

Long-Wavelength and Superlinear Photoinitiation in Vat Photopolymerisation: Action Spectra, Photon Upconversion, Curing Contrast and Qualification

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Statement of Significance

Moving a photopolymer from violet light to green, red or near-infrared excitation is not one change. The absorbed-photon rate, excited-state pathway, coinitiator chemistry, oxygen sensitivity, optical evolution and intensity dependence can all change. A long-wavelength resin is therefore not qualified by a nominal wavelength or by a single cured-depth value. This review separates ordinary one-photon wavelength extension from genuinely superlinear initiation and defines the measurements required to decide whether either mechanism improves penetration, curing contrast or printed fidelity in a specific vat-photopolymerisation workflow.

Keywords: vat photopolymerisation; visible-light photoinitiation; red-light printing; near-infrared photopolymerisation; upconversion nanoparticles; triplet-triplet annihilation; TTAP; superlinear response; action spectrum; absorbed photons; photobleaching; curing contrast

Abstract

Long-wavelength photoinitiation is often presented as a direct route to deeper penetration and lower scattering. That interpretation is incomplete. A visible or red photosystem may be a conventional one-photon Type I or Type II system whose reaction remains sublinear with irradiance, an upconversion-particle system that locally emits shorter-wavelength photons, or a triplet-fusion system whose active-state generation is superlinear over a defined intensity range. These mechanisms require different evidence. The source spectrum must be combined with dynamic absorption, absorbed-photon rate, excited-state transfer, active-species yield, oxygen or inhibitor history, local intensity exponent, conversion and feature response. This review distinguishes direct visible sensitisation, photoredox coinitiator systems, lanthanide-upconversion routes, homomolecular triplet fusion and triplet-triplet-annihilation photopolymerisation. Source-specific demonstrations range from visible Type II hydrogel printing and low-intensity red DLP to NIR-assisted polymerisation and TTAP at continuous-wave intensities. A qualification matrix is proposed around an operational action spectrum, an effective intensity exponent and an application-specific curing-contrast test. The central conclusion is that wavelength extension and superlinearity are independent design variables: longer wavelength can improve optical access without improving confinement, while a superlinear photosystem can improve contrast only within the irradiance, oxygen and concentration regime in which the nonlinearity is demonstrated.

1. Scope and evidence-selection method

ER-77 addresses the generation of initiating radicals or photoacids under visible, red or near-infrared excitation and the evidence needed to convert that mechanism into a VPP printing claim. It includes direct one-photon sensitisation, visible photoredox initiation, upconversion-nanoparticle-assisted initiation, homomolecular triplet fusion and sensitiser-annihilator TTAP. It does not catalogue commercial photoinitiators and does not publish a universal optimum wavelength, intensity or initiator loading.

Peer-reviewed studies were selected when they reported at least one mechanism-resolving measurement such as source spectrum, absorption or action spectrum, photon-upconversion behaviour, intensity dependence, oxygen control, conversion, cure geometry or printed fidelity [1-11]. Numerical results remain tied to the reported formulation, optical system, atmosphere, geometry and criterion. Manufacturer material is segregated and used only to define current implementation boundaries.

2. Mechanism classes that must not be conflated

A wavelength written on a printer or product page does not identify the active photochemical pathway. The same nominal wavelength can drive direct cleavage, electron transfer, energy transfer, upconverted emission or a multi-

photon-equivalent sequence. Conversely, a two-photon-equivalent mechanism can operate with continuous-wave visible light without being conventional femtosecond two-photon polymerisation [1-4].

Table 1. Long-wavelength initiation classes and the evidence needed to identify them.

Mechanism class	Initiating sequence	Characteristic evidence	Critical limitation
Direct one-photon Type I	One absorbed photon produces bond cleavage and radicals.	Initiator action spectrum, photolysis products, conversion and intensity response.	Longer absorption alone does not prove high quantum yield or confinement.
One-photon Type II / photoredox	Excited sensitizer transfers an electron, hydrogen atom or energy to a coinitiator.	Quenching, redox or transfer feasibility, component-resolved absorption and active-radical evidence.	Efficiency and oxygen response depend on all components and concentrations.
Lanthanide upconversion nanoparticles	Several NIR photons populate higher lanthanide states; UV/visible emission activates a conventional initiator nearby.	Excitation-emission spectrum, absorbed NIR power, upconversion exponent/efficiency and PI spectral overlap.	Particle dispersion, emitter-initiator distance and local scattering can dominate.
Homomolecular triplet fusion	Two triplet-excited molecules form one higher singlet state that transfers an electron to monomer.	Triplet population, delayed/upconverted emission, power-law regime and radical evidence.	Triplet quenching and very short reactive singlet lifetime.
Sensitizer-annihilator TTA / TTAP	Sensitizer triplets transfer energy to an annihilator; triplet fusion creates a higher singlet that activates an initiator.	Energy-level compatibility, triplet transfer, threshold behaviour, intensity exponent and print contrast.	Oxygen sensitivity, diffusion, concentration quenching and saturation.
Conventional two-photon absorption	Simultaneous absorption of two photons in a high-intensity focal field.	Quadratic focal response, pulse and peak-intensity record, voxel-growth curve.	Separate ER-29 scope; high peak intensity and small writing volume.

3. Wavelength extension and superlinearity are independent

A bathochromically shifted initiator or sensitizer may absorb green or red light through an ordinary one-photon event. Such a system can reduce scattering or avoid absorption by other resin components, but its polymerisation rate can still scale sublinearly with irradiance because termination, depletion or bimolecular inefficiency increases with radical flux. In the matched comparison by O'Dea and co-workers, the tested Type I and Type II acrylate systems were sublinear, whereas TTAP showed a superlinear initiation response and lower overcure [4]. This is a formulation- and regime-specific comparison, not a universal exponent for all Type I or Type II systems.

Superlinearity means that the chosen response increases faster than linearly with local intensity over a declared interval. It is not established by observing a threshold or by using two photons somewhere in a mechanism. An inhibition period can create a thresholded dose response without a superlinear steady-state initiation law, while upconversion can become approximately linear after saturation. The intensity range and response variable must therefore be stated.

4. Direct visible and red one-photon systems

Visible photoredox systems can make wavelength extension practical without relying on upconversion. Stevens and co-workers quantified dynamic photon absorption during green-light LCD polymerisation and linked it to cure depth through a modified working-curve model [5]. This approach shows why the incident spectrum and static absorbance are insufficient when photospecies bleach, form new absorbers or change concentration during exposure.

Shin and co-workers combined a cyanine photocatalyst with borate and iodonium coinitiators to print under low-intensity red light, reporting 22.5 mm h⁻¹ and approximately 20 µm features in the studied platform [6]. The same formulation used photobleaching to produce optically clear objects and a separate HABI response under violet/blue light. ER-77 treats the speed and resolution as source-specific outcomes; the mechanism must be reconstructed from the complete multicomponent photosystem.

Lopez-Larrea and co-workers developed a riboflavin/triethanolamine/PEDOT:PSS Type II system and reported full monomer conversion in less than two minutes under visible light, with DLP demonstration at 405 nm (violet, at the UV boundary) and 500 µm holes [7]. PEDOT:PSS accelerated electron transfer while also providing conductivity. This example shows that a functional additive can be part of the initiation pathway and cannot be treated only as an inert optical filler.

5. Action spectrum and dynamic absorbed-photon dose

The useful excitation range is an action spectrum, not an absorption spectrum. It links wavelength to a defined response under a specified photon flux and composition. Absorption by a sensitizer is necessary but does not establish radical

yield, photoacid yield, gelation or print fidelity. Emission bandwidth, optical filters, container transmission and the absorption of coinitiators, monomer, fillers and photoproducts belong to the measurement.

$$H_{ph,abs} = \iint \Phi_{abs}(\lambda,t) \, d\lambda \, dt$$

Here $H_{ph,abs}$ is the time-integrated absorbed-photon exposure for the defined path and Φ_{abs} is the absorbed spectral photon flux. The expression is a reporting descriptor, not a standard. It becomes meaningful only when path length, spectral irradiance, absorption model and dynamic optical changes are declared. Stevens and co-workers demonstrated that dynamic photon accounting can materially improve visible-light cure-depth prediction [5].

6. Upconversion-nanoparticle-assisted initiation

Lanthanide upconversion routes separate the incident wavelength from the wavelength that activates the photoinitiator. Rocheva and co-workers used 975 nm excitation and UV-emitting core-shell particles, reporting an internal NIR-to-UV upconversion efficiency of approximately 2% for the selected particles under the stated excitation conditions, and polymerisation below 10 W cm⁻² in the abstract, while the macrostructure demonstration used 15 W cm⁻² [8]. Local shell-growth anisotropy around the particles affected resolution. These values are not generic efficiencies or intensity limits for other particles, matrices or focusing geometries.

Zou and co-workers used 980 nm excitation and UCNP-assisted photochemistry to fabricate melanin-containing black objects at centimetre scale, supported by a light-attenuation and dose-kinetics model [9]. Complex objects were processed within dozens of minutes under the reported conditions. The example demonstrates optical access through an absorbing formulation, not automatic high resolution or a direct NIR one-photon initiation mechanism.

7. Triplet fusion and TTAP

Awwad and co-workers used green or yellow excitation of ZnTPP to populate triplets and, through homomolecular annihilation, the highly reducing S2 state that transferred an electron to acrylate monomer [1]. The work verified radical polymerisation and macro- and microscopic objects, and reported quadratic excitation-power dependence in the weak-annihilation regime. Oxygen scavenging or degassing was needed because oxygen quenches triplets.

Limberg, Kang and Hayward demonstrated TTAP printing with a continuous visible LED at approximately 10 W cm⁻², submicrometre features and exposures near 0.1 s per voxel [2]. Sanders and co-workers encapsulated a sensitizer-annihilator system in upconversion nanocapsules and reported volumetric printing under continuous-wave excitation at optical powers below 4 mW at the focus, with a chemistry-tunable upconversion threshold [3]. The two studies occupy different optical and materials architectures; neither provides a universal TTAP threshold or resolution.

O'Dea and co-workers compared Type I, Type II and TTAP resins with matched optical density in DLP. At 525 nm and 100 mW cm⁻², the TTAP formulation printed at approximately 45 mm h⁻¹ and reproduced features down to approximately 20 μm in the reported demonstrations [4]. The effective critical energy decreased as intensity increased for TTAP over the tested interval, while the comparator systems did not. This directly links superlinear initiation to curing contrast, but only for the tested concentration, atmosphere, intensity range and optical density.

Visible thioxanthone photoredox catalysts by Hola and co-workers were characterised kinetically under 420, 455 and 470 nm LED excitation, with a separate printing demonstration at 405 nm [10].

Table 2. Source-specific demonstrations and the boundary on transfer.

Route and source	Source-specific result used in ER-77	Boundary on interpretation
Homomolecular ZnTPP triplet fusion [1]	Green/yellow Q-band excitation generated an S2 state that initiated acrylate polymerisation; quadratic power dependence was shown in the weak-annihilation regime.	Not a universal exponent; degassing/oxygen-scavenging and concentration were material.
Focused-LED TTAP [2]	Approximately 10 W cm ⁻² CW visible excitation, submicrometre features and about 0.1 s per voxel.	Focused-voxel result; not equivalent to whole-layer DLP or CAL.
Upconversion nanocapsules [3]	Volumetric printing at optical powers below 4 mW at the focus and a chemistry-tunable upconversion threshold.	Threshold belongs to the encapsulated photosystem and measurement criterion.
Matched Type I/II/TTAP DLP [4]	TTAP showed superlinear response, lower overcure, about 45 mm h ⁻¹ and about 20 μm minimum demonstrations at 525 nm, 100 mW cm ⁻² .	All source conditions must be re-verified before release.
Dynamic photon accounting [5]	Green-light LCD and projection printing linked dynamic absorption to cure depth using a modified working-curve model.	Model parameters are formulation-, spectrum- and platform-specific.

Route and source	Source-specific result used in ER-77	Boundary on interpretation
Cyanine red-light DLP [6]	22.5 mm h ⁻¹ , about 20 µm features and photobleached clear objects in the selected multicomponent resin.	Long wavelength and bleaching do not establish superlinearity.
Riboflavin/TEA/PEDOT:PSS [7]	Full conversion below 2 min and 405 nm DLP (violet, at the UV boundary) with 500 µm holes; PEDOT:PSS accelerated initiation.	Functional additive participates in photochemistry; no automatic biomedical or NIR inference.
975 nm UCNP route [8]	Approximately 2% internal NIR-to-UV upconversion efficiency under the stated conditions, polymerisation below 10 W cm ⁻² and local anisotropic shell growth.	Particle efficiency, bulk printing intensity and local voxel behaviour must remain distinct.
980 nm black-object UCAP [9]	Centimetre-scale melanin objects and a dose/attenuation model; complex objects within dozens of minutes.	Penetration result is not a universal speed, resolution or direct-NIR mechanism claim.
Visible thioxanthone sensitisation [10]	Kinetic characterisation at 420, 455 and 470 nm; separate printing demonstration at 405 nm.	Cationic mechanism details remain with ER-65; wavelength extension is the ER-77 boundary.
One-component stilbene iodonium salts [11]	Photoacid yields up to tenfold above benzylidene analogues; 365/405/430 nm activity and cationic VPP.	Absorption and photoacid yield are separate variables; not a TTAP or superlinear route.

8. Effective intensity exponent and operational threshold

A local intensity exponent should be extracted from the measured response rather than assigned from mechanism name. The response can be initiation rate, polymerisation rate, conversion rate or another declared quantity. The interval must avoid detector limits, oxygen-induction transients and saturation unless those regimes are the intended subject.

$$n_{\text{eff}} = d \ln(r_p) / d \ln(I_{\text{ex}})$$

n_{eff} is a local reporting descriptor. A value above one demonstrates superlinearity only for the chosen response and intensity interval. An operational threshold, $I_{\text{th,op}}$, is the intensity at which a declared conversion, rate, gel or print criterion is reached under a specified exposure time and atmosphere. It is not necessarily the physical onset of upconversion and must not be transferred between path lengths, concentrations or source spectra.

9. Curing contrast is a coupled optical-chemical quantity

For a target region and a background region receiving different local intensities, a useful reporting ratio is:

$$C_r = r_p(I_T) / r_p(I_B)$$

If both intensities fall inside the same local power-law regime, then C_r is approximately $(I_T/I_B)^{n_{\text{eff}}}$. This relation illustrates why superlinearity can amplify optical contrast. It does not account automatically for oxygen depletion, diffusion, cumulative dose, photobleaching, scattering, heating or saturation. Printed positive and negative features remain necessary to validate the mechanism under the full process history.

10. Oxygen, triplet lifetime and containment

Triplet-based systems are especially vulnerable to oxygen quenching. Awwad and co-workers used degassing or dimethylfuran scavenging [1]. Upconversion nanocapsules can isolate a photosystem prepared under inert conditions while allowing use in an external resin [3]. Ambient TTAP has also been demonstrated using annihilator chemistry that assists singlet-oxygen scavenging [4]. These are distinct strategies and should not be collapsed into a generic oxygen-tolerant label.

Oxygen control changes induction, radical availability, threshold and spatial response. Report dissolved-oxygen preparation, headspace, container permeability, scavenger identity, concentration, storage and reuse. A print obtained once in air does not prove that the triplet population, threshold or contrast remains stable through a vat-residence window.

11. Minimum qualification architecture

Table 3. Minimum evidence architecture for a long-wavelength or superlinear VPP claim.

Domain	Minimum record	Decision supported
Source field	Spectral irradiance, bandwidth, temporal mode, spatial map, beam or pixel geometry and exposure history.	Defines incident photons and local intensity.

Domain	Minimum record	Decision supported
Optical path	Container transmission, resin path length, absorption/scattering and refractive interfaces.	Defines photons reaching the photosystem.
Photosystem identity	Sensitiser, initiator, annihilator, coinitorator or UCNF identity, concentration and dispersion.	Defines the proposed mechanism.
Action response	Conversion, radical/photoacid yield, gel or rate against wavelength at controlled photon flux.	Separates absorption from productive initiation.
Dynamic optics	Bleaching, darkening, emission, photoproduct absorption and reuse history.	Shows whether the optical state changes during printing.
Intensity response	r_p or declared response against I_ex over multiple decades where practicable; n_eff and regime bounds.	Tests sublinear, linear or superlinear behaviour.
Oxygen and transport	Atmosphere, dissolved oxygen, scavenger, triplet lifetime, diffusion and temperature.	Defines induction and quenching conditions.
Upconversion route	Excitation/emission spectra, quantum or relative efficiency, threshold, exponent, particle state and PI overlap.	Shows that NIR photons generate useful shorter-wavelength excitation.
Chemical state	Conversion/gel criterion, through-depth state and post-exposure reaction.	Prevents optical initiation becoming a uniform-network claim.
Printed fidelity	Positive/negative features, z-overcure, enclosed cavities, build rate and dimensional uncertainty.	Tests whether mechanism improves the actual print.
Stability and safety	Photodegradation, leachables where relevant, storage, repeated cycles and source-specific optical-safety controls.	Bounds practical operation without implying biological suitability.

12. Standards and method boundaries

ISO/ASTM 52900:2021 supplies additive-manufacturing vocabulary, and ISO/ASTM 52927:2024 identifies general AM part and feedstock quality characteristics and corresponding test methods [S1,S2]. Neither defines an action spectrum, absorbed-photon exposure, upconversion threshold, TTA exponent, TTAP curing contrast or visible-light VPP qualification route. ISO 11146-1:2021 specifies laser-beam width, divergence and propagation-ratio methods for stigmatic and simple astigmatic beams [S3]. It can support source-field characterisation but does not validate resin photochemistry.

No published ISO, ASTM or DIN standard is identified here as a complete method for long-wavelength or superlinear photoinitiation in VPP. Each laboratory method must therefore report spectrum, photon flux, intensity regime, path, oxygen state, concentration, response criterion and uncertainty. A general AM, optical or laser standard cannot substitute for mechanism-specific measurements.

13. Failure modes and interpretation errors

Table 4. Common interpretation failures in long-wavelength and superlinear photoinitiation.

Observation	Interpretation error	Required response
Absorption extends to red light	Efficient red photoinitiation assumed.	Measure action response, active-species yield and conversion at equal photon flux.
Deeper cure at longer wavelength	Lower scattering declared as the only cause.	Measure absorption, bleaching, initiator efficiency, path and conversion.
A threshold is visible	Superlinear mechanism claimed.	Measure n_eff over a declared intensity interval and separate inhibition.
Two photons participate sequentially	Conventional 2PP claimed.	Identify whether the route is UCNF, TTA/TTAP or simultaneous two-photon absorption.
NIR excites UCNF-filled resin	Direct NIR photoinitiator claimed.	Measure upconverted emission and spectral overlap with the actual initiator.
High upconversion emission	High polymerisation efficiency inferred.	Measure productive radical/photoacid yield, conversion and geometry.
One intensity exponent reported	Universal n assigned.	Report low-intensity, crossover and saturation regimes with uncertainty.

Observation	Interpretation error	Required response
Photobleaching increases depth	Fidelity improvement assumed.	Track time-dependent lateral and depth overcure in printed features.
Ambient print succeeds	Oxygen tolerance claimed.	Repeat across oxygen, vat-residence and reuse conditions.
One product is called 2PP or NIR-ready	TTAP, action spectrum or threshold inferred.	Treat manufacturer identity as implementation context only.
20 μm feature demonstrated	Universal resolution claimed.	Report feature type, optics, dose, threshold, development and measurement uncertainty.

14. Scope boundaries within the Engineering Review series

- ER-29 addresses material photophysics for conventional two-photon polymerisation. ER-77 uses 2PP only as a mechanism boundary and does not repeat focal-volume or femtosecond-writing qualification.
- ER-58 and the Spatial Selectivity Perspective address xolography and cross-architecture selectivity. ER-77 does not review dual-colour photoswitch geometry or rank volumetric methods.
- ER-65 addresses cationic ring-opening photopolymerisation. ER-77 includes visible photoacid generation only to compare long-wavelength initiation pathways and does not re-teach cationic propagation or dark cure.
- ER-27 addresses conversion metrology and spatial cure heterogeneity. ER-77 defines the source and mechanism variables that such conversion measurements must resolve.
- ER-30 addresses oxygen inhibition at free and vat interfaces. ER-77 treats oxygen only as a quencher or induction variable in long-lived excited-state systems.
- ER-61 addresses gelation, vitrification and mobility arrest. ER-77 uses a declared gel or conversion criterion to define operational threshold but does not replace network-state analysis.
- ER-75 addresses the material operating window for tomographic VAM. ER-77 can supply a photosystem to such a process but does not define tomographic projection or dose-accumulation algorithms.

15. 3Dresyns implementation boundary

Current 3Dresyns documentation includes conventional UV-visible photoaccelerants and products positioned for two-photon polymerisation at selected wavelength ranges [M1-M4]. Those pages establish product identity and intended formulation context only. They do not independently establish an action spectrum, absorbed-photon yield, TTAP mechanism, UCNP threshold, red-light one-photon cure law, superlinear intensity exponent, voxel size or transferable printing speed.

No current standard 3Dresyns product is identified in ER-77 as an independently validated TTAP, triplet-fusion, UCNP-assisted NIR or red-light one-photon VPP platform. A custom long-wavelength system would require full source, optical, photochemical, oxygen, conversion, dimensional and final-property qualification. Product terms such as fast, photoaccelerant, 2PP, NIR, visible or biocompatible must not be converted into mechanism, safety or finished-device claims.

16. Design rules

- Specify the active photochemical sequence before choosing a wavelength label.
- Measure spectral photon flux at the resin, not only electrical source power.
- Build an action spectrum using a declared chemical or mechanical endpoint.
- Separate static absorbance from dynamic bleaching, darkening and emission.
- Report intensity response over enough range to identify crossover and saturation.
- Define $I_{\text{th,op}}$ by the criterion used; do not call it an intrinsic material threshold.
- Control oxygen, headspace, scavenger and vat residence for triplet-based systems.
- For UCNP routes, report particle state, excitation-emission efficiency and initiator overlap.
- For TTAP, report sensitiser, annihilator, initiator, triplet-transfer and concentration regime.
- Validate curing contrast with positive, negative and enclosed printed features.
- Keep wavelength extension, penetration, superlinearity, resolution and final properties as separate claims.

17. Limitations

This review does not provide a universal action spectrum, intensity exponent, upconversion efficiency, threshold, maximum depth, voxel size or printing speed. The evidence spans thin-film photopolymerisation, DLP/LCD printing, focused-voxel writing and volumetric printing with different chemistries, optical fields and atmosphere. Quantitative values are not pooled across those states.

The term superlinear is retained only when a measured response exceeds first-order intensity dependence over a stated interval. Mechanism assignment should be supported by spectroscopy, transfer or radical/photoacid evidence rather than inferred from print shape alone. Reference [4] is assigned to Advanced Functional Materials 2026, 36(41), e30758; all source conditions was re-verified for this release.

18. Conclusions

- Longer excitation wavelength and superlinear initiation are independent design variables.
- An absorption spectrum does not establish a productive photochemical action spectrum.
- Dynamic photon absorption and photobleaching can change the exposure field during a print.
- UCNP-assisted initiation and TTAP are distinct upconversion architectures with different transfer and transport limits.
- A superlinear exponent is local to a response, intensity interval, composition and oxygen state.
- Curing contrast must be validated in printed positive and negative features, not inferred from mechanism name.
- Manufacturer wavelength or 2PP positioning is implementation context, not independent mechanism evidence.

The central engineering principle is: qualify the complete photon-to-active-species-to-network pathway. A resin is not long-wavelength qualified because it absorbs red or NIR light, and it is not high-contrast because its mechanism contains two photons; the productive action spectrum, intensity regime and printed response must all be demonstrated.

Declarations

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Standards and series framework

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