

Dual-Colour Photoinitiator Design Space for Xolography: Photochemical Requirements, Molecular Variability, Patent Boundaries and Resin-Matrix Opportunities

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Abstract

Xolography achieves volumetric photopolymerisation through chemical rather than purely dose-integrated spatial selectivity. A photoswitchable photoinitiating system is converted by light of a first wavelength from a substantially dormant state into an intermediate state capable of absorbing a second wavelength. Polymerisation is therefore preferentially initiated where the two optical fields act sequentially or simultaneously within the relevant lifetime of the intermediate state.

This mechanism creates a materials-design problem substantially more demanding than conventional single-wavelength vat photopolymerisation. A useful dual-colour photoinitiator must not merely absorb at convenient wavelengths or generate radicals efficiently. It must simultaneously provide spectral orthogonality, sufficiently rapid photoswitching, controlled thermal relaxation, adequate initiation efficiency in the activated state, low single-colour background polymerisation, formulation solubility, chemical stability and compatibility with the reactive resin matrix.

The original xolography work demonstrated this concept using a spiropyran/merocyanine-based dual-colour photoinitiator incorporating a benzophenone-type, Type II photoinitiating motif that requires a co-initiator [1,5]. Subsequent work has demonstrated that substantial structural modification of this architecture is possible, including the introduction of hydrophilic functionality and optimisation of substitution patterns for aqueous hydrogel systems. More recent patent filings also describe alternative naphthopyran-based photoswitchable photoinitiators. These developments show that xolographic photochemistry should be regarded as a molecular design space rather than as a single immutable molecule.

This paper examines that design space from a photochemical and materials-engineering perspective. Particular attention is given to the distinction between chemically plausible substitutions and experimentally demonstrated dual-colour initiators, to the unusually broad structural language found in the original patent family, and to the consequences for attempts to develop lower-hazard, more readily available or more formulation-compatible photoinitiating systems. No freedom-to-operate, patentability or non-infringement conclusion is made. Instead, a qualification framework is proposed in which molecular design, photophysical behaviour, polymerisation selectivity and resin-matrix compatibility are treated as coupled variables.

Keywords

volumetric additive manufacturing; xolography; dual-colour photopolymerisation; photoswitchable photoinitiator; spiropyran; merocyanine; photopolymer; VAM; photochemistry; spatial selectivity

1. Introduction

Volumetric additive manufacturing departs from conventional stereolithographic manufacturing because spatial selectivity does not necessarily arise from sequentially defining a two-dimensional layer at a free

surface or release interface. Instead, polymerisation can be generated inside a volume of photoreactive material.

Different volumetric printing architectures solve the spatial-selectivity problem by fundamentally different mechanisms. In computed axial lithography and related tomographic approaches, three-dimensional selectivity arises primarily from the accumulation of optical dose. Multiple projected dose distributions are combined so that target regions exceed the material's polymerisation threshold whereas surrounding regions remain below it.

Xolography introduces a different concept. Rather than relying exclusively on accumulated dose contrast, it incorporates a chemical gate into the initiating system. A first optical input changes the molecular state of the photoinitiator, and a second optical input subsequently generates the polymerisation-active state. The original publication describes this as dual-colour volumetric printing using intersecting light fields and photoswitchable photoinitiators [1].

The distinction is important. Algorithmic optimisation can improve dose-distribution fidelity in tomographic systems, but it does not change the physical origin of selectivity. In dual-colour systems, by contrast, spatial selectivity depends directly on molecular kinetics and spectroscopy.

Consequently:

spatial selectivity $\neq$ optical resolution alone

and:

photoinitiator efficiency $\neq$ xolographic suitability

A photoinitiator can be highly efficient under conventional illumination and still be unsuitable for xolography if it generates excessive polymerisation under either wavelength individually.

The central materials problem is therefore the creation of a sufficiently large difference between the desired dual-colour reaction channel and every undesired single-colour or thermally persistent reaction channel.

2. Chemical gating in dual-colour volumetric photopolymerisation

The core sequence can be represented conceptually as:

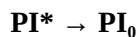


followed by:



where PI_0 is the initial photoinitiator state and PI^* is a photogenerated intermediate with optical properties different from those of PI_0 .

For useful spatial gating, regions exposed only to λ_1 should predominantly return toward the inactive population rather than polymerise:



The rate of this reverse process becomes a processing variable. If the intermediate survives for too long, spatial information written by the first light field becomes temporally delocalised. If it decays too rapidly, the overlap tolerance between the two optical events becomes unnecessarily restrictive.

The published WO disclosure and granted European patent include thermal return of the intermediate state and define broad wavelength ranges encompassing ultraviolet and visible excitation. The disclosure gives successively preferred lower bounds for the apparent thermal back-reaction rate constant, culminating in $k_{\text{back}} > 0.08 \text{ s}^{-1}$ in its most-preferred statement [2,3].

The useful xolographic operating window can therefore be viewed as bounded by at least four competing processes:

1. productive conversion of the dormant state into the photoswitched intermediate; 2. productive excitation of the intermediate followed by initiation; 3. thermal or photochemical loss of the intermediate before productive second-colour excitation; 4. unwanted polymerisation produced by λ_1 or λ_2 independently.

This can be expressed schematically as:

$$\text{desired dual-colour rate} \gg \text{undesired } \lambda_1 \text{ rate} + \text{undesired } \lambda_2 \text{ rate}$$

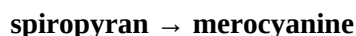
within a sufficiently useful temporal and spatial coincidence window.

The original patent examples include operation at 375/565 nm and, for particular formulations, 405/565 nm; a further described experiment uses approximately 375 and 617 nm [2,3].

These values should not be interpreted as universally optimal wavelengths. They are consequences of the absorption spectra, excited-state behaviour and optical hardware used with the corresponding initiating systems.

3. The published spiropyran/merocyanine DCPI architecture

The original xolography system combined a photochromic transformation with photoinitiating functionality in one molecular architecture. In simplified form:



is induced by the first illumination.

The thermodynamically favoured spiropyran state is substantially less responsive to the second wavelength, whereas ring opening produces a coloured merocyanine state having visible absorption. Subsequent excitation can generate the photochemical pathway required for polymerisation.

The patent describes the spiropyran/merocyanine system as a representative positive, thermally reversible photochromic architecture and discusses Type II initiation pathways involving co-initiators and hydrogen abstraction or electron-transfer chemistry.

This architecture couples several functions that cannot be independently optimised without consequences:

photoswitch core

→ determines ring-opening/ring-closing kinetics and much of the spectral behaviour

electronic substituents

→ modify state energies, absorption bands and thermal stability

photoinitiating moiety

→ controls reactive excited-state formation and radical-generating efficiency

co-initiator

→ affects electron or hydrogen transfer kinetics

resin environment

→ influences polarity, viscosity, diffusion, protonation, aggregation and excited-state behaviour.

The molecule should consequently be treated as a coupled photochemical system rather than as a conventional photoinitiator carrying interchangeable decorative substituents.

4. The original XOLO patent family: an important distinction

The international application **WO 2020/245456 A1**, claiming priority from the German filing **DE 10 2019 115 336** of 6 June 2019, was drafted with a notably broad combination of functional and structural language. No separate DE-A publication was identified for that priority filing; the readable disclosure is provided by the WO publication and its regional or national descendants [2,7].

WO 2020/245456 A1 claim 1 describes a process in which light of the first and second wavelengths acts simultaneously or sequentially to transfer the photoinitiator from an initial state through an intermediate state that absorbs the second wavelength into a reactive state that locally triggers polymerisation; outside the local volume, the intermediate returns toward the initial state [2].

WO 2020/245456 A1 dependent claim 8 then introduces an extensive Markush definition around the photoswitchable photoinitiator [2]. The allowable substituent classes include, among many others, halogens, CN, hydroxyl, alkyl, cycloalkyl, aryl, heteroaryl, acyl, alkoxy, aryloxy, amides, esters, sulfonyl-related groups, boronic and phosphonic functionality, ketones, imines, carbamates and ethers. Adjacent substituents may also be linked to produce fused ring structures.

The breadth is chemically significant because it attempts to reserve a large substituent space around the functional concept.

However, the international application should not be treated as if its original claims were identical to the rights eventually granted in every jurisdiction.

4.1 The granted European patent

WO 2020/245456 A1 claim 1 defines the functional dual-colour polymerisation sequence without a structural formula, while dependent claim 8 limits the photoinitiator to formula (I). In granted EP 4 224 253 B1, claim 1 incorporates the same functional sequence together with formula (I). The granted European independent process claim therefore narrows the functional mechanism by importing a structural Markush definition into claim 1 [2,3].

European patent EP 4 224 253 B1, granted on 15 November 2023, is a divisional under Article 76 EPC of European application EP20733372.5, published as EP3980847A1, which is the European regional phase of the PCT application and remained pending at the review date. A further divisional, EP23202739.1, published as EP4282655A1, also remained pending at that date [10,11]. A divisional claim set need not correspond to the pending parent claim set.

This distinction is essential.

It would be incorrect to reason:

any dual-colour photoinitiator necessarily infringes EP4224253B1.

It would be equally unjustified to reason:

a modified substituent necessarily avoids EP4224253B1.

The correct analysis requires mapping the actual molecule and intended process against the claims as granted in the jurisdiction of interest.

4.2 National and regional descendants

The original family has proceeded beyond the ceased international PCT phase. Public records checked during the independent review identified granted members including EP 4 224 253 B1, US 12,179,419 B2 [7], [US 12,296,531 B2](#), [CN 113993906 B](#), [KR 102765093 B1](#) and [JP 7781413 B2](#). The PCT application's cessation therefore does not imply disappearance of corresponding national or regional rights.

For scientific discussion this is sufficient to establish that the patent landscape remains relevant.

For a commercial freedom-to-operate opinion, the authoritative registers, prosecution histories, claim interpretation and territorial status would need to be examined separately.

5. The second German patent cited in the Nature paper

The 2020 *Nature* publication itself states that two German patent applications related to the reported work had been filed [1]:

DE 10 2019 115 336

and

DE 10 2019 129 868.

The second application is publicly available as **DE 10 2019 129 868 A1**, “**Method and device for processing an optically reactive material**” [4].

Its priority date is 6 November 2019. In contrast with the chemical emphasis of DE102019115336 and its descendants, DE102019129868 is primarily concerned with the optical processing sequence and apparatus. It describes sequential processing of different partial layer volumes using light of first and second wavelengths and projection of the second wavelength into the corresponding volume.

The family includes the granted European member **EP 4 054 827 B1** [8] and the granted US member **US 11,999,099 B2** [9]. **EP 4 360 853 A1** is a later pending divisional of EP 4 054 827 rather than a source for the subsequent US grant [12].

The two original German filings should therefore be considered complementary:

DE102019115336 family

→ dual-colour polymerisation mechanism and photoswitchable photoinitiator chemistry

DE102019129868 family

→ optical processing method and apparatus architecture.

This separation is relevant to materials developers. Avoiding one particular molecular structure would not by itself answer questions concerning process or apparatus claims, just as use of a different optical implementation would not automatically answer questions concerning chemical claims.

6. Broad Markush language does not demonstrate universal chemical feasibility

One of the most striking features of the original chemical disclosure is the size of the substituent space.

From a synthetic and photochemical perspective, however:

a substituent being textually permitted is not equivalent to a molecule being demonstrated.

Nor does textual enumeration establish that every formally included structure:

- can be prepared in useful yield;
- possesses the required photochromism;
- has the required thermal back-isomerisation;
- remains soluble in the formulation;
- generates radicals efficiently;
- avoids single-colour polymerisation;
- survives storage;
- works at technologically useful concentrations;
- produces a practical xolographic process window.

This distinction is familiar in pharmaceutical, agrochemical and functional-material patent drafting, where Markush structures may encompass a very large theoretical chemical space while experimental examples investigate only a small fraction of that space.

For scientific purposes, the consequence is straightforward:

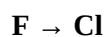
claim coverage and demonstrated structure-property relationships are different questions.

Patent-law concepts including sufficiency, enablement, support, novelty and inventive step can affect the enforceable significance of very broad structural language, but those are legal questions and are outside the scope of this paper.

The scientifically relevant point is that extensive enumeration of substituents does not eliminate the need to determine experimentally which structures actually produce the unusually constrained photophysics required for dual-colour volumetric printing.

7. Why simple substituent replacement is not a sufficient design strategy

Consider apparently modest changes such as:



or replacement of a strongly electron-withdrawing substituent by a different electronic or fused-ring motif.

From a conventional synthetic viewpoint these may look like small structural changes.

From the standpoint of xolographic function they may not be small.

A substituent can modify:

- ground-state absorption;
- merocyanine absorption maximum;
- oscillator strength;
- quantum yield of ring opening;
- equilibrium between closed and open forms;
- thermal merocyanine lifetime;
- intersystem crossing;
- excited-state energy;
- electron-transfer potential;
- hydrogen-abstraction efficiency;
- polarity;
- aggregation;
- resin solubility.

Changing halogen identity, for example, changes not only steric and inductive properties but potentially excited-state behaviour.

Conversely, introducing a fused oxygen-containing motif can influence conjugation and molecular rigidity as well as electronic donation.

Therefore:

chemical plausibility $\neq$ preserved photophysical function

and:

preserved photophysical function $\neq$ patent independence.

The F $\rightarrow$ Cl example is particularly illustrative from a claim-analysis perspective because granted EP 4 224 253 B1 claim 1 expressly uses the broader category “halogen” in the relevant Markush definitions [3]. A chlorine analogue therefore cannot sensibly be presumed to fall outside solely because the demonstrated compound contained fluorine.

More complex changes require correspondingly more careful structural mapping.

The useful research question is thus not:

Which atom can be changed?

but:

Which molecular changes improve the complete two-colour reaction network while maintaining synthetic practicality, formulation compatibility and an acceptable safety profile?

8. Evidence that the DCPI architecture tolerates substantial molecular modification

Subsequent experimental work provides important evidence that the original DCPI should not be regarded as the only chemically viable member of the design space.

In 2025, Stoecker and co-workers reported xolography of hydrogel systems for biomedical applications [5]. The previously reported DCPI was unsuitable for aqueous use because of its limited water solubility. The authors therefore functionalised the DCPI with water-solubilising functionality and further optimised the substitution pattern for the desired photophysical behaviour in water.

The resulting system retained the central sequential principle. UV irradiation at 375 nm generated the merocyanine absorption band in the visible region, enabling subsequent visible-light activation.

The study is especially instructive because it also demonstrates why molecular optimisation cannot be reduced to solubility modification. The activated form retained absorption at 375 nm, opening an undesired UV-only reaction pathway at sufficiently high UV dose.

This observation reinforces the concept of a finite processing window.

Increasing sensitivity is not automatically beneficial if it simultaneously increases one-colour leakage.

A useful figure of merit should therefore include a ratio resembling:

dual-colour polymerisation efficiency / maximum single-colour polymerisation efficiency

rather than simply measuring cure speed under combined illumination.

9. The design space is expanding beyond the original spiropyran system

The patent landscape has also evolved.

A later XOLO patent application published in 2025 describes **[2,1-b]naphthopyran photoswitchable photoinitiators** for dual-colour photopolymerisation [6]. The application claims priority from December 2023 and explicitly presents naphthopyran-based initiators as xolography photoinitiators.

This later development is scientifically relevant independently of its eventual patent scope.

This later disclosure is consistent with an expansion from optimisation of one specific spiropyran DCPI toward exploration of alternative photoswitch families [6].

The most useful conceptual decomposition is therefore:

photoswitch
plus
photoinitiating function
plus
co-initiator/redox partner
plus
reactive resin matrix
plus
two-colour optical protocol

rather than:

one proprietary molecule = xolography chemistry.

This broader framework creates legitimate scientific opportunities for investigating alternative photoswitch classes, alternative photochemical activation mechanisms and different resin environments.

It does not, however, imply freedom to commercialise any particular implementation without patent analysis.

10. Lower-hazard molecular design: the correct scientific question

A rational materials-development objective would be to reduce hazards associated with synthesis, raw materials, purification and formulation while retaining the complete photochemical performance envelope.

The design objective should therefore be written as a multi-objective optimisation problem:

minimise

- precursor hazard;
- synthesis complexity;
- number of purification operations;
- cost;
- environmentally problematic solvents or reagents;
- residual hazardous impurities;
- photoinitiator loading;
- single-colour background reactivity;

while **maximising**

- synthetic yield and robustness;
- commercial precursor availability;
- formulation solubility;

- λ_1 switching efficiency;
- λ_2 initiation efficiency;
- spectral separation;
- thermal reset kinetics appropriate to printing;
- storage stability;
- resin compatibility;
- printable process-window width.

This is fundamentally different from searching for a one-for-one precursor replacement.

A less hazardous precursor is only technologically advantageous if the resulting molecule preserves or improves the overall functional landscape.

11. A qualification cascade for alternative DCPI candidates

Alternative molecules should be evaluated progressively rather than taken directly from synthesis to printing.

Stage 1. Chemical identity and stability

Confirm:

- molecular identity;
- purity;
- thermal stability;
- dark stability;
- resin stability;
- resistance to irreversible photobleaching under expected exposure conditions.

Stage 2. Ground-state spectroscopy

Measure spectra of the dormant material and determine:

$$A_0(\lambda_1) \text{ and } A_0(\lambda_2)$$

An ideal starting state should permit efficient activation at λ_1 while providing minimal direct response to λ_2 .

Stage 3. Photoswitched-state spectroscopy

Generate the intermediate state and measure:

$$A^*(\lambda_1) \text{ and } A^*(\lambda_2)$$

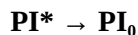
A useful system requires sufficiently large switching contrast at the second wavelength:

$$A^*(\lambda_2) \gg A_0(\lambda_2)$$

The exact magnitude required will depend on irradiation intensity, quantum yield and resin kinetics.

Stage 4. Thermal relaxation

Determine the lifetime or rate constant for:



under actual resin conditions.

Measurements in dilute spectroscopic solvent alone are insufficient because polarity, viscosity and specific interactions in the reactive matrix can change the kinetics.

Stage 5. Single-colour controls

Quantify polymerisation under:

λ_1 only

and

λ_2 only

across doses extending beyond the intended printing window.

This step is mandatory. A candidate producing rapid cure under combined illumination can appear attractive while being unusable because of weak but cumulative background cure under one wavelength.

Stage 6. Dual-colour cure map

Construct a two-dimensional parameter map:

$$\mathbf{Dose\ \lambda_1 \times Dose\ \lambda_2}$$

and record conversion, gel formation or mechanical response.

The objective is not merely to identify one successful point but to quantify the dimensions of the usable process window.

Stage 7. Temporal-offset mapping

Determine response as a function of delay:

$$\mathbf{\Delta t = t_2 - t_1}$$

This experimentally connects the molecular lifetime of the intermediate to printing velocity and spatial localisation.

Stage 8. Resin-specific validation

Repeat the relevant experiments after changing:

- monomer/oligomer composition;
- polarity;
- viscosity;
- co-initiator concentration;
- inhibitor concentration;

- temperature;
- photoinitiator concentration.

A DCPI cannot be fully characterised independently of the formulation in which it is intended to operate.

12. The resin matrix is an independent technology layer

The emphasis placed on the DCPI should not obscure the role of the base resin.

The initiating system determines when and where polymerisation begins.

The resin matrix determines what material is ultimately produced.

These functions can be separated conceptually:

optical/chemical gate

→ spatial polymerisation selectivity

reactive matrix

→ viscosity, conversion, crosslink density, mechanical response, thermal response, optical quality and post-processing behaviour.

This separation is strategically important because an equipment manufacturer does not necessarily need to develop every resin chemistry, and a resin developer does not necessarily need to commercialise the proprietary photochemical gate.

The original patent itself demonstrates formulations based on different polymerisable systems, including tetrafunctional acrylates, dimethacrylate systems and an aqueous acrylamide/bis-acrylamide formulation, showing that dual-colour initiation is not intrinsically tied to one monomer matrix [2].

13. 3Dresyns materials and xolography compatibility

3Dresyns develops VAM-compatible photopolymer matrices intended for third-party volumetric platforms.

This positioning should be interpreted narrowly and accurately.

It does **not** demonstrate ownership of the xolography photoinitiating mechanism.

It does **not** establish a general licence to the protected DCPI chemistry.

It supports a technically important development principle:

the photopolymer matrix and the dual-colour photochemical gate can constitute distinct development layers.

A commercially and scientifically coherent materials strategy can therefore concentrate on engineering photopolymer matrices compatible with third-party volumetric platforms while leaving proprietary initiator chemistry and optical mechanisms with the corresponding technology owner.

This produces the architecture:

XOLO or other platform developer

hardware + optical process + proprietary dual-colour initiating technology

3Dresyns

engineered photopolymer matrices + mechanical/thermal/functional material performance + formulation adaptation to the optical platform.

Such a division is not merely an intellectual-property strategy. It is also a rational specialisation of materials engineering.

14. Public molecular-design hypotheses versus commercial products

Any alternative molecular concepts discussed in this work should be described as:

publicly disclosed molecular-design hypotheses within the dual-colour photoinitiator design space

and not as:

3Dresyns alternative DCPI products.

This distinction should remain explicit.

A chemically reasonable molecular proposal can occupy four different states:

1. **conceived structure** a molecule that can be drawn and for which a rationale exists; 2. **synthetically demonstrated structure** identity and purity experimentally established; 3. **photochemically demonstrated DCPI** switching and dual-colour initiation experimentally established; 4. **qualified xolography photoinitiator** process window demonstrated in a relevant resin and printing architecture.

Only the fourth category establishes technologically relevant xolographic performance.

A further, independent question is whether a molecule and its use can be commercially practised in a specific jurisdiction.

Consequently:

chemical hypothesis $\neq$ synthesis
synthesis $\neq$ DCPI function
DCPI function $\neq$ printable process window
printable process window $\neq$ freedom to operate

This hierarchy should be maintained throughout future experimental and technical communications.

15. Patent breadth and the scientific value of alternative chemistry

The presence of broad patent claims does not make exploration of molecular alternatives scientifically irrelevant.

On the contrary, it highlights how little can be inferred from a Markush formula alone.

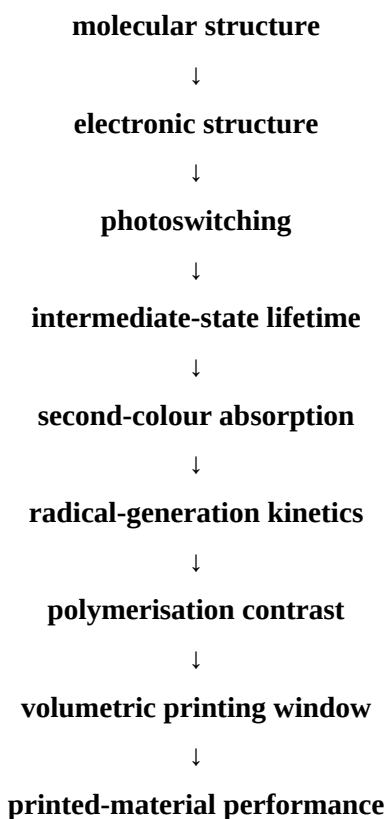
A large patent-defined structural space can contain:

- non-synthesizable structures;
- unstable structures;

- compounds without useful photochromism;
- compounds with inappropriate thermal lifetimes;
- weak photoinitiators;
- photoinitiators exhibiting unacceptable one-colour curing;
- highly effective candidates.

Determining which region of that space actually produces the coupled properties required for volumetric dual-colour polymerisation is a legitimate structure-property research problem.

The scientific contribution therefore lies not in presenting a trivial substituent change as an invention, but in establishing the relationships:



This chain is substantially more informative than a catalogue of theoretically possible substituents.

16. Implications for future materials development

The evidence considered here suggests four particularly valuable research directions.

First, **DCPI performance should be characterised quantitatively as a selectivity problem rather than only as a sensitivity problem.** Cure speed alone is an inadequate screening parameter.

Second, **molecular optimisation should be performed inside representative resin environments.** Solvent-phase spectroscopy remains useful for mechanistic interpretation, but industrial performance depends on the complete formulation.

Third, **hazard reduction should be evaluated across the full chemical lifecycle**. Replacing one precursor with a nominally less hazardous reagent provides little benefit if synthesis subsequently requires additional transformations, difficult purification or greater initiator loading.

Fourth, **photoinitiating technology and functional resin technology should remain conceptually separable**. This allows resin developers to improve final material properties without unnecessarily claiming ownership of the optical gating mechanism.

16.1 Scope boundaries within the Engineering Review series

Within the 3Dresyns Engineering Review series, ER-44 addresses externally introduced photoabsorbing materials and cure-depth control in layerwise VPP, while ER-43 addresses interfaces between intentionally different materials and graded networks. ER-58 remains limited to photoswitchable dual-colour initiation, molecular-design boundaries and the corresponding material/process qualification problem.

17. Patent and technology map

For materials-development purposes, the early xolography intellectual-property landscape can be separated into at least two technically distinct layers.

Table 1. Principal early XOLO patent families relevant to dual-colour volumetric printing

Original German filing	Representative later publication	Principal technical emphasis	Relevance to materials development
DE 10 2019 115 336, priority filing	WO 2020/245456 A1; EP 4 224 253 B1, granted divisional; US 12,179,419 B2	Sequential dual-colour photopolymerisation and photoswitchable photoinitiator chemistry	Relevant to DCPI molecular structures, photochemical sequence and use of the initiating system
DE 10 2019 129 868	DE 10 2019 129 868 A1; EP 4 054 827 B1; US 11,999,099 B2	Optical processing of reactive material, including sequential treatment of partial volumes and corresponding apparatus architecture	Relevant to implementation of the optical process independently of the exact resin chemistry

The distinction is useful but should not be interpreted as an exhaustive legal classification. Individual claims can combine chemical, process and apparatus limitations. EP 4 224 253 B1 is a granted divisional of the still-pending regional-phase application EP3980847A1 at the review date, and a further divisional EP4282655A1 was also pending [10,11].

The first family originated from the chemical-gating concept in which photoinitiator molecules are converted by the first wavelength into an intermediate state having changed absorption characteristics and are subsequently transferred into a polymerisation-active state through absorption of the second wavelength [2,3,7].

The second family addresses how optically reactive material is processed spatially and sequentially within the working volume [4,8,9,12].

Consequently, a complete technology assessment requires consideration of three separate questions:

What molecule is used?

How is that molecule activated?

How are the optical fields and material volume processed by the machine?

Changing only one of these elements does not necessarily answer questions relating to the others.

This distinction is particularly important when discussing alternative photoinitiator chemistry. A molecular modification can be scientifically substantial while leaving the optical processing architecture unchanged.

Likewise, a different optical architecture can employ chemistry falling within an existing molecular family.

For this reason, the present work deliberately distinguishes:

molecular design space

from

process design space

and from

commercial freedom to operate.

18. Quantitative qualification of a dual-colour photoinitiator

A recurrent weakness in the evaluation of advanced photoinitiators is the use of maximum cure speed as the principal performance criterion.

For xolographic systems this is insufficient.

The relevant property is **conditional reactivity**.

The material should react strongly when the two required optical conditions are fulfilled but react minimally when either condition is applied independently.

A useful qualification framework should therefore measure at least three responses at equivalent experimental conditions:

X_1 = conversion produced by λ_1 alone

X_2 = conversion produced by λ_2 alone

X_{12} = conversion produced by the combined $\lambda_1 + \lambda_2$ sequence

where conversion may be determined by real-time FTIR, photo-DSC, rheology, gel fraction or another appropriately validated method.

A simple experimental selectivity parameter can then be proposed:

$$S_DC = X_{12} / \max(X_1, X_2, X_DL)$$

where measurements are compared at predefined optical doses and reaction times and X_DL is the validated detection limit of the conversion method. The detection limit must be reported with S_DC so that a near-zero single-colour response does not produce an unbounded or method-dependent comparison.

This parameter is proposed here as an engineering descriptor rather than as a standardised photochemical quantity.

A high value of **S_DC** indicates that productive two-colour polymerisation substantially exceeds the strongest single-colour leakage pathway.

However, a single value remains insufficient because the relative responses change with exposure dose.

The more informative representation is therefore a two-dimensional cure map:

$$D_1 \times D_2 \rightarrow \text{polymerisation response}$$

where D_1 and D_2 are the optical doses at the first and second wavelengths.

The useful printing region can then be defined as the set of conditions satisfying simultaneously:

$$X_{12} \geq X_{\text{required}}$$

while

$$X_1 < X_{\text{background}}$$

and

$$X_2 < X_{\text{background}}$$

where X_{required} is the minimum conversion or gelation level required for object formation and $X_{\text{background}}$ is the maximum tolerable conversion outside the intended polymerisation volume.

This produces a measurable **dual-colour process window** rather than a binary statement that a photoinitiator “works”.

18.1 Process-window width

A superior DCPI should tolerate meaningful variation in:

- λ_1 irradiance;
- λ_2 irradiance;
- exposure time;
- resin temperature;
- photoinitiator concentration;
- co-initiator concentration;
- optical attenuation through the build volume.

A molecule that produces excellent selectivity at one narrowly defined exposure pair but fails following minor dose variations may be scientifically interesting yet industrially fragile.

The objective should therefore be:

maximum robust operating window

rather than:

maximum instantaneous photosensitivity.

19. Coupling molecular kinetics to printer dynamics

The lifetime of the activated intermediate is not merely a molecular property.

It directly constrains the machine process.

Consider an intermediate generated by λ_1 whose concentration decays approximately according to:

$$[\text{PI}^*] \text{ at time } t = [\text{PI}^*]_0 \exp(-k_{\text{back}} t)$$

where k_{back} is the apparent thermal back-reaction rate constant under the formulation conditions.

The corresponding characteristic lifetime is:

$$\tau = 1 / k_{\text{back}}$$

for a simple first-order approximation. In the original disclosure, the most-preferred lower bound $k_{\text{back}} > 0.08 \text{ s}^{-1}$ corresponds to $\tau < 12.5 \text{ s}$ under this approximation [2]. This document-specific ceiling is not a universal optimum.

This lifetime must be considered relative to the time separating activation by λ_1 and productive excitation by λ_2 .

If:

$$\Delta t \gg \tau$$

a large fraction of the activated population disappears before productive initiation.

If:

$$\Delta t \ll \tau$$

efficient activation can occur, but an excessively long τ may increase spatial or temporal persistence beyond the intended illumination region.

The optimum lifetime is therefore printer-dependent.

This leads to an important design principle:

There is no universally optimum DCPI thermal lifetime independently of the optical architecture.

The desired value depends on:

- light-sheet velocity;
- image refresh rate;
- spatial separation between optical events;
- beam geometry;
- irradiance;
- resin reactivity;
- desired build rate.

Photochemistry and machine dynamics must consequently be co-designed.

20. Proposed experimental qualification matrix

A candidate should not be designated a viable xolographic photoinitiator until it has passed a structured qualification sequence.

Table 2. Proposed qualification matrix for alternative dual-colour photoinitiators

Domain	Measurement	Principal question
Chemical identity	NMR, MS and purity analysis	Was the intended molecule actually obtained?
Dark stability	Storage under defined temperature and light exclusion	Is the dormant state sufficiently stable?
Dormant-state absorption	UV-Vis spectrum before activation	Does the initial state respond appropriately to λ_1 while remaining sufficiently inactive toward λ_2 ?
Activated-state absorption	Time-resolved UV-Vis after λ_1 exposure	Is sufficient absorption generated at λ_2 ?
Photoswitching kinetics	Formation rate of activated state	Can the active intermediate be produced rapidly enough?
Thermal relaxation	Decay of activated-state absorption	Is the intermediate lifetime compatible with machine dynamics?
λ_1 -only control	Conversion versus D_1	Does the activation wavelength itself cause unwanted polymerisation?
λ_2 -only control	Conversion versus D_2	Does the projection wavelength cure dormant resin?
Dual-colour response	Conversion versus D_1 and D_2	Is productive polymerisation strongly enhanced by the combined sequence?
Temporal offset	Response versus Δt	What time interval can separate the two optical events?
Concentration dependence	Response versus DCPI loading	Can useful selectivity be obtained without excessive initiator concentration?
Co-initiator dependence	Response versus donor/co-initiator concentration	Is radical formation limited by the secondary reaction partner?
Resin compatibility	Solubility, haze, precipitation and stability	Can the DCPI remain homogeneous in the target formulation?
Optical depth	Response through increasing resin thickness	Does attenuation compromise volumetric uniformity?
Printing demonstration	Defined calibration geometry	Does the measured photochemistry translate into spatially selective printing?

This matrix deliberately separates **chemical existence**, **photochemical function** and **printing performance**.

A candidate that fails at an early stage should not proceed to increasingly expensive printer testing.

21. Separating photoswitch performance from polymerisation performance

Another useful distinction is between:

photoswitching efficiency

and

polymerisation efficiency.

A molecule can produce an intense visible merocyanine band and nevertheless be a poor dual-colour initiator if excitation of that state does not efficiently generate initiating radicals.

Conversely, a strongly initiating excited state can be unsuitable if the dormant form absorbs enough of λ_2 to generate unacceptable background cure.

At minimum, four molecular characteristics should therefore be considered independently:

21.1 Activation contrast

How strongly does λ_1 alter absorption at λ_2 ?

A useful optical descriptor is:

$$C_{\text{abs}}(\lambda_2) = A_{\text{activated}}(\lambda_2) / A_{\text{dormant}}(\lambda_2)$$

under defined concentration, path length and activation conditions.

21.2 Activated-state lifetime

How long does the useful intermediate survive?

This determines the available temporal coincidence window.

21.3 Radical-generation efficiency

How efficiently does excitation of the activated state produce radicals capable of initiating the selected monomer system?

This depends not only on the chromophore but also on the co-initiator and resin chemistry.

21.4 Single-colour leakage

How much polymerisation occurs without the complete two-colour sequence?

This ultimately determines the chemical component of spatial contrast.

An apparently improved candidate must therefore be assessed across all four dimensions.

Improvement in only one dimension can reduce overall xolographic performance.

22. Resin composition as a variable in DCPI behaviour

The behaviour of the initiating system cannot be assumed to transfer unchanged between formulations.

Changes in resin composition can modify:

- dielectric environment;
- hydrogen-bonding interactions;
- viscosity;
- mobility of reactive intermediates;
- co-initiator encounter frequency;
- oxygen solubility;
- proton-transfer equilibria;
- aggregation of the photoswitch;
- spectral position and band shape;

- thermal back-reaction rate.

Consequently, spectroscopy performed in a convenient analytical solvent is useful for molecular characterisation but cannot substitute for measurements in the actual printing formulation.

This is particularly relevant when comparing hydrophobic engineering resin matrices with aqueous hydrogel formulations.

The subsequent demonstration of modified dual-colour photoinitiators for hydrogel xolography confirms experimentally that changes in formulation environment can require substantial changes to the molecular structure of the DCPI itself [5].

The implication for platform development is significant:

DCPI optimisation and resin optimisation are coupled iterative processes.

A practical workflow should therefore alternate between molecular and formulation development rather than completing either independently.

23. A more rigorous definition of an “alternative DCPI”

The term **alternative DCPI** should be reserved for a molecule for which the required function has actually been demonstrated.

Four levels should be distinguished.

Level A: structural hypothesis

A chemically drawn structure proposed on mechanistic grounds.

No synthesis has been demonstrated.

Level B: synthesised candidate

The structure has been prepared and analytically confirmed.

No dual-colour initiating function has yet been demonstrated.

Level C: validated dual-colour photoinitiator

Sequential optical activation and polymerisation selectivity have been experimentally demonstrated under controlled formulation conditions.

Level D: xolographically qualified DCPI

The molecule has demonstrated a useful process window in an actual volumetric printing configuration.

This terminology prevents a common scientific error:

a patent-defined possible structure should not automatically be described as a demonstrated photoinitiator.

Equally:

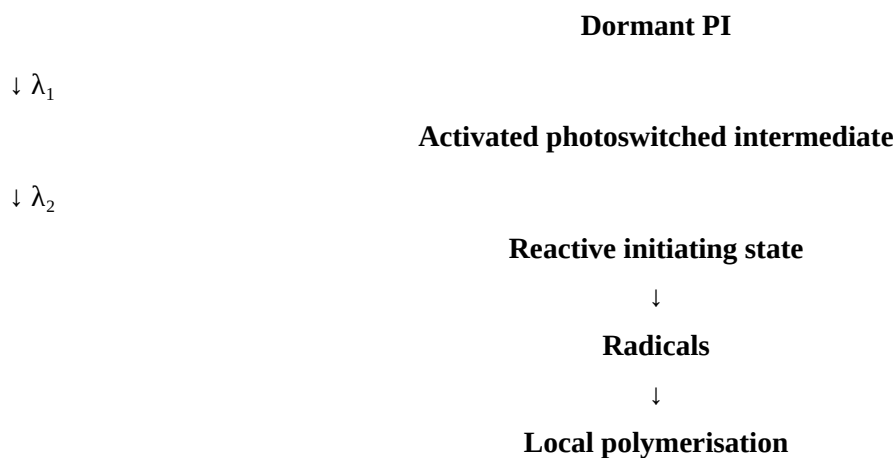
a synthesised photoswitch should not automatically be described as an xolographic DCPI.

The distinction becomes particularly important when analysing large Markush disclosures containing many theoretically permitted structures but comparatively few experimentally demonstrated examples.

24. Proposed figures

Figure 1. Chemical gating principle in xolography

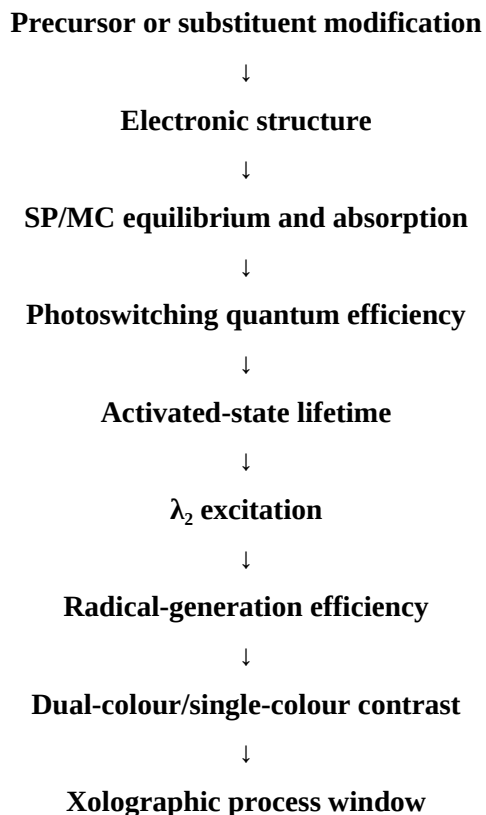
Schematic sequence:



A competing arrow from the activated state back to the dormant state should represent thermal relaxation.

Single-colour leakage pathways should be shown as undesirable side reactions.

Figure 2. Structure-property cascade for molecular modification



This figure would visually explain why simple atom replacement cannot be evaluated solely from synthetic similarity.

Figure 3. Dual-colour process-window map

Horizontal axis:

Dose λ_1

Vertical axis:

Dose λ_2

Three conceptual regions:

No cure

Selective dual-colour cure

Background / non-selective cure

The technologically valuable quantity is the size and robustness of the central selective region.

Figure 4. Technology-layer separation

Optical platform



light-sheet generation + projection + scanning/control

Photochemical gate



photoswitchable DCPI + co-initiator

Reactive matrix



monomers + oligomers + additives

Final printed material



mechanical + thermal + optical + functional properties

The figure should show that these layers interact but do not necessarily originate from the same technology provider.

For the specific commercial positioning considered here:

XOLO

optical platform + proprietary dual-colour technology

and

3Dresyns

engineered VAM-compatible reactive matrices.

25. Recommended terminology

For consistency throughout the paper, the following terminology should be used.

Use:

dual-colour photoinitiator

or

DCPI

for a photoinitiating system whose required two-colour behaviour has been experimentally demonstrated.

Use:

candidate DCPI

for a synthesised structure undergoing photochemical evaluation.

Use:

molecular-design hypothesis

for an unsynthesised structural proposal.

Use:

dual-colour process window

for the exposure domain in which the combined illumination produces the required polymerisation while single-colour exposure remains below the tolerated background threshold.

Avoid using:

alternative XOLO photoinitiator

unless the comparison is purely descriptive and appropriately qualified.

Avoid using:

non-infringing photoinitiator

without a formal legal analysis.

Avoid using:

patent-free

unless the statement has been independently established for the intended jurisdictions, molecule and use.

The scientifically preferable wording for speculative structures is:

Publicly disclosed molecular-design concepts for investigating structure-property relationships within dual-colour photoinitiation.

This accurately describes the research contribution without converting a chemical hypothesis into either a commercial claim or a legal conclusion.

26. Limitations and intellectual-property notice

This work is a scientific and materials-engineering analysis.

Patent documents are discussed to understand the disclosed technological design space and to avoid scientifically misleading descriptions of apparently simple molecular substitutions.

The discussion is **not a legal opinion** and does not provide:

- freedom-to-operate analysis;
- infringement analysis;
- non-infringement analysis;
- patentability analysis;
- validity analysis.

Patent scope can differ materially between jurisdictions and between published applications and granted claims.

In particular, the claim hierarchy of WO 2020/245456 A1 should not be assumed to represent unchanged granted protection, and the granted divisional EP 4 224 253 B1 should not be treated as the complete or final European family position while related applications remain pending at the review date. Conversely, the

structural limitations introduced during prosecution should not be interpreted without analysing the complete granted claims and relevant national law.

Before commercial development of an alternative dual-colour initiating system, the intended molecule, formulation, process and jurisdiction should be reviewed claim-by-claim by qualified patent counsel.

27. Conclusions

Xolography transforms the materials problem of volumetric additive manufacturing by placing part of the spatial-selectivity function inside the photochemistry.

The resulting dual-colour photoinitiator must perform a carefully balanced sequence of molecular events. A first wavelength must efficiently create an intermediate state; that state must exhibit suitable absorption at the second wavelength; the second excitation must efficiently generate initiating species; and the intermediate must disappear rapidly enough outside the intended coincidence region. At the same time, polymerisation produced independently by either optical channel must remain sufficiently low.

The original spiropyran/merocyanine DCPI is therefore best understood as one successful solution to a demanding multidimensional optimisation problem rather than simply as a conventional photoinitiator carrying a photoswitch.

The original XOLO patent family intentionally describes a broad structural space around this concept. WO 2020/245456 A1 claim 1 states the functional sequence while dependent claim 8 introduces formula (I); granted EP 4 224 253 B1 claim 1 combines the sequence with that structural Markush requirement. The granted patent is a divisional, and related European applications remained pending at the review date. Simple substitutions such as replacement of one halogen by another cannot consequently be presumed either scientifically equivalent or legally independent.

At the same time, subsequent experimental development confirms that substantial molecular modification is possible. Hydrophilic derivatives have enabled xolography in aqueous biomedical formulations, and later patent filings investigate naphthopyran-based photoswitchable initiators. The chemistry should therefore be treated as an evolving molecular design field.

For future development, the most productive objective is not to search for superficial substitutes for the original DCPI. It is to identify structure-property relationships that increase the difference between productive dual-colour initiation and every undesired competing pathway, while improving synthesis, availability, formulation compatibility and hazard profile.

For 3Dresyns, a particularly coherent technological position is the development of advanced VAM photopolymer matrices compatible with third-party volumetric platforms. This approach exploits materials expertise in final resin performance without requiring the proprietary dual-colour photochemical mechanism itself to be presented as a 3Dresyns technology.

The central engineering principle can therefore be stated succinctly:

In chemically gated volumetric photopolymerisation, the relevant material property is not maximum photosensitivity, but maximum spatially selective reactivity.

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