Quinizarin derivatives as photoinitiators for free-radical and cationic photopolymerizations in the visible spectral range

*Pauline Sautrot-Ba,¹ Steffen Jockusch,² Jean-Pierre Malval,³ Vlasta Brezova,⁴ Michael Rivard,¹ Samir Abbad-Andaloussi,⁵ Agata Blacha-Grzechnik,⁶ Davy-Louis Versace*¹*

¹Institut de Chimie et des Matériaux Paris-Est (ICMPE) – UMR-CNRS 7182 Equipe Systèmes Polymères Complexes (SPC) 2-8, rue Henri Dunant, 94320 Thiais, France.

²Department of Chemistry, Columbia University, 3000 Broadway, New York, NY 10027, United States.

³Institut de Chimie des Matériaux de Mulhouse (IS2M)-UMR 7361, 15 rue Jean Starcky - BP 2488, 68057 Mulhouse cedex, France.

⁴Slovak University of Technology in Bratislava, Institute of Physical Chemistry and Chemical Physics, Department of Physical Chemistry, Radlinského 9, SK-812 37 Bratislava, Slovak Republic.

⁵Université Paris-Est Créteil (UPEC), Laboratoire Eau, Environnement, Systèmes Urbains (LEESU), UMR-MA 102, 61 avenue Général de Gaulle, 94010 Créteil Cedex, France.

⁶Faculty of Chemistry, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland

*Corresponding author: versace@icmpe.cnrs.fr

Figure S1. ^1H NMR spectra of A) QA and B) QE in CDCl_3

Figure S2. ^{13}C NMR spectra of A) QA and B) QE in CDCl_3

A

B

Figure S3. HSQC NMR spectra of A) QA and B) QE in CDCl₃.

Figure S4. Emission spectrum of the lamps used during the antibacterial tests. Light intensity = $170 \mu\text{mol}/\text{m}^2/\text{s}$

Figure S5. Steady state photolysis of **A)** QE, **B)** QE/Iod, **C)** QE/Iod/Rhodamine B in acetonitrile, **D)** QE/MDEA and **E)** QE/Trithiol after irradiation by LED@405 nm (60 mW/cm²) under air conditions. [QE]= 0.14 mM; [Iod] = 13 mM; [RhB] = 10⁻⁶ M; [MDEA] = 30 mM and [Trithiol] = 10 mM.

Figure S6. Determination of the bimolecular quenching rate constants k_q of quenching of **QA** and **QE** triplet states by molecular oxygen using laser flash photolysis ($\lambda_{\text{ex}} = 355 \text{ nm}$, 7 ns pulse width). Pseudo-first-order decay rate constant of **QA** and **QE** triplet state absorbance monitored at 580 nm vs. varying concentration of dissolved molecular oxygen in acetonitrile.

Figure S7. Determination of the bimolecular quenching rate constants k_q^{Iod} of quenching of **QA** and **QE** triplet states by Iod using laser flash photolysis ($\lambda_{\text{ex}} = 355 \text{ nm}$, 7 ns pulse width). Pseudo-first-order decay rate constant of **QA** and **QE** triplet state absorption monitored at 580 nm vs. varying concentration of Iod in acetonitrile.

Figure S8. Cyclic voltammogram of quinizarin (QZ), allyl quinizarin (QA) and epoxidized quinizarin (QE) in acetonitrile + 10^{-3} M $n\text{Bu}_4\text{NBF}_4$ measured at a scan rate of 100 mV/s. $[\text{QZ}] = [\text{QA}] = [\text{QE}] = 10^{-3}$ M.

Figure S9. Determination of the bimolecular quenching rate constants k_q of quenching of **QA** and **QE** triplet states by MDEA using laser flash photolysis ($\lambda_{\text{ex}} = 355 \text{ nm}$, 7 ns pulse width). Pseudo-first-order decay rate constant of **QA** and **QE** triplet state absorption monitored at 490 nm vs. varying concentration of MDEA in acetonitrile.

Figure S10. Determination of the bimolecular quenching rate constants k_q of quenching of **QA** and **QE** triplet states by trithiol using laser flash photolysis ($\lambda_{\text{ex}} = 355 \text{ nm}$, 7 ns pulse

width). Pseudo-first-order decay rate constant of **QA** and **QE** triplet state absorption monitored at 580 nm vs. varying concentration of trithiol in acetonitrile.

Figure S11. Photopolymerization profiles of TMPTA (acrylate function) in the presence of QZ/MDEA (0.5%/2%, w/w) in laminate upon (1) LED@405 nm, (2) LED@455 nm, (3) Xe lamp and (4) LED@470 nm. Thickness of the film = 25 μm .

Figure S12. Photopolymerization profiles of TMPTA (acrylate function) in the presence of CQ/MDEA (0.5%/2%, w/w) in laminate upon (1) LED@470 nm, (2) Xe lamp and (3) LED@455 nm. No polymerization occurs under air. Thickness of the film = 25 μm .

Figure S13. Photopolymerization profiles of TMPTA (acrylate function) in the presence of QE/MDEA (0.5%/2%, w/w) **A)** under air and **B)** in laminate upon (1) LED@405 nm, (2) LED@455 nm, (3) Xe lamp and (4) LED@470 nm. Thickness of the film = 25 μm .

Figure S14. Photopolymerization profiles of TMPTA (acrylate function) in the presence of QZ/Iod (0.5%/2%, w/w) upon LED@405 nm (1) under air and (2) in laminate. Thickness of the film = 25 μm .

Figure S15. Photopolymerization profiles of TMPTA (acrylate function) in the presence of QE/Iod (0.5%/2%, w/w) in laminate upon (1) LED@405 nm, (2) Xe lamp, (3) LED@455 nm and (4) LED@470 nm. Thickness of the film = 25 μm .

Figure S16. Photopolymerization profiles of TMPTA (acrylate function) in the presence of CQ/Iod (0.5%/2%, w/w) in laminate under (1) LED@455 nm (2) Xe lamp and (3) LED@470 nm exposure. Thickness of the film = 25 μm .

Figure S17. Photopolymerization profiles of a TMPTA/Trithiol blend (43%/57%, w/w) in the presence of A) **QA** (0.5%) and B) **QA/Iod** (0.5%/2%, w/w) **under air** upon LED@405 nm (curves 1 and 2), Xe lamp (curves 3 and 4) and LED@455 nm (curves 5 and 6). Curves 1, 3 and 5 = acrylate conversions; Curves 2, 4 and 6 = thiol conversions. Thickness of the film = 25 μm .

Figure S18. Photopolymerization profiles of a TMPTA/Trithiol blend (43%/57%, w/w) in the presence of A) **QE** (0.5%) and B) **QE/Iod** (0.5%/2%, w/w) **in laminate** upon LED@405 nm (curves 1 and 2), Xe lamp (curves 3 and 4) and LED@455 nm (curves 5 and 6). Curves 1, 3 and 5 = acrylate conversions; Curves 2, 4 and 6 = thiol conversions. Thickness of the film = 25 μm .

Figure S19. Photopolymerization profiles of a TMPTA/Trithiol blend (43%/57%, w/w) in the presence of A) QE (0.5%) and B) QE/Iod (0.5%/2%, w/w) **under air** upon LED@405 nm (curves 1 and 2), Xe lamp (curves 3 and 4) and LED@455 nm (curves 5 and 6). Curves 1, 3 and 5 = acrylate conversions; Curves 2, 4 and 6 = thiol conversions. Thickness of the film = 25 μm .

Figure S20. Photopolymerization profiles of a TMPTA/Trithiol blend (43%/57%, w/w) in the presence of A) QZ (0.5%) and B) QZ/Iod (0.5%/2%, w/w) **in laminate** upon LED@405 nm (curves 1 and 2), Xe lamp (curves 3 and 4) and LED@455 nm (curves 5 and 6). Curves 1, 3 and 5 = acrylate conversions; Curves 2, 4 and 6 = thiol conversions. Thickness of the film = 25 μm .

Figure S21. Photopolymerization profiles of a TMPTA/Trithiol blend (43%/57%, w/w) in the presence of A) QZ (0.5%) and B) QZ/Iod (0.5%/2%, w/w) **under air** upon LED@405 nm (curves 1 and 2), Xe lamp (curves 3 and 4) and LED@455 nm (curves 5 and 6). Curves 1, 3 and 5 = acrylate conversions; Curves 2, 4 and 6 = thiol conversions. Thickness of the film = 25 μm .

Figure S22. Photopolymerization profiles of a TMPTA/Trithiol blend (43%/57%, w/w) in the presence of A) CQ (0.5%) and B) CQ/Iod (0.5%/2%, w/w) **in laminate** upon LED@455 nm (curves 1 and 2), Xe lamp (curves 3 and 4) and LED@470 nm (curves 5 and 6). Curves 1, 3 and 5 = acrylate conversions; Curves 2, 4 and 6 = thiol conversions. Thickness of the film = 25 μm .

Figure S23. Photopolymerization profiles of a TMPTA/Trithiol blend (43%/57%, w/w) in the presence of A) CQ (0.5%) and B) CQ/Iod (0.5%/2%, w/w) **under air** upon LED@455 nm (curves 1 and 2), Xe lamp (curves 3 and 4) and LED@470 nm (curves 5 and 6). Curves 1, 3 and 5 = acrylate conversions; Curves 2, 4 and 6 = thiol conversions. Thickness of the film = 25 μm .

Figure S24. Kinetic profiles of the allyl and thiol functions in the DVE/trithiol formulation (43%/57%, w/w) in the presence of A) QA (0.5 wt%) and B) QA/Iod (0.5%/2%, w/w) **under air** upon LED@455 nm (curves 1 and 2) and LED@470 nm (curves 3 and 4) exposure. Curves 1 and 3 = acrylate conversions; Curves 2 and 4 = thiol conversions. Thickness of the film = 25 μm .

Figure S25. Kinetic profiles of the allyl and thiol functions in the DVE/trithiol formulation (43%/57%, w/w) in the presence of A) CQ (0.5 wt%) and B) CQ/Iod (0.5%/2%, w/w) **in laminate** upon LED@455 nm (curves 1 and 2) and LED@470 nm (curves 3 and 4) exposure. Curves 1 and 3 = acrylate conversions; Curves 2 and 4 = thiol conversions. Thickness of the film = 25 μm

Figure S26. Kinetic profiles of the allyl and thiol functions in the DVE/trithiol formulation (43%/57%, w/w) in the presence of A) CQ (0.5 wt%) and B) CQ/Iod (0.5%/2%, w/w) **under air** upon LED@455 nm (curves 1 and 2) and LED@470 nm (curves 3 and 4) exposure. Curves 1 and 3 = acrylate conversions; Curves 2 and 4 = thiol conversions. Thickness of the film = 25 μm .

Figure S27. Photopolymerization profiles of an EPOX/TMPTA blend (50%/50%, w/w) under air in the presence of **QA**/Iod (0.5%/2%, w/w) (1 and 3); and in the presence of **QE**/Iod (0.5%/2%, w/w) (2 and 4) upon LED@455 nm light exposure. Curves 1 and 4 = epoxy conversions; Curves 2 and 3 = acrylate conversions. Thickness of the film = 25 μm .

Figure S28. Photopolymerization profiles of an EPOX/TMPTA blend (50%/50%, w/w) in laminate, in the presence of **QA**/Iod (0.5%/2%, w/w) (2 and 3); and in the presence of **QE**/Iod (0.5%/2%, w/w) (1 and 4) upon LED@455 nm light exposure. Curves 1 and 2 = acrylate conversions; Curves 3 and 4 = epoxy conversions. Thickness of the film = 25 μm .

Figure S29. A) Schematic representation of the evaluation of singlet oxygen and B) UV-vis spectra of 1,3-diphenylisobenzofuran (DPBF) recorded during irradiation of **QA**/Iod/TMPTA/EPOX film under a Xenon lamp source. Inset: drop in the absorbance at 410 nm during illumination of **QA**/Iod/TMPTA/EPOX film with respect to the blank test.