Supporting information

NIR Photothermal Activation in Epoxy/Thiol Polymerization

Rania Rejeb^{1,2}, Philibert Lenormand ³, Didier Gigmes ⁴, Frédéric Dumur ⁴, Michael Schmitt ^{1,2}, Julien Pinaud ^{3*}, Jacques Lalevée^{1,2*}

¹Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France ²Université de Strasbourg, France ³ ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France ⁴ Aix Marseille Univ, CNRS, ICR, UMR 7273, F-13397 Marseille, France Corresponding authors: jacques.lalevee@uha.fr, julien.pinaud@umontpellier.fr

Table S1. Overview of the chemical compounds used in this study.

	Full names	Abbreviation s	Molar masses (g.mol ⁻¹)	Weight Content	CAS
Thermal initiator	1,3- Dimesitylimidazolium-2- carboxylate	NHC-G	348.45	0.5 phr	675877- 56-2
	Bis(2,4-pentanedionato) zinc (II)	Zn 1	263.60	0.5 phr	14024- 63-6
	Zinc (II) acetate hydrate	Zn 2	219.51	0.5 phr	5970-45-6
	Manganese (III) acetylacetonate	Mn 1	352.26	0.5 phr	14284-89- 0
	Manganese (III) acetate dihydrate	Mn 2	268.10	0.5 phr	19513-05- 4
	Copper (II) acetate monohydrate	Cu	199.65	0.5 phr	6046-93-1
	Tetrakis(acetylacetonato) zirconium (IV)	Zr	487.66	0.5 phr	17501-44- 9
	Iron (III) Stearate	Fe	906.27	0.5 phr	
Photoinitiator	2-Isopropylthioxanthone	2-ITX	254.35	0.5 phr	5495-84-1
NIR dyes	The NIR dyes 2-(2-(3- (2-(1,3-dihydro-1,3,3- trimethyl-2 <i>H</i> -indol-2- ylidene)ethylidene)-2- ((1-phenyl-1 <i>H</i> -tetrazol- 5-yl)thio)-1-cyclohexen- 1-yl)ethenyl)-1,3,3- trimethyl chloride	IR785		0.1 phr	
	2-[2-[2-chloro-3-[2-(1,3- dihydro-1,1,3-trimethyl- 2H-benz[e]indol-2- ylidene)ethylidene]-1- cyclohexen-1-	IR813		0.1 phr	134127- 48-3

	yl]ethenyl]-1,1,3- trimethyl-1 <i>H</i> - benz[<i>e</i>]indolium 4- Methylbenzenesulfonate				
Thiols	Pentaerythritol tetrakis (3-mercaptopropionate)	PETMP	488.66	42wt%	7575-23-7
	<i>Tris</i> [2-(3- mercaptopropionyloxy) ethyl] Isocyanurate	TEMPIC	525.61	50wt%	36196-44- 8
	Ethylene glycol <i>bis</i> (3-mercaptopropionate)	GDMP	238.32	42wt%	22504-50- 3
EPOXY	Bisphenol A diglycidyl ether	BADGE	340.4	50wt% ^a 58wt%	1675-54-3

a) 42 wt% for PETMP and GDMP and 50 wt% for TEMPIC. phr of the chromophores are relative to the total amount of resin (thiol and epoxy)



Figure S1. Examples of FTIR spectra before and after polymerization.



Figure S2. (A) Temperature profiles for Epoxy/PETMP blend (58/42 (wt%/ wt%)) and corresponding/simultaneous (B) Photopolymerization profiles (epoxy functions conversion in relation to irradiation time) for irradiation by Laser Diode@785 nm (0.4 W cm⁻²) in presence of (1) 0.1 phr IR785; (2) 0.1 phr IR785 and 0.5 phr Zn 1; (3) 0.1 phr IR785 and 0.5 phr Zn 2; (4) 0.5 phr Zn 1; (5) 0.5 phr Zn 2; and (6) without both IR785 and thermal initiator. The irradiation starts at t = 10s.



Figure S3. SEM Analysis of polymers post-irradiation: (A) Epoxy/Thiol/Zn 1 and (B) Epoxy/Thiol/Zn 2.



Figure S4. (A) Temperature profiles for Epoxy/PETMP blend (58/42 (wt%/ wt%)) and corresponding/simultaneous (B) Photopolymerization profiles (epoxy functions conversion in relation to irradiation time) for irradiation by Laser Diode@785 nm (0.4 W cm⁻²) in presence of 0.1 phr IR785 and 0.5 phr Zn 1. The irradiation starts at t = 10s.



Figure S5. (A) Temperature profiles for Epoxy/ PETMP blend (58/42 (wt%/ wt%)) and corresponding/simultaneous (B) Photopolymerization profiles (epoxy functions conversion in relation to irradiation time) for irradiation by Laser Diode@785 nm (0.4 W cm⁻²) in presence of (1) without both dye and thermal initiator; (2) 0.5 phr Fe; (3) 0.5 phr Mn 1; (4) 0.5 phr Mn 2. The irradiation starts at t = 10s.



Figure S6. (A) Temperature profiles for Epoxy/ PETMP blend (58/42 (wt%/ wt%)) and corresponding/simultaneous (B) Photopolymerization profiles (epoxy functions conversion in relation to irradiation time) for irradiation by Laser Diode@785 nm (0.4 W cm⁻²) in presence of (1) 0.1 phr IR785 and 0.5 phr Fe; (2) 0.1 phr IR785 and 0.5 phr Cu; (3) 0.1 phr IR785; (4) 0.1 phr IR785 and 0.5 phr Zr; (5) 0.1 phr IR785 and 0.5 phr Mn 1; (6) 0.1 phr IR785 and 0.5 phr Mn 2; and (7) without both IR785 and thermal initiator. The irradiation starts at t = 10s.