

Supporting Information

Phenothiazine Derivatives as Photoredox Catalysts for Cationic and Radical

Photosensitive Resins for 3D Printing Technology and Photocomposites

Synthesis

Mira Abdallah^{1,2,3}, Thanh-Tuân Bui^{4*}, Fabrice Goubard⁴, Dimitra Theodosopoulou,⁴ Frédéric Dumur⁵, Akram Hijazi³, Jean Pierre Fouassier¹, Jacques Lalevée^{*1,2}

¹Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

²Université de Strasbourg, France

³ EDST, Université Libanaise, Campus Hariri, Hadath, Beyrouth, Liban.

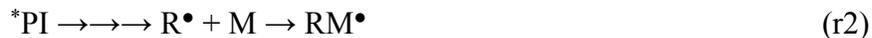
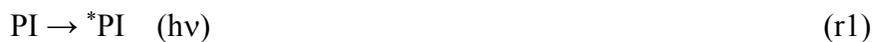
⁴ Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 mail Gay Lussac, 95000 Neuville-sur-Oise, France.

⁵ Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France

***Corresponding author:** tbui@u-cergy.fr (T.-T.Bui), jacques.lalevee@uha.fr (J. L.)

(A): Reaction Mechanisms for Free Radical Photopolymerization:

1) Photoinitiation:



2) Propagation:



3) Termination:

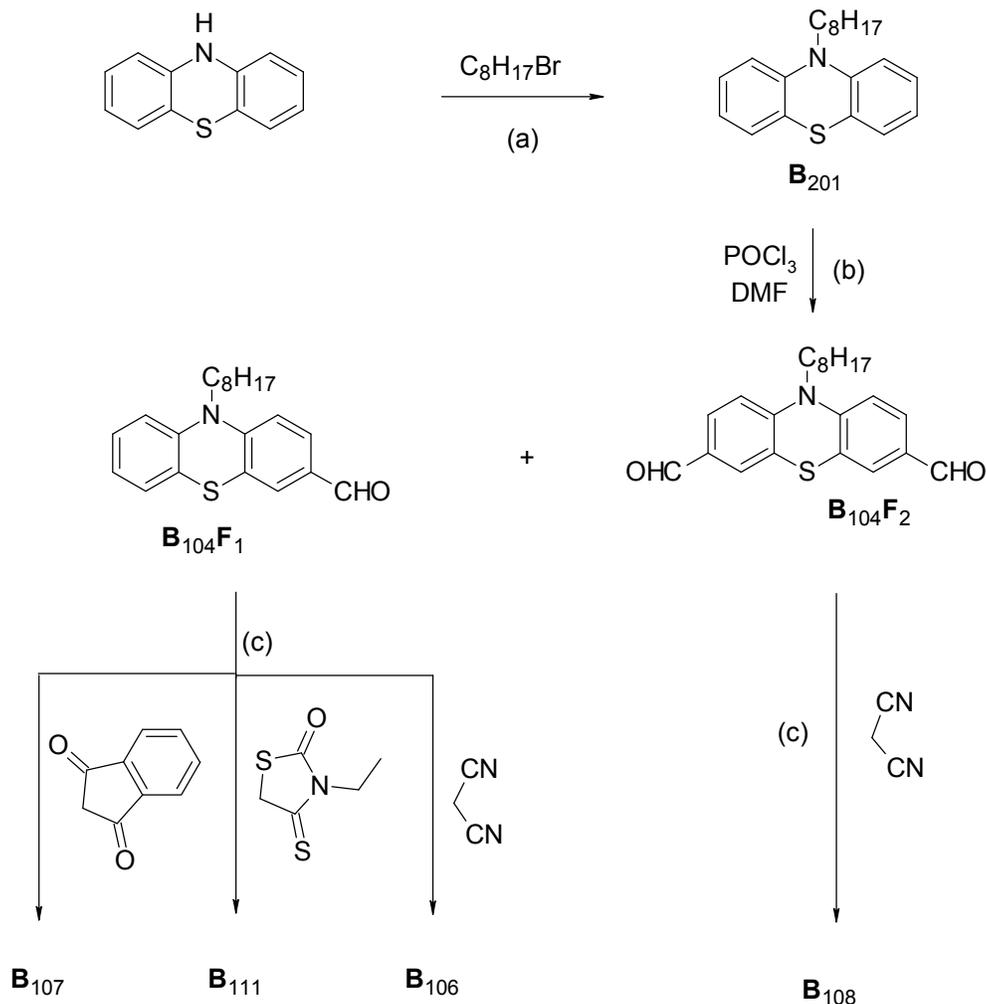


(B): Reaction Mechanisms for Cationic Photopolymerization:



Scheme S1. (A): General reaction mechanisms for FRP; and (B): General reaction mechanisms for CP, respectively.

Synthesis of studied compounds (B106, B107, B108, B111)



Synthesis of B201: The compound B201 is already reported in the literature. (Ref : RSC Adv., 2016,6, 91546-91556. DOI:10.1039/C6RA13839J)

Synthesis of B104F1 and B104F2: In a 250ml round bottom flask, DMF (30ml) was added first and then $POCl_3$ (12ml) by dropwise following stirring for 30 min. Compound **B201** (2.74 g, 8.8 mmol) was added and the reaction mixture was heated at $60^\circ C$ overnight. Reaction was stopped by pouring portionwise into ice water and then was neutralized with aqueous solution of K_2CO_3 . Afterwards, the mixture was extracted with chloroform and washed 3 times with water. After evaporation the crude product (light brown color) was purified over silica gel column

chromatography using a 3:1 mixture of hexane and ethyl acetate as eluent. Yield: compound **B104F1** (2g, 5.89 mmol, 67 % yield) and compound **B104F2** (250 mg, 0.68 mmol, 7.7 % yield).

B104F1: $^1\text{H NMR}$ (250MHz, DMSO- d_6 , δ ppm) 9.78 (s, 1H), δ 8.31 (s, 1H), δ 7.72-7.68 (m, 1H), δ 7.58-7.57 (m, 1H), δ 7.21-6.95 (m, 5H), δ 3.94-3.88 (t, 2H), δ 1.69-1.63 (t, 2H), δ 1.61-1.17 (m, 12H), δ 0.82-0.79 (q, 3H).

B104F2: $^1\text{H NMR}$ (250MHz, DMSO- d_6 , δ ppm) 9.81-9.82 (d, 2H), δ 7.76 (s, 1H), δ 7.72-7.73 (d, 1H), 7.64-7.63 (m, 1H), 7.26-7.23 (d, 2H), δ 3.94-3.88 (t, 2H), δ 1.69-1.63 (t, 2H), δ 1.61-1.17 (m, 12H), δ 0.82-0.79 (q, 3H).

Synthesis of B106: In a 100ml round bottom flask, 513 mg (1.51 mmol) of **B104F1** were mixed with 150mg (2.27 mmol) malononitrile, 11.3mg (0.147 mmol) NH_4OAc and 5ml THF/15ml EtOH. The color changes rapidly from yellow to deep red. The reaction mixture was stirred at room temperature overnight. After evaporation of the solvent the crude product was purified over silica gel column chromatography using a 5:1 mixture of petroleum ether and ethyl acetate as eluent. Purple solid was obtained (m= 490 mg, yield: 83.7 %). $^1\text{H NMR}$ (250 MHz, CDCl_3 , δ_{ppm}) δ 7.73-7.72 (d, 1H), 7.54-7.53 (d, 1H), 7.48 (s, 1H), δ 7.2-7.1 (d, 1H), δ 7.07-7.06 (d, 1H), δ 7.01-6.98 (d, 1H), δ 6.9-6.83 (t, 2H), δ 3.91-3.85 (t, 2H), δ 1.84-1.79 (t, 2H), δ 1.44-1.1.17 (m, 12H), δ 0.93-0.88 (q, 3H). $^{13}\text{C NMR}$ (62.5 MHz, CDCl_3 , δ_{ppm}): 157.3, 150.8, 142.4, 131.4, 129.5, 127.8, 125.1, 124.8, 124.2, 122.9, 116.1, 114.9, 113.6, 48.2, 31.7, 29.2, 29.1, 26.8, 26.7, 22.6, 14.1. **HRMS** (ESI+): Calculated for $\text{C}_{24}\text{H}_{26}\text{N}_3\text{S}^+$ ($[\text{M}+\text{H}]^+$): 388.1842 /found: 388.1840

Synthesis of B107: In a 100ml round bottom flask, 400 mg (1.18 mmol) of **B104F1** were mixed with 230 mg (1.57 mmol) 1,3 indandione, 9.1 mg (0.12 mmol) NH_4OAc and 5ml THF/15ml EtOH. The color changes rapidly from yellow to deep red. The reaction mixture was stirred at room temperature overnight. After evaporation of the solvent the crude product was purified over silica gel column chromatography using a 5:1 mixture of petroleum ether and ethyl acetate as eluent. Purple solid was obtained. (m= 360 mg, yield: 65.3 %). $^1\text{H NMR}$ (250 MHz, CDCl_3 , δ_{ppm}) δ 8.38 (d, 1H), δ 7.98-7.94 (m, 1H), δ 7.88-7.71 (m, 2H), δ 7.12-7.09 (d, 1H), δ 6.89-6.86 (d, 2H), δ 3.90 (t, 2H), δ 1.86-1.81 (t, 2H), δ 1.45-1.26 (m, 12H), δ 0.87-0.85 (q, 3H). $^{13}\text{C NMR}$

(62.5 MHz, CDCl₃, δ_{ppm}) 190.9, 189.5, 149.8, 145.6, 142.9, 142.4, 140.0, 135.6, 135.5, 135.0, 143.8, 133.1, 127.7, 127.5, 127.4, 126.3, 123.8, 123.0, 115.8, 114.6, 53.5, 48.1, 31.7, 31.0, 29.2, 26.8, 22.6, 14.1. **HRMS** (ESI+): Calculated for C₃₀H₃₀NO₂S⁺ ([M+H]⁺): 468.1992 /found: 468.1993

Synthesis of B108: In a 100ml round bottom flask, 210 mg (0.62 mmol) of **B104F2** were mixed with 80 mg (1.3 mmol) malononitrile, 8.8 mg (0.13 mmol) NH₄OAc and 3ml THF/8ml EtOH. The color changes rapidly from yellow to purple. The reaction mixture was stirred at room temperature overnight. After evaporation of the solvent the crude product was purified over silica gel column chromatography using dichloromethane as eluent. Purple solid was obtained (m= 60 mg, yield 22.6 %). **¹H NMR** (250 MHz, CDCl₃, δ_{ppm}) δ 7.82-7.81 (d, 1H), δ 7.79-7.78 (d, 1H), 7.54-7.52 (m, 4H), δ 6.95-6.84 (d, 2H), δ 3.95-3.89 (t, 2H), δ 1.86-1.77 (t, 2H), δ 1.45-1.25 (m, 12H), δ 0.91-0.85 (q, 4H). **¹³C NMR** (62.5 MHz, CDCl₃, δ_{ppm}) 157.2, 157.0, 148.03, 138.2, 131.3, 129.6, 123.9, 115.9, 114.1, 113.1, 48.74, 31.9, 31.7, 26.9, 26.8, 26.7, 22.6, 14.1. **HRMS** (ESI+): Calculated for C₂₈H₂₆N₅S⁺ ([M+H]⁺): 464.1903/found: 464.1903. Calculated for C₂₈H₂₉N₆S⁺ ([M+NH₄]⁺): 481.2169/found: 481.2168

Synthesis of B111: In a 100ml round bottom flask, 350 mg (1.03 mmol) of **B104F1** were mixed with 175 mg (1.08 mmol) 3-ethylrhodanine, 10 mg (0.1 mmol) of NH₄OAc and 5ml THF/15ml EtOH. The color changes rapidly from yellow to deep red. The reaction mixture was stirred at room temperature overnight. After evaporation of the solvent the crude product was purified over silica gel column chromatography using a 5:1 mixture of cyclohexane/dichloromethane (5/5 to 0/10 v/v) as eluent. Purple solid was obtained (m= 450 mg, yield: 90.5 %). **¹H NMR** (250 MHz, CDCl₃, δ_{ppm}): 7.58 (s, 1H), 7.18 (d, *J*=6.75 Hz, 2H), 7.12 (d, *J* = 8 Hz, 1H), 6.95 (t, *J* = 7.75 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.3 (s, 1H), 4.14 (q, *J* = 7.5 Hz, 2H), 3.85 (br, 2H), 1.80 (m, 2H), 1.42-1.21 (m, 10H), 0.86 (t, *J*=6.25 Hz, 3H). **¹³C NMR** (62.5 MHz, CDCl₃, δ_{ppm}): 192.8, 167.7, 165.1, 149.8, 147.5, 143.5, 132.1, 130.8, 129.1, 127.5, 125.4, 123.4, 121.1, 120.1, 115.7, 115.3, 53.5, 47.9, 39.8, 31.7, 29.2, 27.1, 22.6, 21.7, 14.1, 12.3. **HRMS** (ESI+): Calculated for C₂₆H₃₀N₂OS₃⁺ ([M]⁺): 482.1515/found: 482.1513

Figure S1. (A): B106/NPG photolysis; (B): B107/NPG photolysis; (C): B108/NPG photolysis; and (D): B111/NPG photolysis; upon exposure with LED@375 nm in ACN.

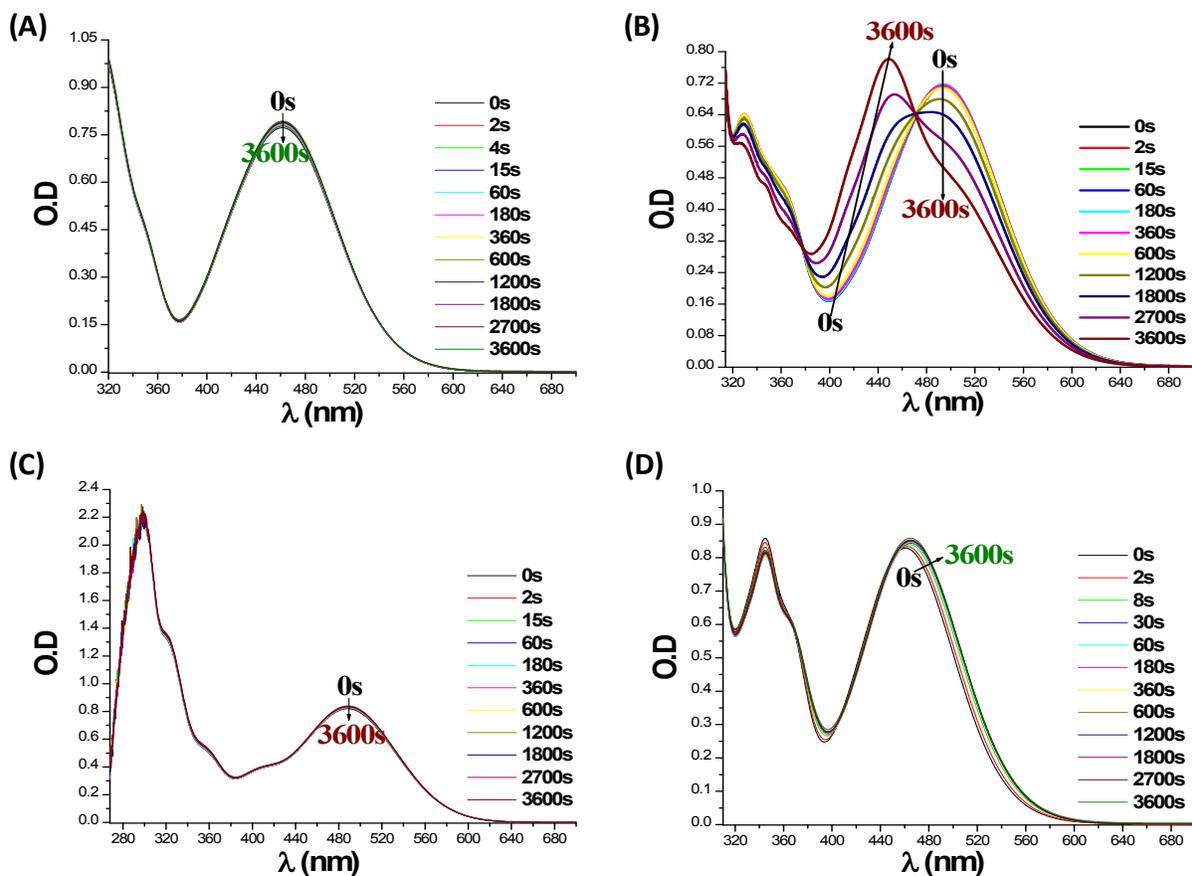


Figure S2. Free radical photopolymerization experiments for 3D printing upon laser diode @405 nm: Characterization of the 3D patterns by numerical optical microscopy; (A) B107/Iod/NPG (0.018%/0.091%/0.091% w/w) in BisGMA/TEGDMA (thickness = 2940 μm for B107 and 2570 μm for IOD); (B) B107/NPG (0.05%/0.25% w/w) in TMPTA (thickness = 1920 μm); and (C) B107/Iod/NPG (0.016%/0.083%/0.083% w/w) in BisGMA/TEGDMA (thickness = 3280 μm); respectively.

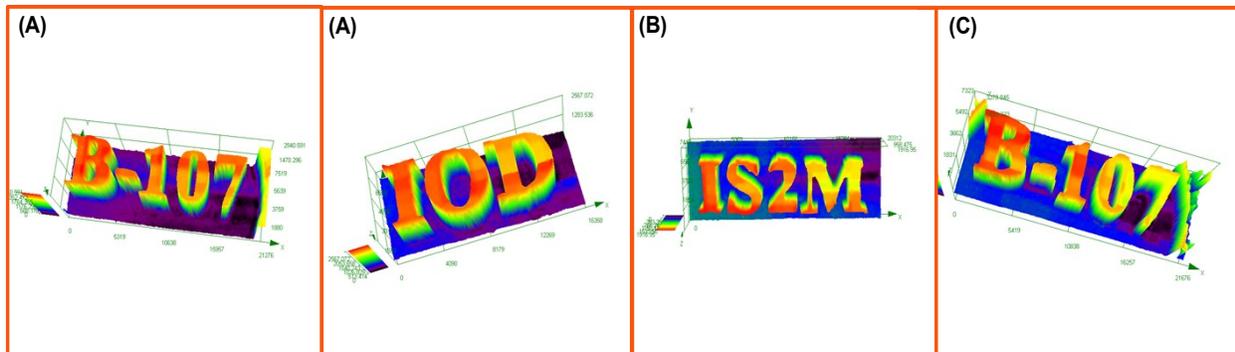


Figure S3. Photocomposites produced upon Near-UV light (LED @395 nm), Belt Speed = 2 m/min, using the free radical polymerization (FRP) in the presence of glass fibers/(meth)acrylate resin for different systems : (1): 0.05% B107 + 1% Iod + 1% NPG in TMPTA (2): 0.05% B107 + 1% Iod + 1% NPG in BisGMA/TEGDMA; (3): 0.05% B106 + 1% NPG in BisGMA/TEGDMA; (4): 0.05% B107 + 1% NPG in BisGMA/TEGDMA; (5): 0.05% B111 + 1% Iod + 1% NPG in TMPTA; and (6): 0.2% B106 + 1% Iod + 1% NPG in BisGMA/TEGDMA. Glass fibers: ~ 2 mm of thickness for one layer; 50% glass fibers/50% organic resin.

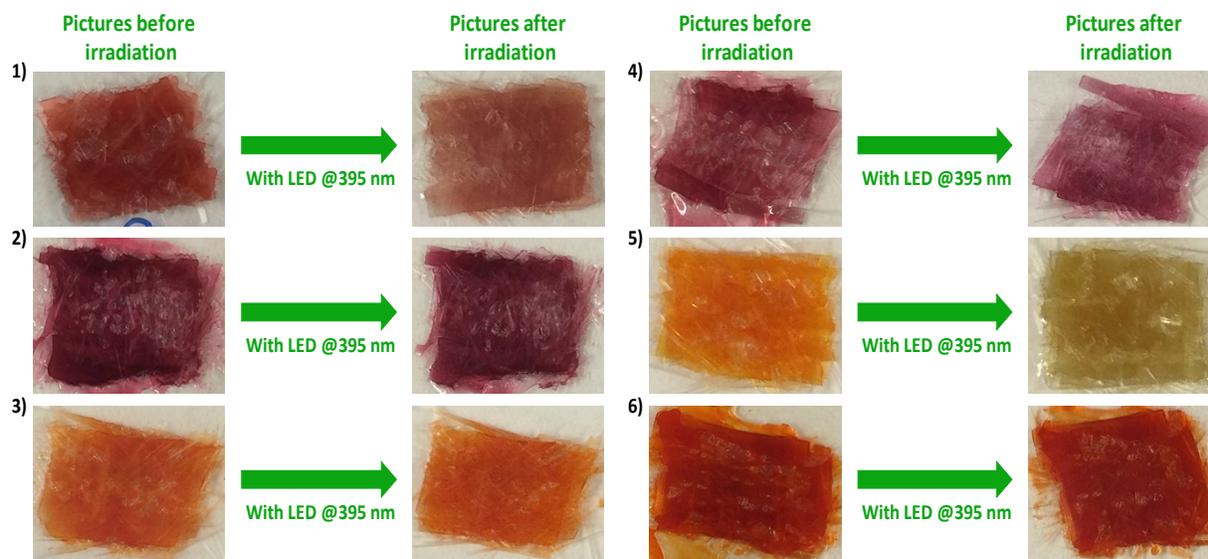


Table S1. Number of passes to be tack-free for impregnated glass fibers with (meth)acrylate resins using Near-UV conveyor (LED @395 nm), belt speed used = 2 m.min⁻¹.

One layer of glass fibers (50% glass fibers/50% (meth)acrylate resin)	At the surface	On the bottom
1) 0.05% B106 + 1% Iod + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 1 pass

2) 0.05% B108 + 1% lod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 1 pass
3) 0.05% B111 + 1% lod + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 1 pass
4) 0.05% B107 + 1% lod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 2 passes
5) 0.05% B107 + 1% lod + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 2 passes
6) 0.05% B106 + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 6 passes
7) 0.05% B107 + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 8 passes
8) 0.05% B111 + 1% lod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 8 passes
9) 0.2% B106 + 1% lod + 1% NPG in BisGMA/TEGDMA	T.F. after 1 pass	T.F. after 11 passes

T.F.: Tack-free