1+1 Photon Absorption Processes and New Photoinitiators

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3D Printing with Light

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Two-step absorption instead of two-photon absorption in 3D nanoprinting

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Perspective

Challenges and Opportunities in 3D Laser Printing Based on (1 + 1)-Photon Absorption

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Search for Alternative Two-Step-Absorption Photoinitiators for 3D Laser Nanoprinting

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2022

From Karlsruhe Inst. Tech. (KIT)

Free-Radical Photopolymerization

Initiation

$$Initiator + h_{\nu} \longrightarrow \mathrm{R}^{\bullet}$$
$$\mathrm{R}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{RM}^{\bullet}$$

Propagation

$$\mathrm{RM}^{\bullet} + \mathrm{M}_n \longrightarrow \mathrm{RM}^{\bullet}_{n+1}$$

Termination

combination

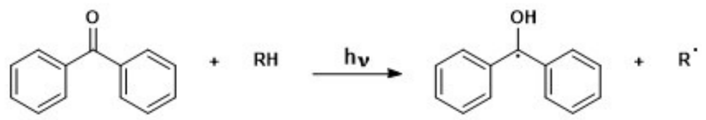
$$\mathrm{RM}^{\bullet}_n + {}^{\bullet}\mathrm{M}_m\mathrm{R} \longrightarrow \mathrm{RM}_n\mathrm{M}_m\mathrm{R}$$

disproportionation

$$\mathrm{RM}^{\bullet}_n + {}^{\bullet}\mathrm{M}_m\mathrm{R} \longrightarrow \mathrm{RM}_n + \mathrm{M}_m\mathrm{R}$$

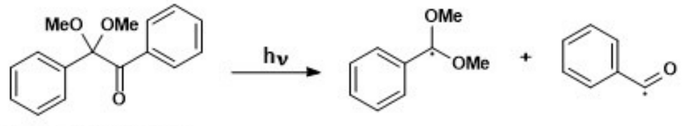
Free-Radical Photoinitiation

Abstraction



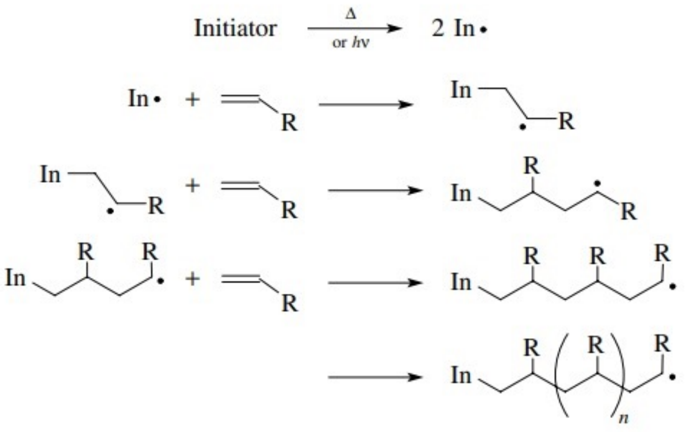
Benzophenone

Cleavage

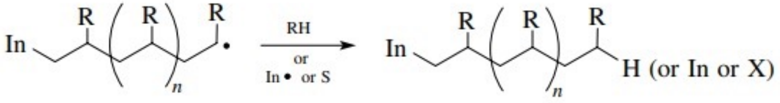


Benzil dimethyl acetal

Example Process



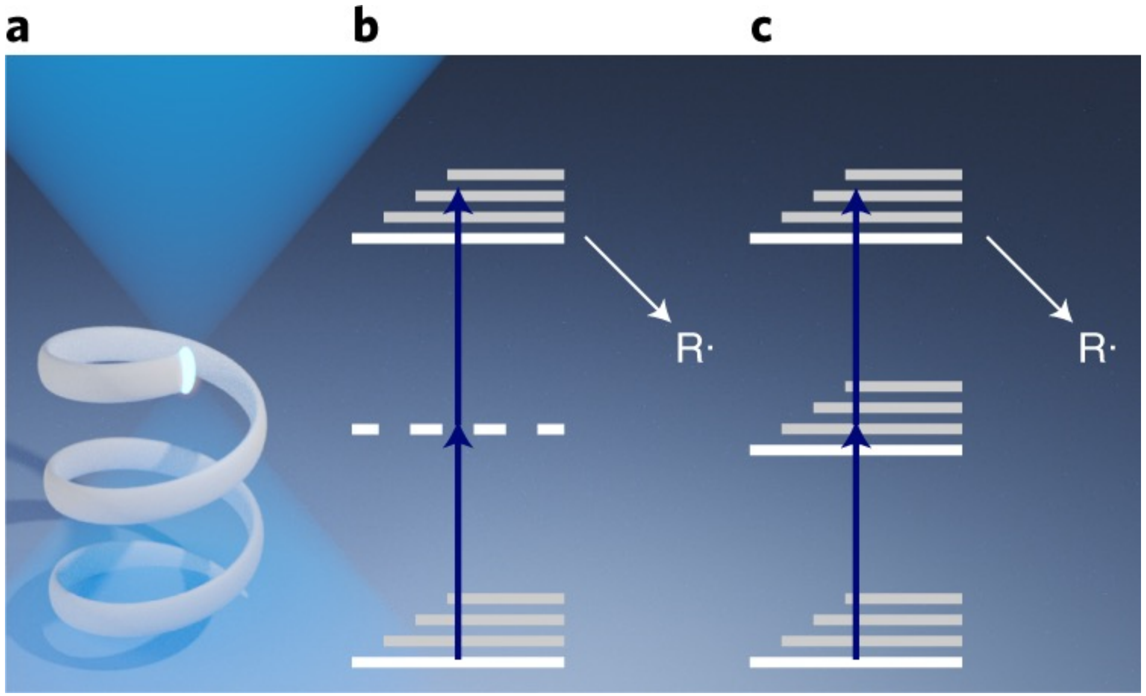
Termination



Problem:

without non-linear reactions with photo-intensity, exposure dose accumulates along the optical path rendering precision control impossible.

Two-Photon Absorption vs. Two-Step Absorption

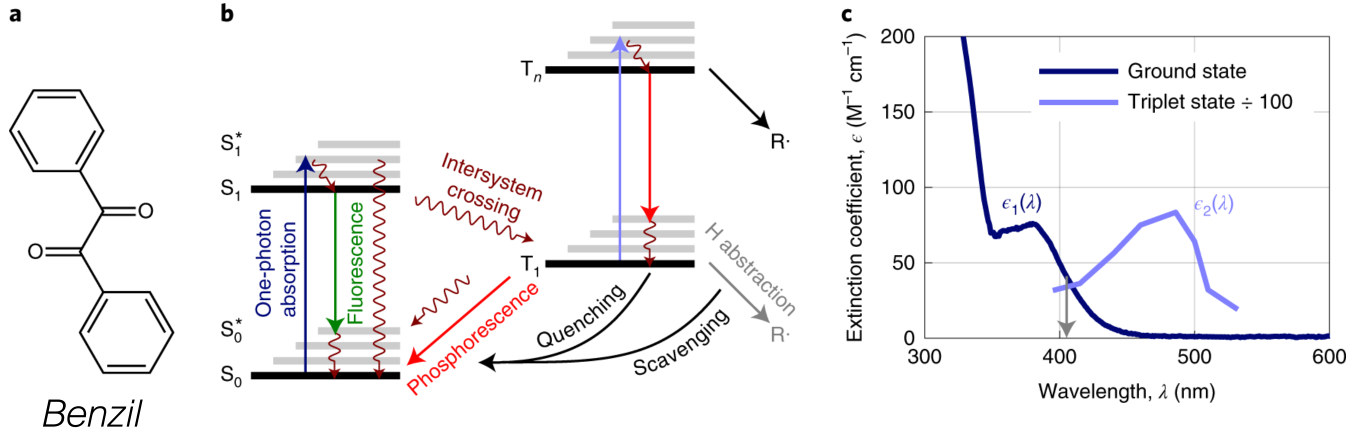


B) Two Photon Absorption (established)

- Enables $D \propto I^2$
  - Quadratic relationship implies smaller voxel size for more focused exposure and cross-linking
- Electrons are excited to a virtual state, which only exists when light is applied continuously
- Another photon provides the missing energy to complete the excitation

C) Two-Step Absorption (new)

- There is a real electronic state for the electron to occupy.
- Can use the same photoinitiator and one or two colors



Quenching: anything that reduces fluorescence intensity (O_2)
Scavenging: reducing hydrogen concentration

Two-step absorption instead of two-photon absorption in 3D nanoprinting

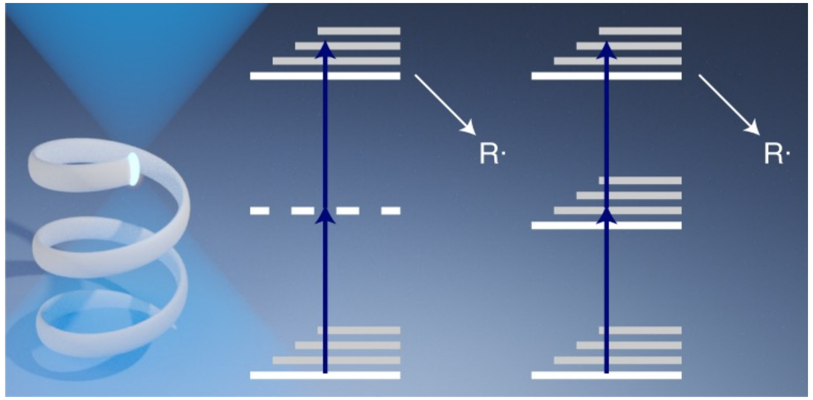
Pros and Cons

Two-Photon Absorption

Cons

- Laser cost: mode-locked pico- or femtosecond lasers (10^{12} W/cm^2)
  - Tens of thousands of euros
- Size of femtosecond lasers is large
- Microexplosions
  - 3-4 photons absorbed creates high population of high-energy states.
  - Laser power at which this occurs varies.

Two-photon processes are still limited in commercial scope



Two-Step Absorption (new)

Lifetime of electrons is determined by non-radiative decay (much longer than virtual-state lifetime)

Pros

- Can use continuous laser systems with μW level doses
  - More efficient process due to longer excitation lifetimes
  - Tens of euros, not tens of thousands.

Cons

- Added chemical complexity
- A single absorption may prematurely trigger a polymerization reaction
- Non-linear exposure scalability
  - Real state decay lifetime, $\tau = k_D^{-1}$
  - For $tk_D << 1 \rightarrow D \propto t^2 I^2$
  - For $tk_D \approx 10 \rightarrow D \propto t I^2$
  - Reference: one-photon absorption, $D \propto tI$

Two-step absorption instead of two-photon absorption in 3D nanoprinting

1+1 Absorption ($D \propto I^2$)

Two-Step Absorption (B)

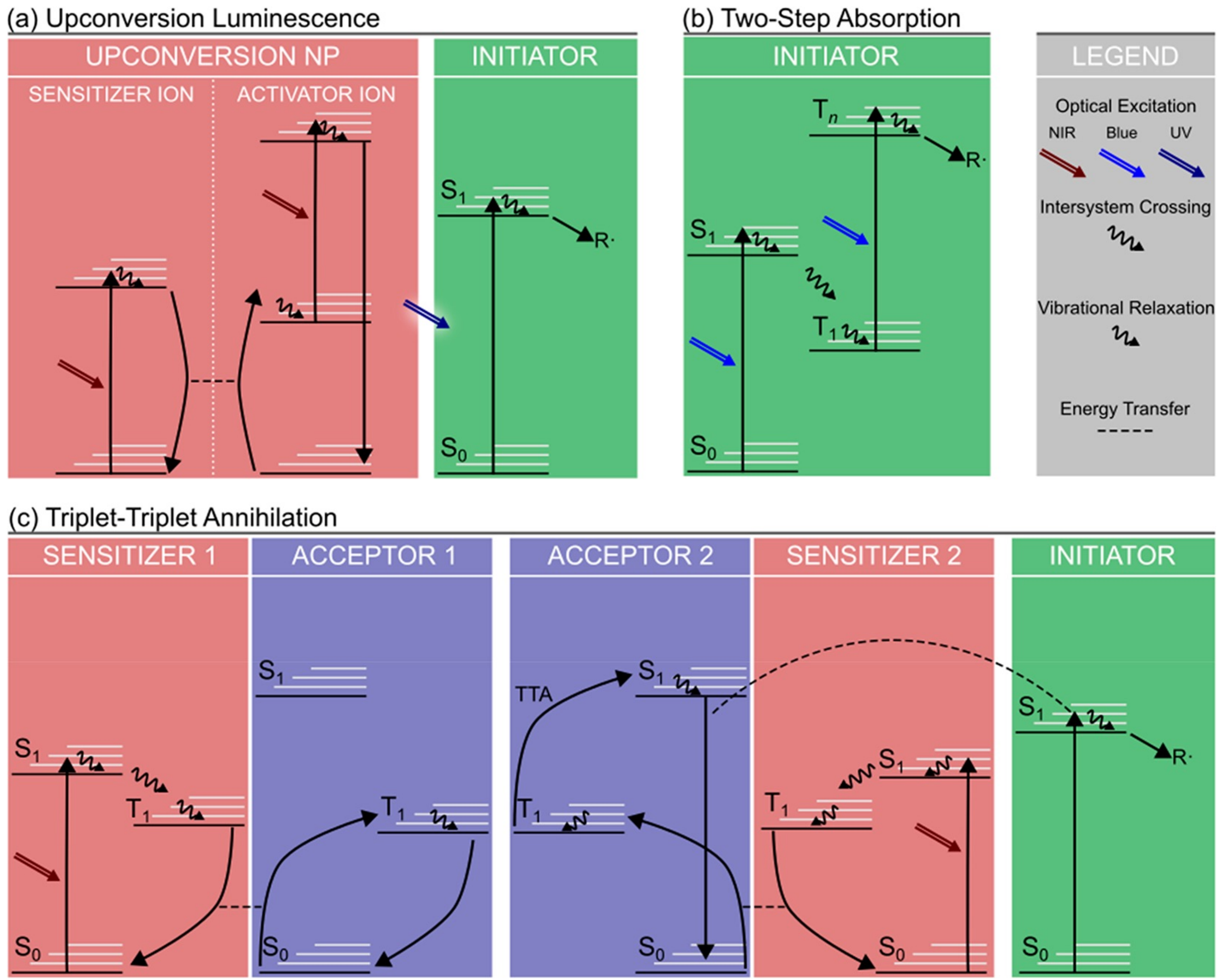
- Two photons generate a total excited state with sufficient energy for radicalization

Upconversion Luminescence (A)

- Two photons generate a single ultraviolet photon that's then absorbed by an initiator
- Voxel size is proportional to absorption length of UV photon
- **UV emission probability $\propto I^2$**

Triplet-Triplet Annihilation (C)

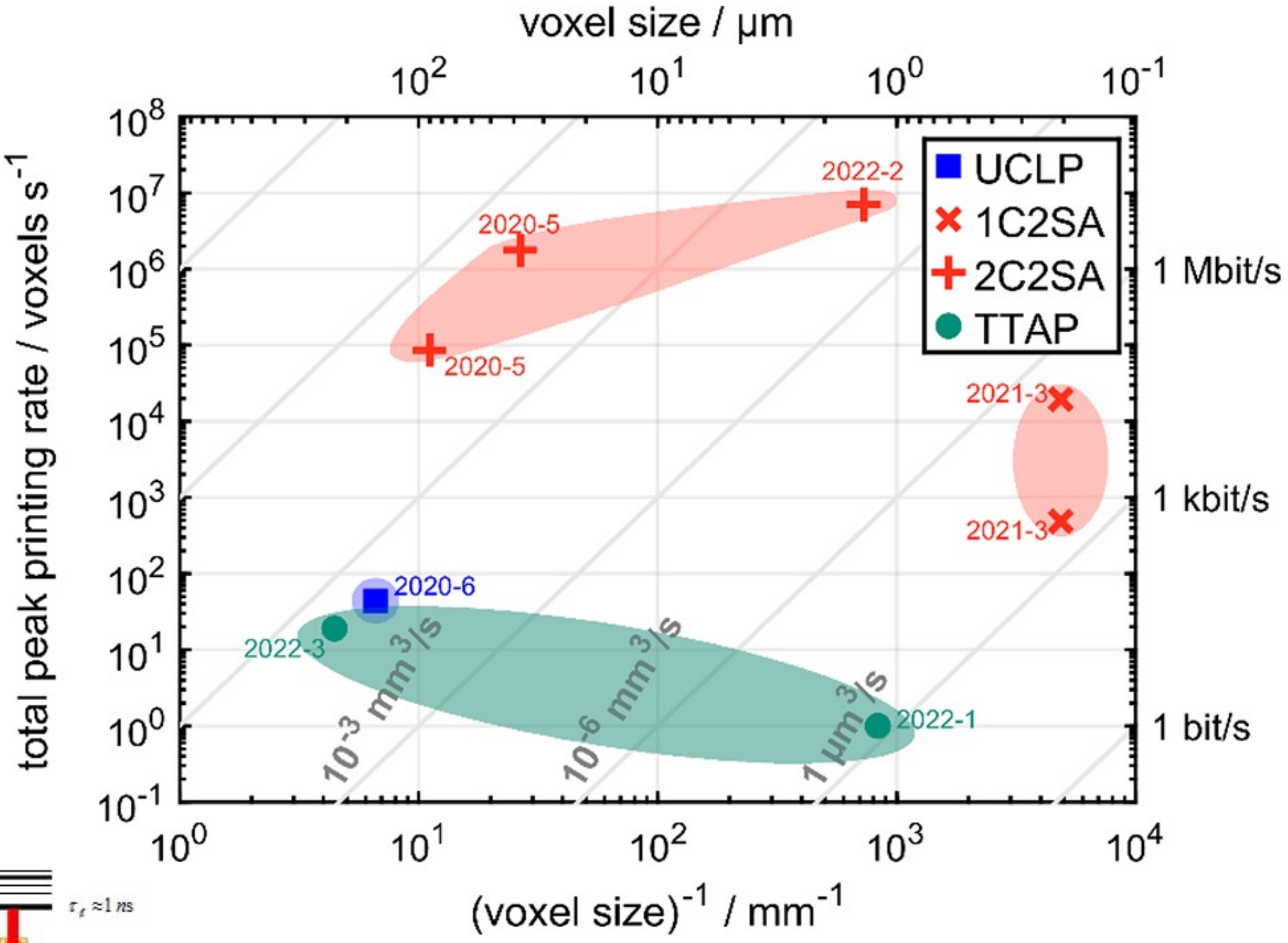
- Two photons fuse energy; one acceptor generates a higher energy photon, sending the other emitter back to ground state.
- Requires a large concentration of sensitizers and excited acceptors, as two molecules need to be proximal
- Diffusion dependent process, determined by photoresin viscosity



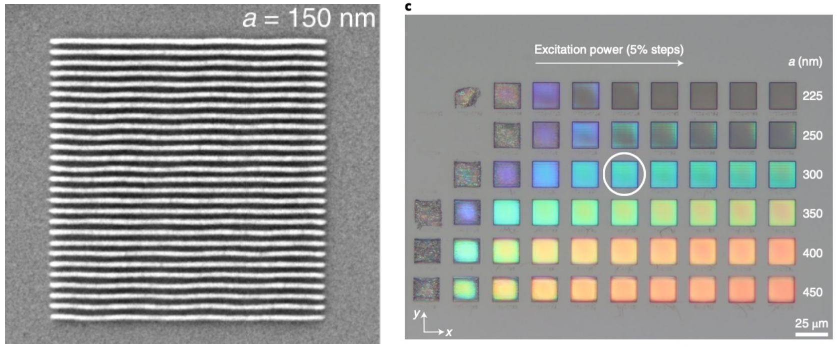
Challenges and Opportunities in 3D Laser Printing Based on (1 + 1)- Photon Absorption

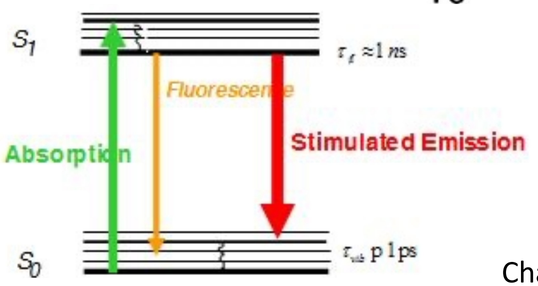
Comparison of (1+1) Techniques

- All can use lower power lasers ($10\text{-}10^6$ W/cm^2, rather than 10^{12})
- All suffer from proximity effect / dose accumulation in unwanted areas
- Upconversion and triplet-triplet annihilation are slowest.
- Voxel size
    - Upconversion: ~150um
    - TTA – 1um
    - 1C, Two-Step with STED - 150nm



1C-2SA
For 150nm, 670 voxel/s used
(Larger structures, 2400-19,400 voxel/s)





Two-step absorption instead of two-photon absorption in 3D nanoprinting
Challenges and Opportunities in 3D Laser Printing Based on (1 + 1)- Photon Absorption

Photoinitiators

Desired Properties

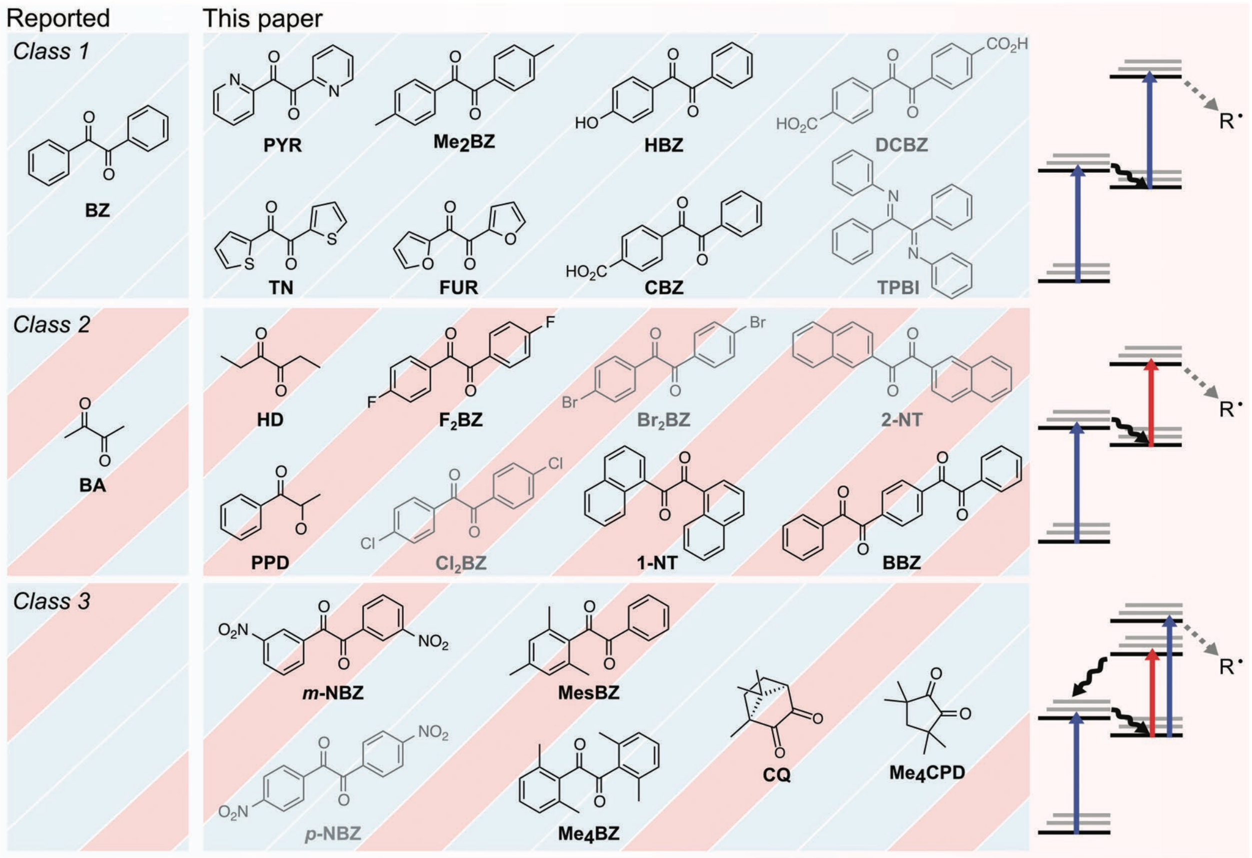
- Balance of triplet (intermediate)-state excitation lifetime
    - High lifetime implies high sensitivity but low printing speeds
- High absorbance
- Low diffusion lengths (physical and optical)
- No side-reactions

Theoretical predictions of reactivity between scavengers, (1+1) photoinitiators, scavengers, and quenchers:
not completed

Tuning Properties for Non-Linear Absorption

- Photoinitiator absorption bands often shift with solvent polarity and pH values
- Photoinhibitors (not done for (1+1))
- Photothermal component (gold nanoparticle) for non-linear localized polymerization

Two-Step Absorption Photoinitiators



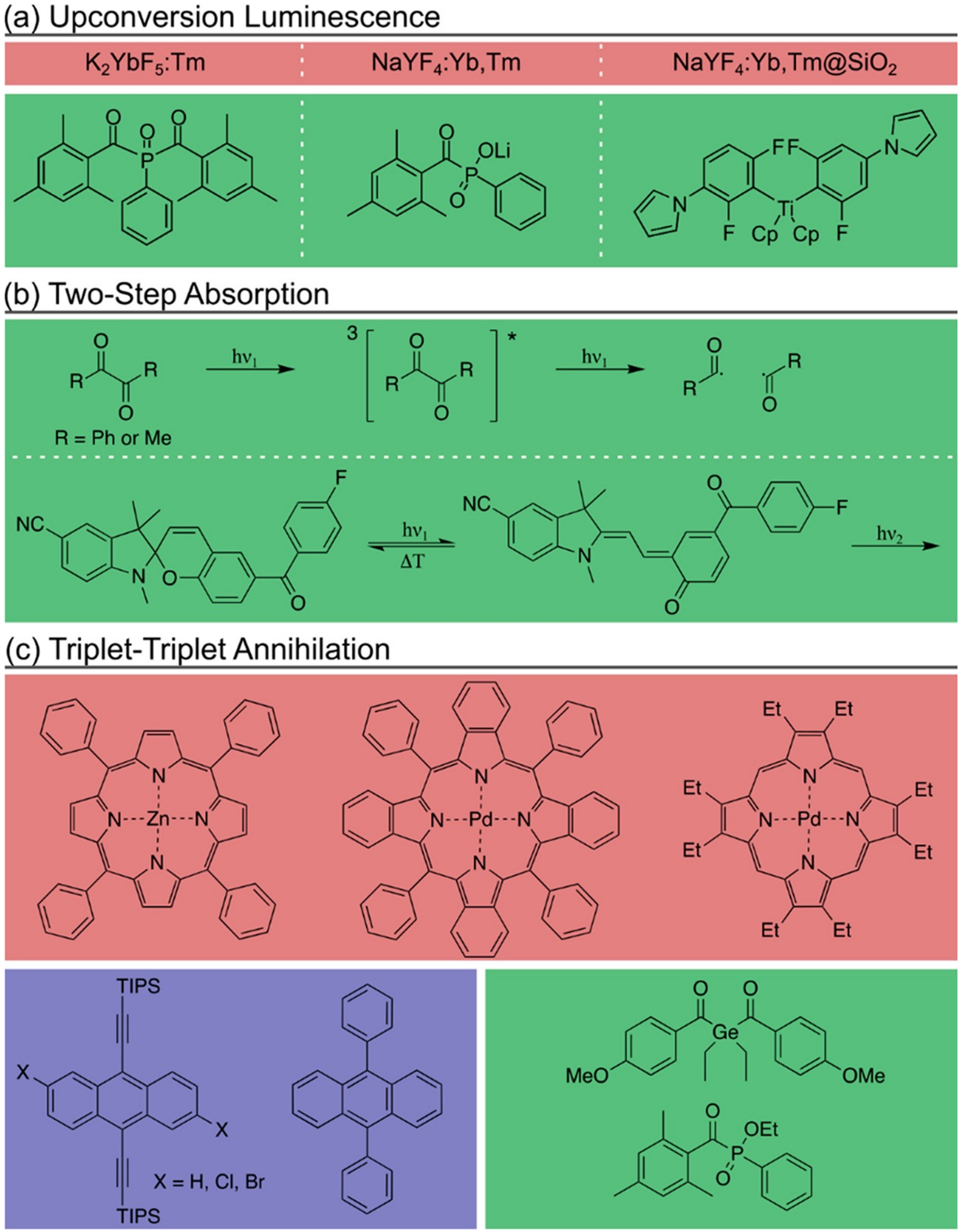
Classes:
one-color two-step absorption, two-color two-step absorption, and one-color two-step absorption combined with a depletion process.
Colors: blue for 405 nm and red for 640 nm.

Search for Alternative Two-Step-Absorption Photoinitiators for 3D Laser Nanoprinting

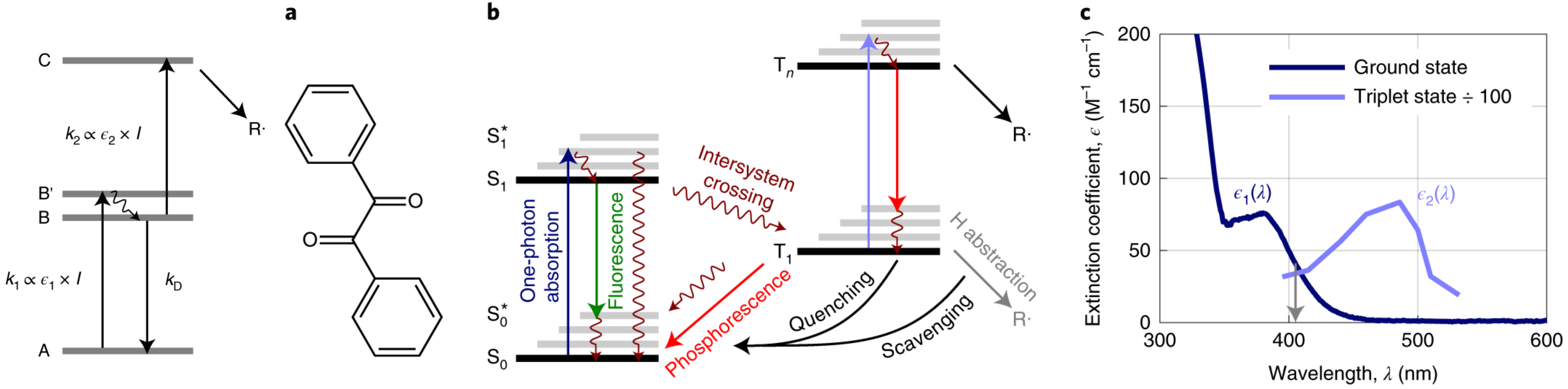
Thank you!

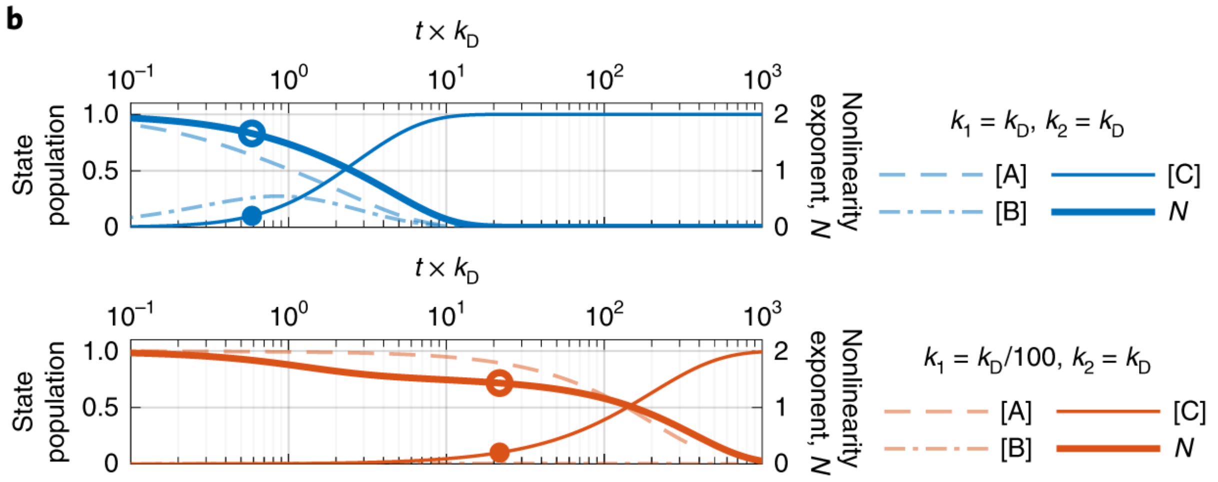
Molecules Used

- Upconversion luminescence
  - Inorganic host matrix dopes with lanthanide ions (e.g., Yb^{+3}/Er^{+3})
- Two-strep absorption
  - Benzil, spiropyran
- Triplet-triplet annihilation
  - Sensitizers: porphyrins
  - Acceptors: anthracene derivatives



Photoinitiation: Benzil





Extinction coefficient; how strongly a chemical species absorbs light

- Higher extinction = more strong absorption.
- Lower ground state extinction means 300um light travel before significant absorption; enables ”dip-in 3D Printing”.

With triplet state 100x higher extinction, relatively efficient absorption of second-excitation reaction.

Stimulated Emission Depletion - STED

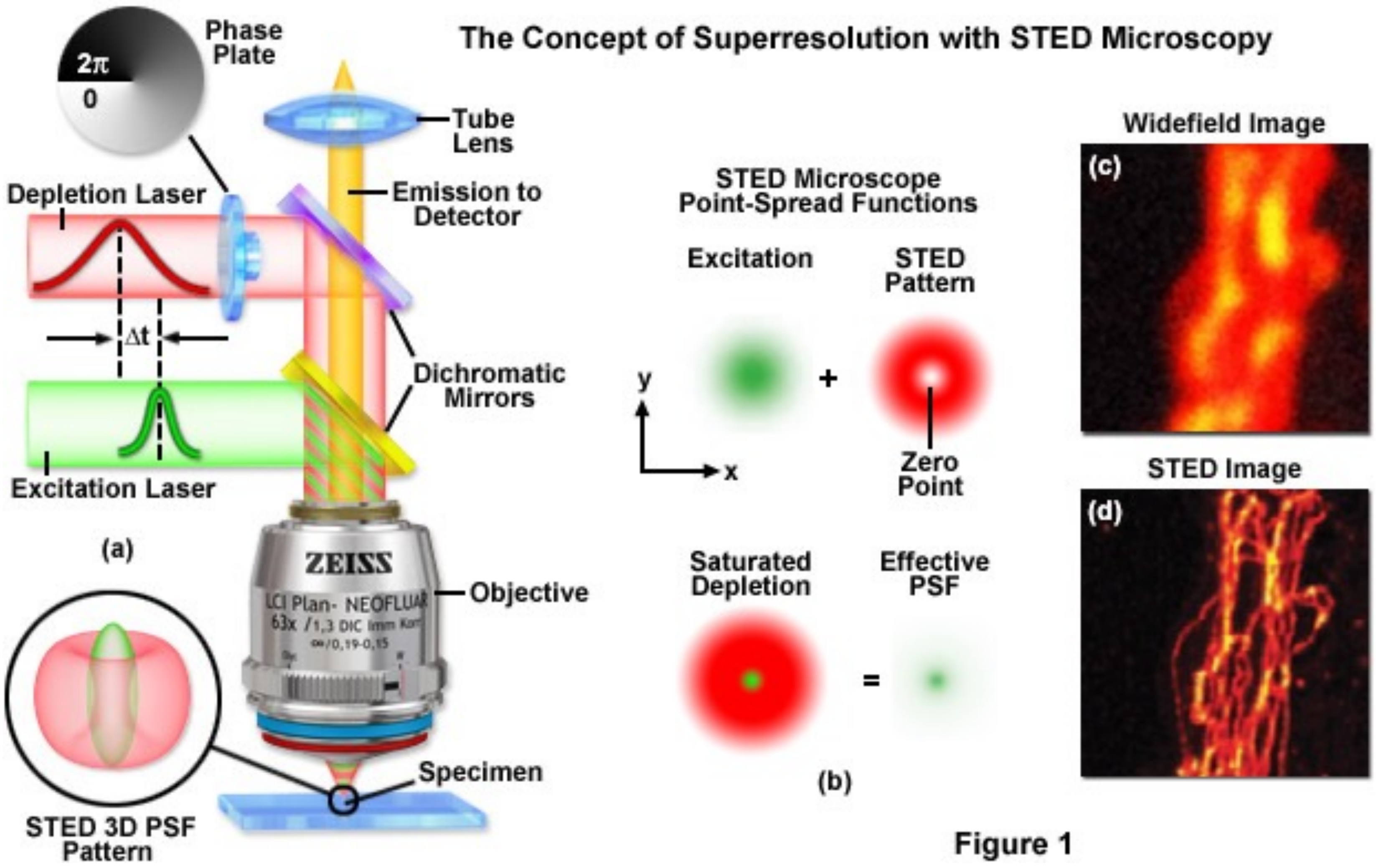


Figure 1