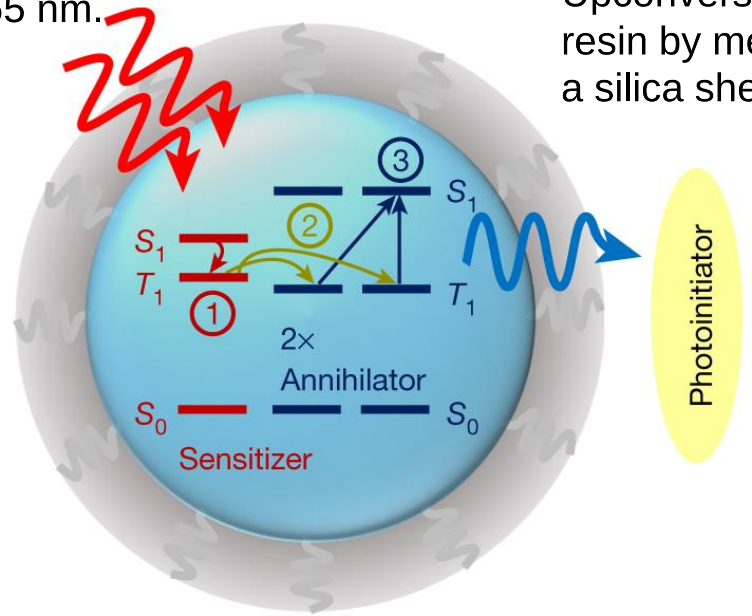



# Triplet fusion upconversion nanocapsules for volumetric 3D printing

The linear laser required to drive printing has limited print size and speed, preventing widespread application beyond the nanoscale.




The linear process results from directly exciting the sensitizer at 635 nm and exciting annihilator triplets at 365 nm.




Upconversion is introduced to the resin by means of encapsulation with a silica shell and solubilizing ligand

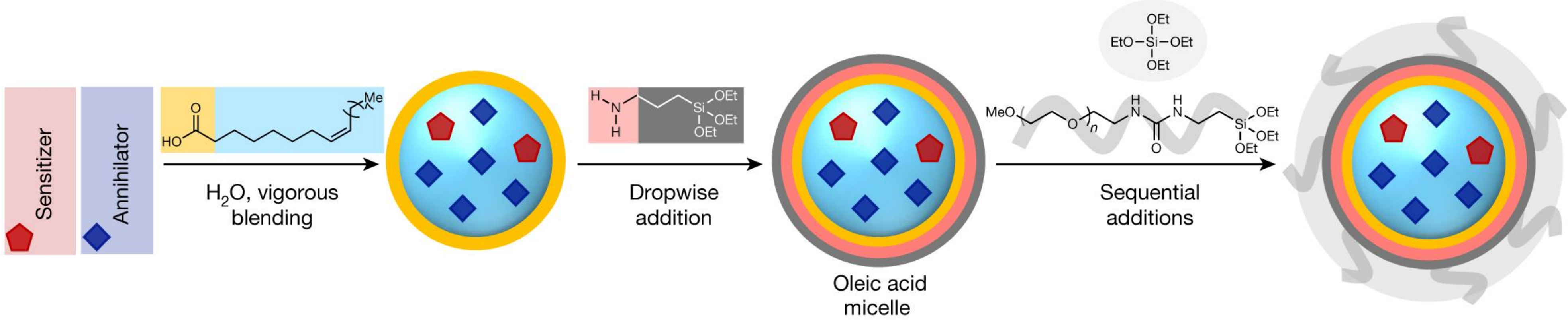
Germanium and titanium-based initiator (Ivocerin, 450 nm)

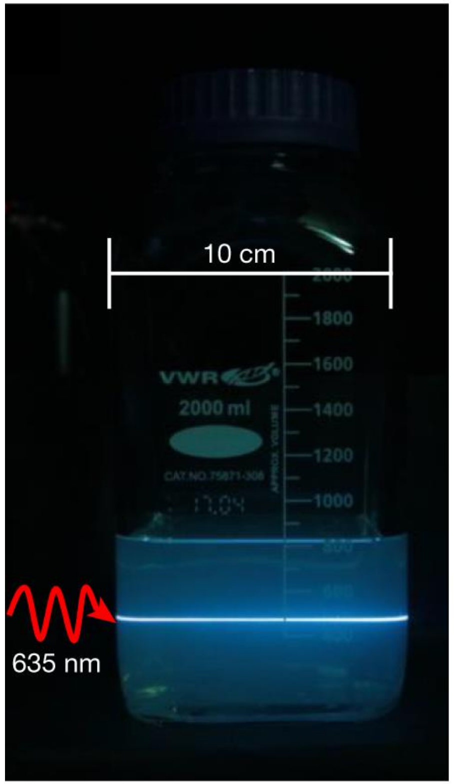
The final upconversion step requires collisions of two excited annihilator triplets, which fuse to form one higher-energy annihilator singlet, which emits blue light that can be used to excite photopolymerization by coupling with a photoinitiator.

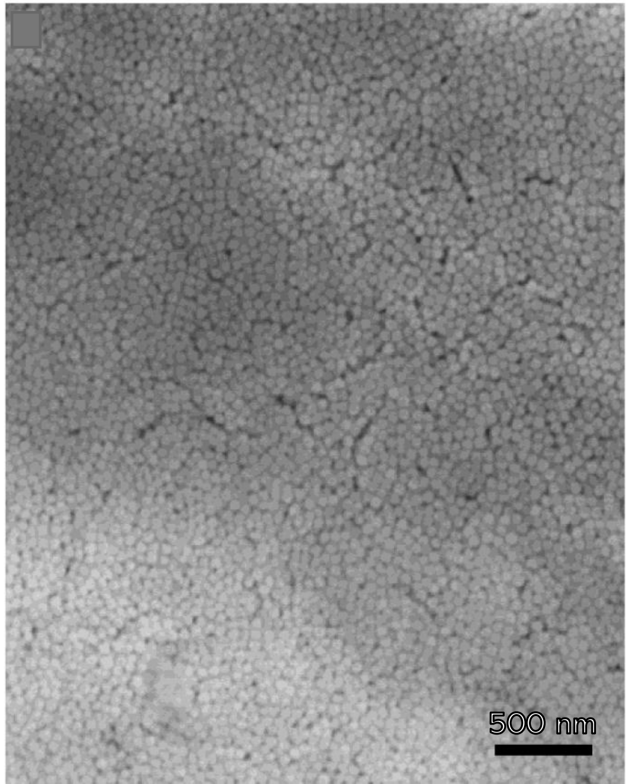

Scan in three dimensions

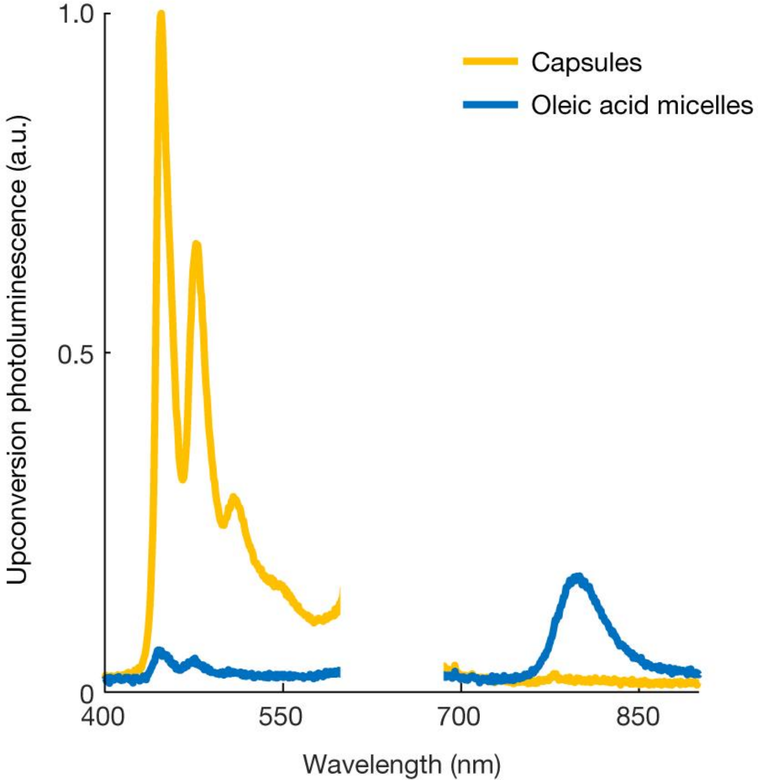
# Triplet fusion upconversion nanocapsules for volumetric 3D printing

A nanoencapsulation that would disperse in organic-solvent-based 3D printing resins without leaking the contents or scattering light.



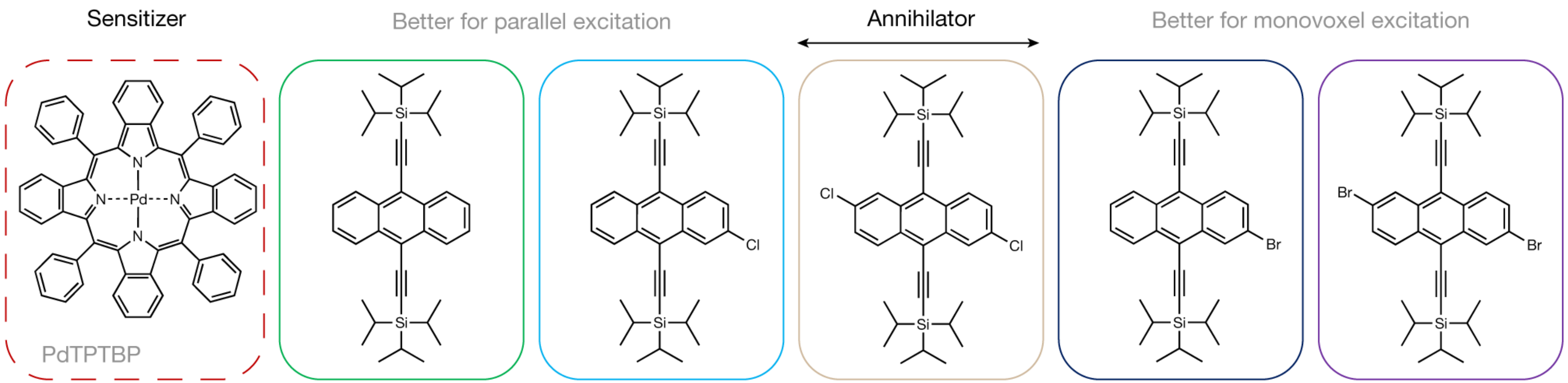



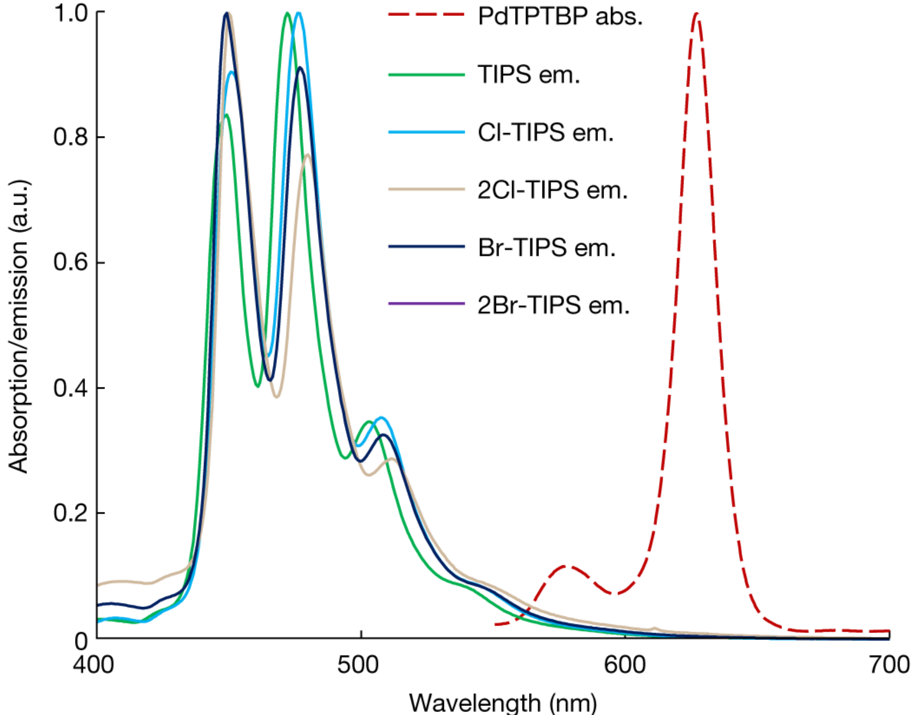



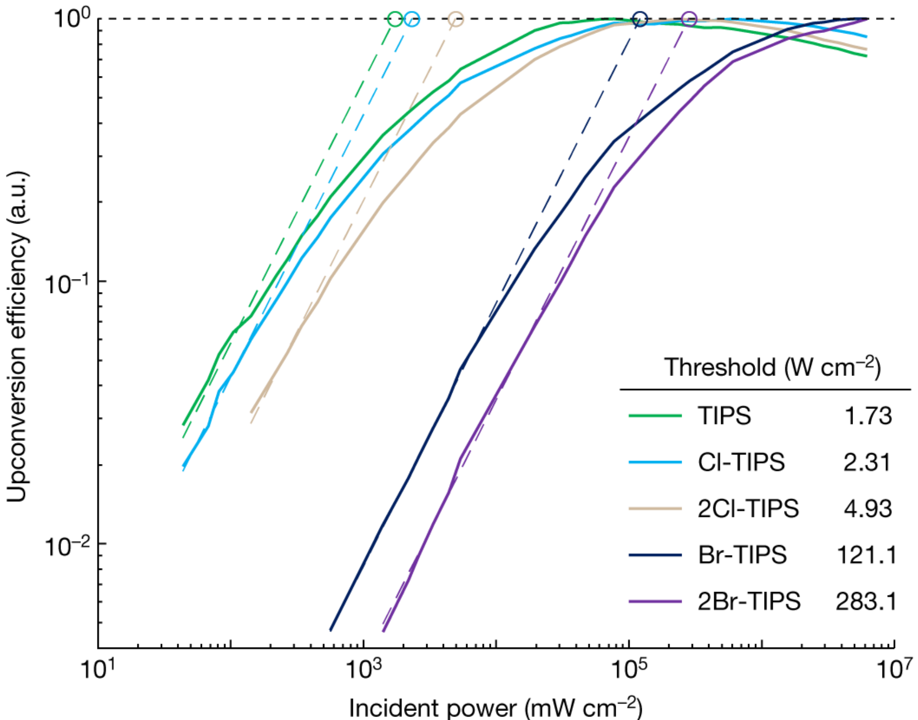
# Triplet fusion upconversion nanocapsules for volumetric 3D printing

An excitonic strategy to systematically control the upconversion threshold to support either monovoxel or parallelized printing schemes, printing at power densities several orders of magnitude lower than the power densities required for two-photon-based 3D printing.

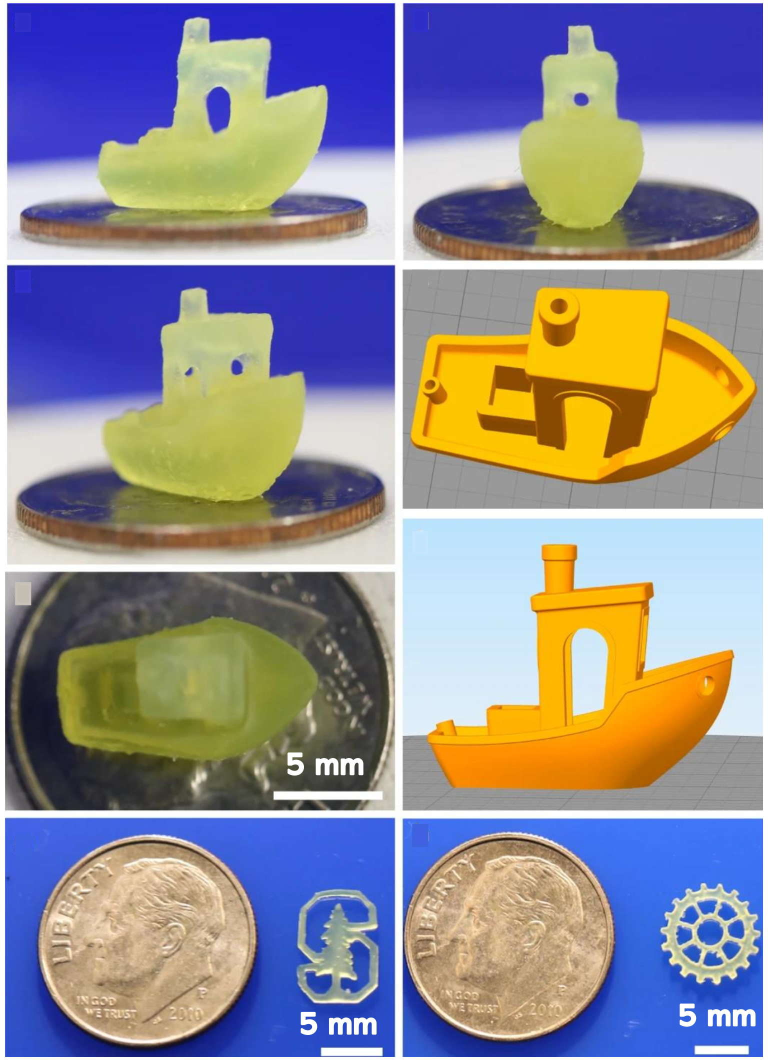


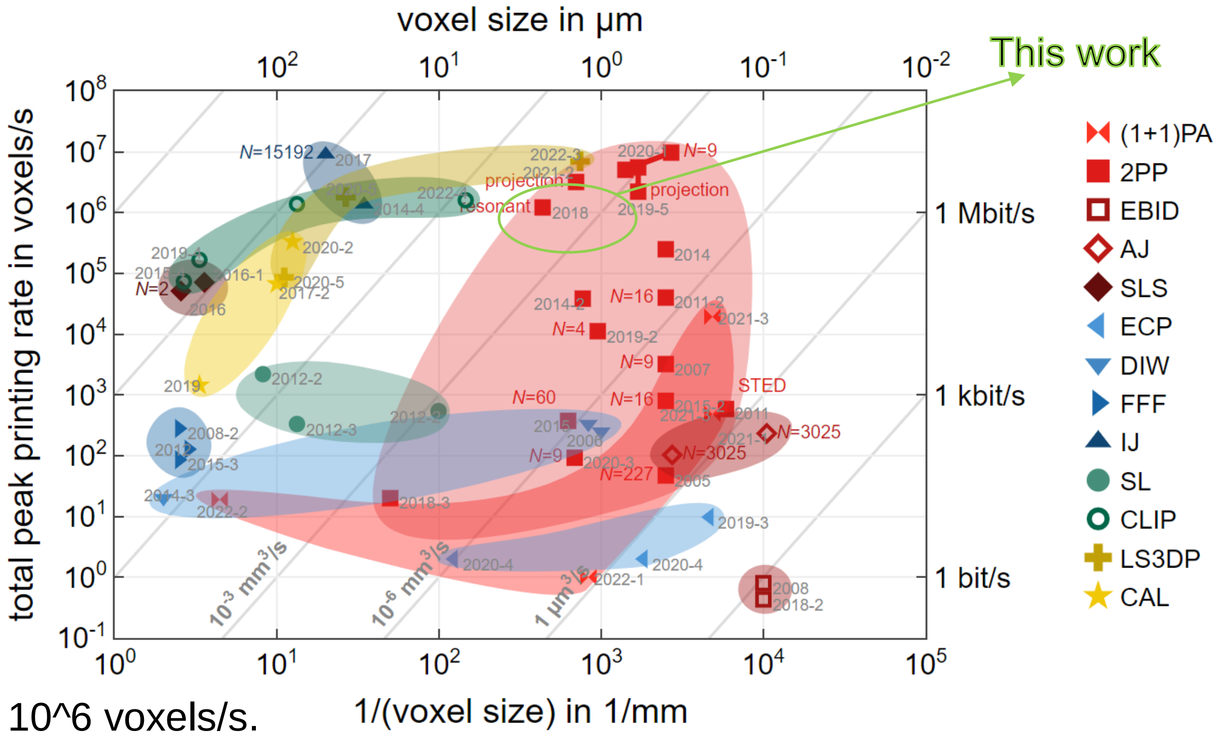

TIPS-anthracene



# Triplet fusion upconversion nanocapsules for volumetric 3D printing




1.6 × 10^6 voxels/s.

- (1+1)PA : (1+1)-Photon Absorption
- 2PP : Two-Photon Printing
- EBID : Electron-Beam-Induced Deposition
- AJ : Aerosol Jet 3D Nanoprinting
- SLS : Selective Laser Sintering
- ECP : Electrohydrodynamic (redox) Printing
- DIW : Direct Ink Writing
- FFF : Fused Filament Fabrication
- IJ : Inkjet 3D Printing
- SL : Stereolithography
- CLIP : Continuos Liquid Interphase Printing
- LS3DP : Light-Sheet 3D Printing
- CAL : Computed Axial Lithography

# THANK YOU FOR YOUR ATTENTION!

## Any Questions?