

Metal–Ligand Dynamic Photopolymer Networks: Coordination State, Stimulus Response, Toughening and Reversibility

Coordination chemistry, DLP compatibility, healing, state variables and service qualification

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Abstract

Metal-ligand coordination provides a reversible crosslinking mechanism whose strength and exchange rate can be tuned through metal identity, ligand field, stoichiometry and local environment. In photopolymer networks this enables stress dissipation, thermally assisted healing and post-print response without relying solely on covalent bond exchange. The central engineering challenge is state control: the same coordination chemistry that supports repair can also introduce creep, humidity sensitivity, ion migration, colour or optical attenuation, and competition between metal-ligand exchange and permanent covalent constraints. Recent DLP-printed metallopolymer studies demonstrate self-healing complex structures using zinc- and nickel-based coordination motifs while retaining overall geometry under selected healing conditions. Broader dynamic metal-ligand literature shows that multiphase architecture and ligand-to-metal ratio strongly affect mechanics and recovery. This review proposes a qualification framework that treats coordination state, activation temperature, environmental exposure, optical compatibility, creep, recovery efficiency and retained geometry as coupled variables rather than independent material properties. Keywords: metal-ligand coordination; metallopolymer; DLP; dynamic network; self-healing; stress relaxation; creep; supramolecular polymer

1. Significance and scope

Metal-ligand interactions occupy an intermediate position between permanent covalent crosslinks and weak physical associations. Their binding strength can be high enough to contribute to load bearing while ligand exchange remains accessible under thermal, chemical or mechanical activation. This review owns metal-ligand dynamic photopolymer networks: coordination state, stimulus response, toughening and reversibility. It includes DLP-compatible metallopolymers and hybrid networks where covalent photopolymerisation fixes geometry while coordination provides recoverable secondary crosslinks.

1.1 Corpus boundary

ER-13 retains the umbrella scope for self-healing and interlayer repair. ER-319 is limited to metal-ligand coordination as a dynamic-network variable in photopolymer systems, including coordination state, optical compatibility, stimulus response, toughening and reversibility. Non-vat coordination literature is used only to define mechanisms and controls, not as direct evidence of DLP performance.

2. Coordination chemistry as a network variable

The mechanical contribution of a coordination bond depends on metal identity, ligand denticity, complex geometry, ligand-to-metal ratio and the surrounding polymer environment. Terpyridine, imidazole, histidine-like and related ligands illustrate how large the design space can be. Network mobility arises when coordination bonds dissociate and reform or exchange ligands. The relevant engineering descriptor is therefore the exchange timescale under a stated temperature and environment, not simply the equilibrium binding strength. Speciation should be verified where possible. Excess free ligand, incomplete complexation or multiple coordination states can change colour, modulus, relaxation and healing behaviour. Nominal formulation stoichiometry is not a substitute for evidence of the state present in the cured material. [2,3]

3. DLP-printed metallopolymers and healing

Recent work on DLP-printed metallopolymers demonstrates that ligand-containing acrylate formulations can be complexed with metal salts before photopolymerisation and printed into three-dimensional structures with thermally activated self-healing. Zinc- and nickel-containing systems showed different healing temperatures and thermal stability windows. [1]

This evidence is important because it demonstrates repair in a genuine printed geometry rather than only in cast films. It also shows the main qualification trade-off: a temperature high enough to accelerate coordination exchange may approach the temperature at which the printed structure softens or collapses. Healing efficiency should therefore be coupled to geometric retention. A material that restores a local scratch while the overall structure deforms has not met a structural repair requirement. [1]

4. Optical and photochemical compatibility

Metal complexes can absorb strongly in the UV-visible range and may compete with photoinitiators for photons. Coordination chemistry can therefore change cure depth, lateral feature growth and conversion even before its dynamic function is used. A DLP qualification should measure resin absorbance at the printing wavelength, cure-depth behaviour, conversion and feature fidelity as metal content or complex state changes. Post-cure colour changes can also indicate oxidation, ligand exchange or further complexation. Metal ions can participate in redox

chemistry or catalyse side reactions. Storage stability and dark reaction should therefore be assessed rather than assuming that the metal complex is a spectroscopically passive additive. [1,4,5]

5. Toughening, relaxation and creep

Dynamic coordination bonds can dissipate energy by reversible dissociation, increasing toughness when the bonds reform after load removal. The same process can produce stress relaxation and long-term creep. Rate-dependent testing is essential. Tensile strength at one strain rate should be supplemented by DMA, stress relaxation and sustained-load creep. Healing temperature and service temperature should be separated by a sufficient kinetic margin. Multiphase architectures can localise dynamic coordination in a softer phase while a harder phase preserves shape. Such designs can improve the balance between repair and stability, but morphology itself becomes a state variable that must be controlled across thermal cycles. [1-3]

6. Environment, ion migration and reversibility

Water, competing ligands, salts and pH can alter coordination equilibria. Applications involving aqueous media, cleaning solutions or biological contact require conditioning studies that include possible metal-ion or ligand release. Reversibility should be demonstrated over repeated damage and healing cycles. A first repair may consume free ligand, redistribute metal ions or change phase morphology. Recovery efficiency should therefore be tracked with composition and dimensions across cycles. Where conductivity or sensing is relevant, ion mobility may be functional. Where dimensional stability or electrical insulation is required, the same mobility may be undesirable. Qualification should be tied to the intended function rather than using a universal healing criterion. [1-3]

7. Minimum qualification matrix

A minimum programme should demonstrate coordination state, optical compatibility, dynamic response, geometric retention and environmental stability with matched controls.

Table 1. Minimum qualification matrix for metal-ligand dynamic photopolymer networks.

Domain	Minimum measurement	Primary failure interpretation
Coordination state	Metal/ligand stoichiometry plus spectroscopic or chemical evidence of cured-state complexation	Nominal recipe may hide free ligand or multiple species
Optics	Absorbance at print wavelength, cure-depth response and feature fidelity	Metal complexes can compete with photoinitiation
Dynamics	Stress relaxation and healing over a defined temperature range	Thermal softening may be mistaken for coordination exchange
Service stability	Creep and dimensional retention below healing conditions	Useful mobility can become structural drift
Environment	Humidity, pH, salt or solvent conditioning and release where relevant	Coordination equilibria and ion mobility can change
Cycling	Repeated healing with mechanical and geometric retention	Metal redistribution or morphology change may accumulate

8. Interpretation matrix

Metal-ligand systems are particularly prone to mechanism overlap because coordination, redox chemistry, phase morphology and ordinary thermal softening can all influence recovery. Multiple measurements are needed to assign cause.

Table 2. Interpretation matrix for common metallopolymer observations.

Observation	Plausible interpretation	Discriminating control
Healing improves at higher temperature	Coordination exchange accelerates, but bulk softening may also increase	Matched non-coordinating control and geometry tracking
Printed structure darkens after cure	Complex-state or redox change may have occurred	UV-visible spectroscopy before and after cure
Toughness rises with metal content	More dynamic crosslinks or phase changes may contribute	DMA, morphology and coordination-state comparison
Repeated healing efficiency falls	Metal/ligand redistribution or irreversible damage may accumulate	Cycle-resolved composition and fracture mapping
Wet conditioning changes modulus	Coordination competition, ion migration or plasticisation may be active	Mass uptake, release and spectroscopy under controlled humidity

9. Limitations and evidence gaps

DLP-printed metallopolymer studies remain relatively few compared with broader supramolecular polymer literature. Metal-ligand combinations that work in bulk or coating systems may not be optically compatible with vat photopolymerisation. Long-duration creep, metal migration and repeated wet-dry ageing are less commonly reported than short healing demonstrations. These variables are central for structural or biomedical translation. Cross-study healing percentages are difficult to compare because damage geometry, temperature, time and recovered property differ. Qualification should therefore prioritise protocol transparency over a single efficiency value. [1-5]

10. Conclusions

Dynamic metal-ligand coordination can provide recoverable crosslinking, toughening and thermally assisted repair in photopolymer networks, and DLP studies now demonstrate these functions in complex printed geometries. The useful design window is bounded by optical compatibility, coordination-state stability, service creep and environmental sensitivity. Metal identity and ligand chemistry should therefore be treated as process and service variables, not merely additives. The strongest qualification couples healing with retained geometry, repeated-cycle stability and direct evidence that the coordination state remains controlled. [1-5]

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Competing interests

The author is Founder, CEO and CTO of 3Dresyns by Resyner Technologies S.L. No comparative product recommendation is made.

Data availability

No new experimental dataset was generated for this review. The analysis is based on the cited literature and the stated engineering scope.