

Charge-Transfer-Complex Photoinitiation for Visible-Light Additive Manufacturing

Ground-State Donor-Acceptor Association, Spectral Emergence, Radical Generation, Dual Photo/Thermal Routes and VPP Qualification Boundaries

Juan Segurolo, PhD

3Dresyns by Resyner Technologies S.L.

Registered tax address: General Etxague 15B, 20003 Donostia / San Sebastián, Gipuzkoa, Spain

VAT number: ESB24827511

Correspondence: info@3Dresyns.com · Website: www.3Dresyns.com

Statement of Significance

Charge-transfer-complex (CTC) photoinitiation is often described as “photoinitiator-free”, but that shorthand can obscure the actual mechanism: a donor and acceptor associate in the ground state, the pair can acquire a new absorption band, and the complex itself functions as the initiating light-absorbing system. ER-98 recovers the specialist source gap deliberately left outside ER-83 and defines the evidence needed before a CTC mechanism is claimed in vat or laser-written photopolymerisation.

Keywords: charge-transfer complex; electron donor-acceptor complex; EDA complex; visible-light photoinitiation; 405 nm; 3D printing; free-radical polymerisation; dual photo/thermal initiation; vat photopolymerisation

Abstract

Charge-transfer complexes, also termed electron donor-acceptor complexes in this context, can form by ground-state association of complementary donor and acceptor molecules and generate an absorption response not present in the separated components. Visible-light excitation can drive electron transfer and create initiating species for radical or cationic photopolymerisation, while some systems also show thermal initiation. A focused 2019-2023 literature set demonstrates additive-manufacturing relevance: phosphine/iodonium CTCs [1], indole/iodonium CTCs [2], a water-compatible dye/triethanolamine CTC used for hydrogel printing [3], and bromoacetophenone/amine CTCs [4] were all taken into 405 nm patterning or 3D-printing demonstrations. The broader CTC review by Garra et al. provides the mechanism boundary between ground-state CTCs and excited-state complexes such as exciplexes [5]. These studies do not support a universal donor/acceptor recipe, induction time, conversion, cure depth, safety or storage-stability claim. ER-98 therefore requires direct evidence of complex formation or a validated mechanistic proxy, the emergent absorption/action window, donor-only and acceptor-only controls where mechanistically relevant, formulation-specific conversion/kinetics, printing evidence under defined optical conditions, and explicit separation of photochemical from thermal initiation. The phrase “photoinitiator-free” is treated as potentially misleading unless it is qualified to mean absence of a conventional single-molecule photoinitiator; the CTC donor/acceptor pair is still the initiating system.

1. Scope and source-recovery boundary

ER-98 is the specialist paper for **charge-transfer-complex photoinitiation used in additive-manufacturing photopolymerisation**. The topic was previously kept outside the ER-83 evidence-backed taxonomy until an exact primary-source set could establish donor/acceptor identity, wavelength, conversion/kinetics and printing evidence. The present source pack satisfies that prerequisite for a narrow specialist review.

ER-98 remains distinct from ER-65 cationic ring opening/PAG chemistry, ER-77 long-wavelength and superlinear photoinitiation, ER-80 in-can stability, ER-81 cationic latency, ER-82 photobase/anionic pathways, ER-83 taxonomy and ER-95 photoinitiator migration/substitution. It may cross-reference those mechanisms but does not inherit their performance or stability conclusions.

The paper is intentionally limited to systems for which a CTC/EDA interpretation is supported by direct spectroscopy, control experiments, calculations or the authors’ explicit mechanistic evidence. A redox pair that works under light is not automatically a ground-state CTC.

2. What constitutes a charge-transfer complex in this review

Garra et al. describe CTCs as ground-state associations between an electron donor and electron acceptor whose combined electronic structure can produce a bathochromically shifted absorption relative to the separated components [5]. This emergent absorption is the key reason that two individually weak visible absorbers can become a useful visible-light initiating system when associated.

The same review distinguishes ground-state CTCs from **exciplexes**, which are excited-state complexes. ER-98 preserves that distinction. A new absorption band before irradiation supports ground-state association; an interaction that exists only after one component is electronically excited belongs to a different mechanistic category.

Because association is an equilibrium, CTC concentration can depend on donor/acceptor concentration, solvent/resin environment and temperature. The nominal stoichiometric mixing ratio therefore does not by itself establish the concentration of the light-absorbing complex.

3. Primary additive-manufacturing demonstrations

Wang et al. reported phosphine donors with an iodonium acceptor as CTCs that functioned as dual photochemical/thermal free-radical initiators. Formation was supported by ^{31}P NMR, UV-vis and molecular-orbital calculations, and 405 nm laser-writing experiments produced spatially resolved polymer patterns [1].

A companion 2019 study replaced the phosphine donor family with indoles while retaining an iodonium acceptor. UV-vis spectroscopy and calculations were used to evaluate CTC formation, and 405 nm laser-writing again provided an additive-manufacturing proof of concept [2]. These studies demonstrate family-level flexibility, not free interchangeability of donors and acceptors. A related study extended the acceptor family to sulfonium salts and likewise reported a dual thermal/photochemical CTC initiating system for composites and 3D printing [6]. The acceptor class is therefore not restricted to iodonium salts, although each donor/acceptor pairing requires its own evidence.

Chen et al. developed a water-compatible visible-light system in which a chalcone-derived dye and triethanolamine formed a CTC that initiated PEG-diacrylate photopolymerisation and was used for 3D printing of hydrogel structures under 405 nm irradiation [3]. The presence of a dye in this system is a useful warning against defining CTC photoinitiation as “photochemistry without any chromophore” in every case.

Ma et al. later used 2-bromoacetophenone as acceptor with amines as donors. The system showed 405 nm photopolymerisation and a thermal-initiation component, and was used for 3D patterning. The authors also reported formulation-specific limitations including induction behaviour, low cure depth and poorer mixed-methacrylate printing under some conditions [4]. Negative or weaker printing outcomes are therefore part of the evidence base, not exceptions to omit.

Table 1. Representative CTC additive-manufacturing source pack.

Source	Donor / acceptor architecture	Printing evidence	Boundary
Wang et al. 2019 [1]	Phosphine donor / iodonium acceptor.	405 nm laser write; free-radical methacrylate system.	Dual photo/thermal behaviour is source-specific.
Wang et al. 2019 [2]	Indole donor / iodonium acceptor.	405 nm laser-write additive-manufacturing proof.	Does not establish all indoles/iodonium salts as equivalent.
Chen et al. 2021 [3]	Chalcone-derived dye / triethanolamine donor pair.	405 nm hydrogel 3D printing in PEG-DA.	Water-compatible hydrogel evidence is not transferable to hydrophobic VPP resins.
Ma et al. 2023 [4]	2-bromoacetophenone acceptor / amine donors.	405 nm 3D patterning; acrylate stronger than tested mixed methacrylate route.	Induction time and cure depth require formulation-specific control.

4. “Photoinitiator-free” requires qualification

Some CTC literature is positioned as an alternative to conventional photoinitiators or dyes, and the phrase “photoinitiator-free” can appear in broader discussions. ER-98 uses a stricter terminology. If a donor/acceptor pair

absorbs light and produces initiating species, that pair is the **photoinitiating system**, even when no conventional single-molecule Type I or Type II PI has been added.

The more defensible wording is “without a conventional single-molecule photoinitiator” when that is factually true. This avoids a category error in which the initiating function disappears linguistically even though it remains chemically essential.

The Chen hydrogel example [3] also shows why “dye-free” and “CTC-based” are not synonyms: their CTC contains a deliberately synthesized dye component. Garra et al. [5] reviewed CTC photochemistry both as “photochemistry without dyes” in many systems and as a broader mechanistic class; the exact formulation must decide the descriptor.

5. Minimum mechanism evidence

A CTC claim should not be based only on faster polymerisation after two additives are mixed. The primary literature commonly uses **UV-vis evidence of a new or shifted absorption**, supported in some systems by NMR, molecular-orbital calculations or other association evidence [1,2,5].

Donor-only and acceptor-only controls are particularly valuable when the individual components absorb weakly at the irradiation wavelength. If either component alone initiates efficiently, the incremental role of a CTC must be demonstrated rather than assumed.

Action-spectrum agreement, concentration dependence and spectroscopy under the actual resin environment can strengthen attribution. Because complexation and absorption depend on medium, evidence generated in dilute solution should not automatically be treated as quantitative evidence for the concentrated printing formulation.

6. Photochemical and thermal initiation are separate axes

Several source-pack systems are explicitly **dual photo/thermal initiators** [1,2,4]. That architecture can be useful, but it creates a qualification obligation: conversion that occurs after light exposure may include a thermal or dark contribution rather than only continued photochemical radical generation.

Ma et al. found that their bromide/amine CTCs had thermal-initiation capability but also reported high thermal-startup temperature and moderate thermal conversion in the tested conditions [4]. This prevents a universal “dark cure” or low-temperature thermal-cure claim.

ER-98 therefore requires time-resolved light/dark controls and temperature records whenever a dual mechanism is claimed. Storage stability remains under ER-80/81; a CTC being thermally capable does not establish acceptable shelf life.

7. Printing qualification: absorption is necessary but not sufficient

An emergent visible absorption band does not establish printable cure depth, lateral fidelity or recoating compatibility. The printing demonstration must record wavelength, irradiance or exposure basis, geometry, resin composition basis, layer/voxel strategy and a direct printed outcome.

Ma et al. provide a useful negative boundary because a system can photopolymerise yet still show long induction, low cure depth or poor pattern quality for a particular methacrylate formulation [4]. Conversely, high conversion in a thin spectroscopy or RT-FTIR geometry cannot be transferred directly to volumetric cure depth.

The qualification sequence is therefore: prove or strongly support CTC formation; establish the useful absorption/action window; quantify formulation-specific kinetics/conversion; measure depth/spatial response; then demonstrate printing. Each step can fail independently.

Table 2. ER-98 minimum evidence architecture.

Axis	Minimum evidence	Claim enabled
Identity / formulation	Exact donor and acceptor identities and concentration basis; other co-initiators disclosed to permitted level.	Defines the system being classified.
Complex formation	UV-vis emergent/shifted band plus appropriate controls; complementary evidence where needed.	Supports a ground-state CTC rather than generic redox synergy.
Photochemical response	Wavelength, irradiance/dose,	Links CTC absorption to productive

Axis	Minimum evidence	Claim enabled
	kinetics/conversion, donor-only and acceptor-only controls when relevant.	polymerisation.
Thermal/dark response	Temperature, dark controls, DSC/kinetic evidence if dual initiation is claimed.	Separates thermal from photochemical conversion.
Printing response	Cure depth/spatial fidelity and direct printed pattern/part under defined optics.	Supports additive-manufacturing relevance.
Final state	Post-cure, dimensions/mechanics and application-specific checks.	Prevents mechanism proof from substituting for delivered-part qualification.

8. Safety, environmental and commercial-availability claims are not mechanism outputs

Some source abstracts describe particular CTC systems as stable, safer or environmentally friendly [1-3]. ER-98 does not generalise those descriptors. Donor and acceptor hazard, impurities, residuals, photoproducts, exposure route and final-part extractables require their own evidence.

Likewise, in-situ association can reduce the need to isolate a conventional thermal initiator in a particular synthesis architecture, but it does not prove safe storage of every mixed CTC formulation. Storage stability is formulation- and temperature-specific and remains an independent qualification endpoint.

No 3Dresyns commercial resin is represented here as a CTC implementation. A future product-specific claim would require controlled composition evidence and independent validation before inclusion.

9. Relationship to the broader photocuring taxonomy

ER-83 classifies trigger, active species, bond-forming transformation, spatial/temporal control and structure evolution as separate axes. CTC photoinitiation belongs primarily at the **trigger/active-species supply** level. It can feed conventional radical chain growth, cationic polymerisation or other downstream chemistry depending on the generated species [5].

Accordingly, “CTC” does not replace a polymerisation-mechanism label. A CTC-triggered free-radical acrylate remains radical chain-growth chemistry at the network-forming step. Dual photo/thermal activation describes an additional control architecture, not a new bond-forming reaction.

This specialist treatment closes the source gap without expanding ER-83 itself. Any update to the ER-83 matrix should occur only through a separate controlled delta after ER-98 passes independent review.

10. Research gaps and priority experiments

The present literature is strong enough to establish additive-manufacturing relevance but still narrow in formulation diversity. Most printing demonstrations come from a limited set of donor/acceptor families and laboratory benchmark resins. A useful next step is a controlled comparison in a printer-native VPP geometry that measures CTC association, working-curve response, conversion, induction time, lateral fidelity and dark/thermal continuation from the same formulation.

The equilibrium nature of CTC formation is another open engineering variable. Donor/acceptor concentration, resin polarity, temperature and competing interactions can alter the population of the absorbing complex. Quantitative spectroscopy in the actual resin, rather than only dilute model solutions, would help connect complex formation to cure depth and optical attenuation.

Oxygen sensitivity also requires explicit treatment for radical CTC systems. A CTC can improve visible-light absorption yet still feed radicals into a propagation chemistry that is oxygen-inhibited. Atmosphere and surface-inhibition effects should therefore be measured rather than inferred from the trigger mechanism; those effects remain mechanistically separate from the existence of the CTC itself.

Finally, any claimed advantage in migration, toxicity, shelf life or environmental profile should be tested as an independent endpoint. ER-98 deliberately stops at initiation mechanism and printing qualification because donor/acceptor complexation does not by itself determine residual chemistry or finished-part risk.

11. Conclusions

Charge-transfer-complex photoinitiation is a real and experimentally demonstrated route for visible-light additive manufacturing, with multiple donor/acceptor families taken into 405 nm patterning or 3D-printing studies [1-4,6].

The core evidence is mechanistic and layered: donor/acceptor association, emergent absorption, productive polymerisation, separation of photochemical and thermal contributions where applicable, and direct printing under defined optical conditions. None of these layers should be inferred from the others.

ER-98 therefore replaces the loose shorthand “photoinitiator-free” with a more precise description of the initiating system and treats CTC performance as formulation-specific. It closes a documented source gap while preserving the boundaries of the existing photocuring reviews.

Scientific literature

- [1] Wang, D.; Garra, P.; Lakhdar, S.; Graff, B.; Fouassier, J.P.; Mokbel, H.; Abdallah, M.; Lalevee, J. Charge Transfer Complexes as Dual Thermal and Photochemical Polymerization Initiators for 3D Printing and Composites Synthesis. *ACS Applied Polymer Materials* 1(3) (2019) 561-570. DOI: 10.1021/acsapm.8b00244. <https://doi.org/10.1021/acsapm.8b00244>
- [2] Wang, D.; Garra, P.; Fouassier, J.P.; Graff, B.; Yagci, Y.; Lalevee, J. Indole-based charge transfer complexes as versatile dual thermal and photochemical polymerization initiators for 3D printing and composites. *Polymer Chemistry* 10 (2019) 4991-5000. DOI: 10.1039/C9PY00878K. <https://doi.org/10.1039/C9PY00878K>
- [3] Chen, H.; Vahdati, M.; Xiao, P.; Dumur, F.; Lalevee, J. Water-Soluble Visible Light Sensitive Photoinitiating System Based on Charge Transfer Complexes for the 3D Printing of Hydrogels. *Polymers* 13(18) (2021) 3195. DOI: 10.3390/polym13183195. <https://doi.org/10.3390/polym13183195>
- [4] Ma, Q.; Zhang, X.; Liu, Y.; Graff, B.; Lalevee, J. Dual photo/thermal initiation with charge transfer complexes based on bromide-based electron acceptors. *Journal of Polymer Science* 61(9) (2023) 741-747. DOI: 10.1002/pol.20220642. <https://doi.org/10.1002/pol.20220642>
- [5] Garra, P.; Fouassier, J.P.; Lakhdar, S.; Yagci, Y.; Lalevee, J. Visible light photoinitiating systems by charge transfer complexes: Photochemistry without dyes. *Progress in Polymer Science* 107 (2020) 101277. DOI: 10.1016/j.progpolymsci.2020.101277. <https://doi.org/10.1016/j.progpolymsci.2020.101277>
- [6] Wang, D.; Kaya, K.; Garra, P.; Fouassier, J.P.; Graff, B.; Yagci, Y.; Lalevee, J. Sulfonium salt based charge transfer complexes as dual thermal and photochemical polymerization initiators for composites and 3D printing. *Polymer Chemistry* 10(34) (2019) 4690-4698. DOI: 10.1039/C9PY00913B. <https://doi.org/10.1039/C9PY00913B>

Version note

Version 0.3 is a literature-based release incorporating source-recovery and independent-review corrections and prepared for independent delta review. It does not classify any commercial 3Dresyns formulation as CTC-based, does not disclose proprietary donor/acceptor identities or concentrations, and does not make universal safety, shelf-life, conversion, cure-depth or wavelength claims. No Zenodo, DOI-registration, Shopify or public-release action is authorised by this document.