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Donor-acceptor-donor structured thioxanthone derivatives as visible photoinitiators

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Abstract

Three thioxanthone derivatives differing by their peripheral groups have been investigated as visible light photoinitiators of polymerisation. Their reactivity and efficiency have been compared with that of a commercial type II photoinitiator (2-isopropylthioxanthone - ITX) in the case of free radical polymerisation, cationic polymerisation and interpenetrated polymer networks synthesis for 25 μm or 1.4 mm thick samples under a 405 nm LED irradiation. They are incorporated into either, a two-component system with an iodonium salt or an amine, or a three-component system combining an iodonium salt and an amine. Using absorption and fluorescence spectroscopies, laser flash photolysis and molecular modelling, optical properties, excited state energies and lifetimes of these thioxanthone derivatives have been determined allowing a better understanding of the associated chemical mechanisms. Interestingly, the main reaction pathway for one of these thioxanthone derivatives in the photoinitiating systems was determined as involving its singlet state S_1 whereas ITX and thioxanthenes are known to react from their triplet excited state T_1 . The high efficiency of the new initiating systems was found as being worthwhile for laser write applications @405 nm but also for high migration stability.

1. Introduction

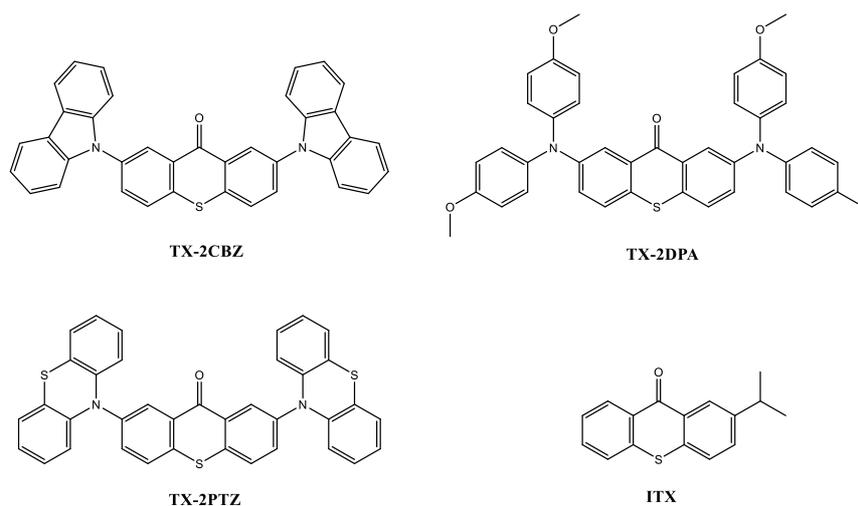
Polymerisation initiated with visible light still remains an important challenge even after four to five decades of development. Indeed, not only the energy consumption is reduced compared to that used for UV-initiated polymerisation and the light penetration capability higher, but this process is also much safer which explained the development of various applications in dentistry¹, coatings² or 3D-printing³. Therefore, different photoinitiators and photoinitiating systems have been developed to initiate either free radical polymerisations or cationic polymerisations under mild reaction conditions (room temperature, visible light, under air). One strategy to achieve this goal consists in designing new photoinitiating systems by modifying the chemical structure of well-known photoinitiators absorbing in near UV such as coumarins⁴ and thioxanthenes^{5 6 7 8}.

Over the past decades, various studies have been conducted on designing thioxanthone-based photoinitiating systems and three main approaches could be inferred: the design of polymeric or macromolecular photoinitiators^{9 10 11 12 13 14 15 16 17}, of one-component molecular photoinitiators^{7 18 19 20} and of multi-component molecular photoinitiating systems^{21 22 23 24}. For example, Dadashi-Silab et al.¹⁴ proposed microporous polymers, where thioxanthone moieties were integrated into the polymer backbones as type II photoinitiators able to initiate both the free radical and cationic polymerisations. Recently, Wu et al.⁹ and Valandro et al.¹¹ developed

44 interesting polymeric photoinitiators with thioxanthone moieties on the side chain of
45 respectively silicone and chitosan-based polymers which allowed a decrease of the
46 photoinitiator migration due to the drastic increase of the photoinitiator molecular weight. Wu
47 et al.⁷ also designed thioxanthone based one-component photoinitiators for the free radical
48 polymerisation of various multifunctional acrylates under xenon lamp. The design of these one-
49 component photoinitiators was based on the functionalisation of thioxanthone with a co-
50 initiator moiety (hydrogen donor). Wu et al.²¹ developed high performance visible light multi-
51 component photoinitiating systems. Based on the reactivity of a substituted
52 isopropylthioxanthone, an iodonium salt and a co-initiator, these multi-component
53 photoinitiating systems could efficiently initiate free radical and cationic polymerisations under
54 405 nm LED irradiation of 40 μm thick samples.

55 In this context, a compound with a donor-acceptor-donor structure (D-A-D structure) where the
56 thioxanthone moiety acts as the acceptor can be an interesting candidate for a photoinitiating
57 system due to its improved light absorption properties associated with the presence of the
58 intramolecular charge transfer. Precisely, compared to the parent thioxanthone, D-A-D triads
59 are expected to exhibit both a red-shifted absorption combined with an enhancement of the
60 molar extinction coefficient. In the literature, such triads have already been designed with
61 carbazole moieties as electron donors²⁵. These structures were notably designed as fluorescent
62 emitters exhibiting thermally activated delayed fluorescence (TADF) properties for the
63 elaboration of high-performance organic light emitting diodes (OLEDs).

64 In this work, three D-A-D structured thioxanthone derivatives, presented in Figure 1, with
65 different peripheral electron donors were investigated as photoinitiators. The free radical
66 polymerisation of acrylates and the cationic polymerisation of epoxides with two-component
67 initiating systems were examined upon visible light irradiation. Finally, the synthesis of
68 interpenetrated polymer networks (IPNs) using three-component initiating systems was also
69 examined. To evidence the interest of these new structures, the reactivity, efficiency and optical
70 properties of the new photoinitiators were compared to that of a benchmark thioxanthone
71 photoinitiator i.e. 2-isopropylthioxanthone ITX.

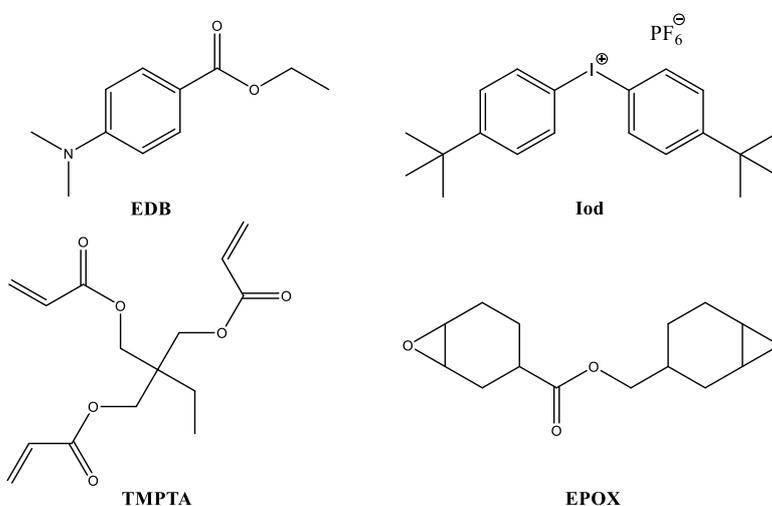


72

73 Figure 1: Chemical structures of the investigated thioxanthenes and the benchmark
74 photoinitiator (ITX)

75 **2. Experimental section**
76 **2.1. Chemical Compounds**

77 *Bis*-(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod; SpeedCure 938), ethyl 4-
78 (dimethylamino)benzoate (EDB; SpeedCure EDB) and 2-isopropylthioxanthone (ITX;
79 SpeedCure 2-ITX) were obtained from Lambson Ltd (UK). Trimethylolpropane triacrylate
80 (TMPTA) and (3,4-epoxycyclohexane)methyl-3,4-epoxycyclohexylcarboxylate (EPOX;
81 Uvacure 1500) were obtained from Allnex and used as benchmark monomers for radical and
82 cationic photopolymerisation, respectively (Figure 2). Dichloromethane (DCM, purity $\geq 99\%$)
83 used as solvent, quinine hemisulphate salt monohydrate (BioReagent, suitable for fluorescence,
84 purity 99.0-101.0%), 1-methylnaphthalene (purity 95%), benzophenone (ReagentPlus, purity
85 99%) and colloidal silica suspension (LUDOX[®] AS 30, 30wt% suspension in H₂O) were
86 purchased from Sigma-Aldrich.



87
88 Figure 2: Chemical structures of additives and monomers

89
90 **2.2. Synthesis of investigated thioxanthone derivatives:**

91 The investigated thioxanthenes were synthesised and characterised according to the following
92 protocol. All the chemicals and solvents were purchased from chemical companies and used as
93 received, unless otherwise mentioned. Purification of products was performed by column
94 chromatography on silica gel from Merck with a grain size of 0.04-0.063 mm (flash silica gel,
95 Geduran Si 60) eluting with analytically pure solvents. NMR (¹H and ¹³C) spectra were
96 recorded on a Bruker DPX-250 FT- NMR spectrometer. Chemical shifts are given in ppm using
97 the residual solvent signal as internal reference. Mass spectroscopy was performed by the
98 Spectropole of Aix-Marseille University. Electron spray ionization (ESI) mass spectral
99 analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer.
100 The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems
101 SCIEX) mass spectrometer. All compounds were prepared from 2,7-dibromo-9*H*-thioxanthen-
102 9-one, a known compound ²⁶. The syntheses of **TX-2DPA** and **TX-2PTZ** have been described
103 elsewhere in a separate publication. The synthesis of **TX-2CBZ**, which was already known in
104 literature ²⁵, was performed according to the following protocol.

105 **2,7-di(9H-carbazol-9-yl)-9H-thioxanthen-9-one (TX-2CBZ)**: In a dried Schlenk flask, the
106 mixture of 2,7-dibromo-9H-thioxanthen-9-one (200 mg, 1.0 eq) and carbazole 96% (300 mg,
107 3.0 eq), CuI (20 mg, 0.2 eq), sodium carbonate (0.3 g, 5.0 eq) and 18-crown-6 (30 mg, 0.2 eq)
108 were added at once. Then, 15 mL of nitrobenzene was supplied. The reaction mixture was
109 stirred under argon atmosphere while the temperature was slowly raised up to 160 °C and kept
110 for 24h before allowed to cool to room temperature. The reaction mixture was then filtered and
111 washed by diethyl ethers through a silica pad to eliminate solid products. Organic layers were
112 collected and evaporated to get the crude product which was then purified by silica gel column
113 chromatography using petroleum ethers: ethyl acetate (4:1 v/v) as eluent to obtain a yellow
114 solid (150 mg, 51% yield). ¹H NMR (250 MHz, DMSO) δ 8.63 (d, *J* = 2.3 Hz, 2H), 8.27 (dd,
115 *J* = 8.1, 4.7 Hz, 6H), 8.15 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.53 – 7.42 (m, 8H), 7.37 – 7.28 (m, 4H).
116 ¹³C NMR (62.5 MHz, DMSO-*d*₆) δ 178.4, 140.3, 136.2, 135.8, 132.0, 129.8, 126.9, 126.6,
117 123.4, 121.1, 109.9. HRMS (ESI⁺): calculated for C₃₇H₂₂N₂OS [M+H]⁺: 543.1453/found:
118 543.1525

119

120 **2.3. UV-visible absorption spectroscopy and colorimetric analysis**

121 UV-visible absorption spectra were acquired in DCM in a quartz cell at room temperature using
122 a Jasco V-750 spectrophotometer. The molar extinction coefficients were determined using the
123 Beer-Lambert law with experimental data obtained on solutions of known concentrations.

124 UV-visible transmission spectra were acquired from 200 to 800 nm on 1.4 mm thick polymer
125 sample at room temperature using a Jasco V-750 spectrophotometer. Colorimetric analysis was
126 given in the CIE L* a* b* colour system with the following parameters: a standard light D55-
127 1, a 10 degrees standard observer, a 5 nm data interval and a colour matching function JIS
128 Z8701:1999 with JIS Z8701:1999 and ASTM E308: 2008 as standard.

129 **2.4. Fluorescence experiment**

130 **2.4.1. Steady state fluorescence**

131 Fluorescence spectra were acquired in a quartz cell at room temperature using a JASCO[®] FP-
132 750 spectrofluorometer. Excitation and emission spectra were recorded in DCM in a quartz
133 cell.

134 **2.4.2. Time correlated single photon counting (TCSPC)**

135 The fluorescence excited state lifetimes were determined using a time-correlated single-photon
136 counting system, a HORIBA[®] DeltaFlex with a HORIBA[®] PPD-850 as detector. The excitation
137 source is a HORIBA[®] nanoLED-370 with an excitation wavelength of 367nm and a pulse
138 duration inferior to 1.4 ns. The fluorescence intensity decay profiles were recorded in DCM in
139 a quartz cell. A silica colloidal solution LUDOX[®] was used to evaluate the impulse response
140 function (IRF) of the apparatus.

141 **2.5. Laser flash photolysis (LFP)**

142 Nanosecond laser flash photolysis (LFP) experiments were performed using a Q-switched
143 nanosecond Nd/YAG laser from Minilite Continuum ($\lambda_{\text{ex}} = 355 \text{ nm}$, 9 ns pulses; energy reduced

144 down to 10 mJ) and an analysing system consisting of a pulsed xenon lamp, a monochromator,
145 a fast photomultiplier, and a transient digitizer²⁷. The decay traces were recorded in DCM in a
146 quartz cell after a deoxygenation of the solution by N₂ bubbling.

147 **2.6. Photopolymerisation kinetics (RT-FTIR)**

148 The experimental conditions for each photosensitive formulation are given in the captions of
149 the figures. The weight percent of the photoinitiating system is calculated from the monomer
150 content. The photoinitiator concentrations in each photosensitive formulation were chosen to
151 ensure the same light absorption at 405 nm.

152 All the polymerisations were performed at ambient temperature (21-25 °C) and irradiation was
153 started at $t = 10$ s. A LED@405 nm (M405L3 - Thorlabs) having an intensity around 50
154 $\text{mW}\cdot\text{cm}^{-2}$ at the sample position was used for the photopolymerisation experiments. The
155 emission spectrum is already available in the literature²⁸.

156 A Jasco 4100 real-time Fourier transform infrared spectrometer (RT-FTIR) was used to follow
157 the conversion of the acrylate functions of the TMPTA and of the epoxide group of EPOX. For
158 the thin samples (~ 25 μm of thickness), the photosensitive formulations were deposited on
159 polypropylene films under air for the cationic polymerisations of EPOX while the free radical
160 polymerisations of TMPTA were performed in laminate (the formulation is sandwiched
161 between two polypropylene films to reduce the O₂ inhibition). The decrease of the C=C double
162 bond band or the epoxide group band was continuously monitored from 1581 to 1662 cm^{-1} or
163 from 768 to 825 cm^{-1} respectively. For the thicker samples (~ 1.4 mm of thickness), the
164 photocurable formulations were deposited on a polypropylene film inside a 1.4 mm thick mould
165 under air. The evolutions of the C=C double bond band and the epoxide group band were
166 continuously followed from 6117 to 6221 cm^{-1} and from 3710 to 3799 cm^{-1} respectively.

167 **2.7. Computational Procedure**

168 Molecular orbital calculations were carried out using the Gaussian 03 package. The electronic
169 absorption spectrum of TX-2CBZ, TX-2DPA, TX-2PTZ and ITX were calculated from the
170 time-dependent density functional theory at the RTD-mPW1PW91-FC/6-31G* level on the
171 relaxed geometries calculated at the uB3LYP/6-31G* level. The geometries were frequency-
172 checked²⁹.

173 **2.8. 3D laser writing experiments**

174 The photosensitive resin was deposited onto a microscope slide (1 mm thick sample). A
175 computer-controlled laser diode at 405 nm (size of the irradiation spot around 50 μm) was used
176 for the spatially controlled irradiation. The generated pattern was analyzed by a numerical
177 optical microscope (DSX-HRSU from OLYMPUS Corp)

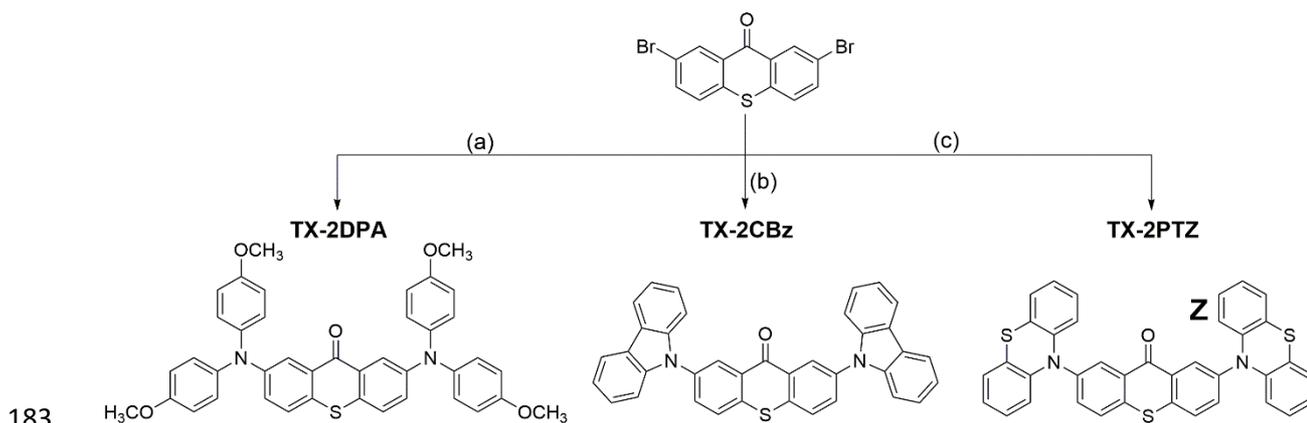
178

179 **3. Results and discussion**

180 **3.1. Photoinitiator synthesis**

181 The synthetic routes toward the different thioxanthone derivatives are outlined in Scheme 1.

182



184 Scheme 1: Synthesis of thioxanthone-based photoinitiators. Reagents and conditions (a) di(4-
185 methoxyphenyl)amine, NaOtBu, PdCl₂(PPh₃)₄, Toluene, 110°C, 24h. (b) Carbazole, Na₂CO₃,
186 CuI, 18-crown-6, Nitrobenzene, 160°C, 24h. (c) phenothiazine, NaOtBu, PdCl₂(PPh₃)₄,
187 Toluene, 110°C, 24h.

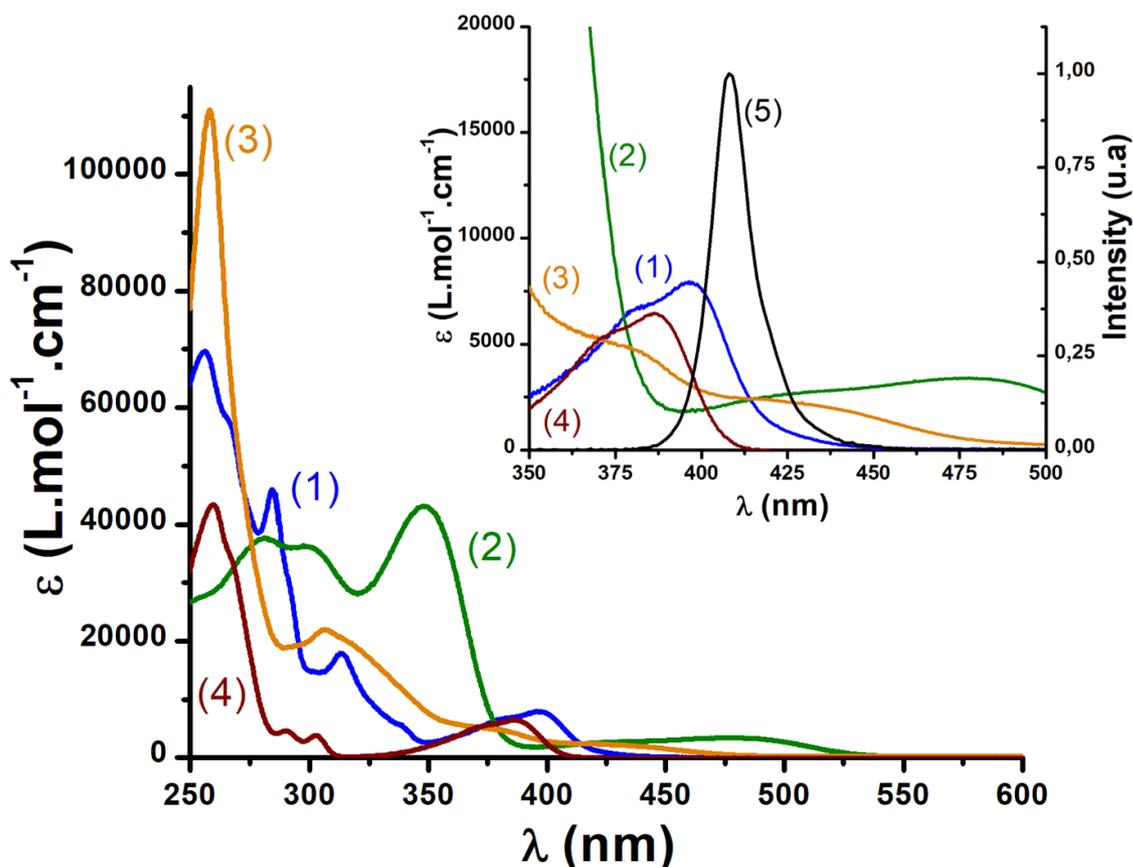
188 Briefly, all compounds were synthesized in one step from 2,7-dibromo-9H-thioxanthen-9-one
189 ²⁶ and the corresponding diarylamine using twofold C-N coupling reactions. While **TX-2DPA**
190 and **TX-2PTZ** were obtained by using Pd-catalyzed Buchwald-Hartwig amination, the copper-
191 catalyzed Ullmann amination was used to afford **TX-2CBZ**.

192

193 3.2. Photochemical properties

194 3.2.1. Ground state: UV-visible absorption and molecular modelling

195 Absorption spectra of the selected thioxanthone derivatives (Figure 1) and of ITX in
196 dichloromethane are depicted in Figure 3. TX-2CBZ, TX-2DPA, TX-2PTZ and ITX show
197 mainly an ultraviolet absorption. However, their lowest energy transition corresponds to a near
198 UV-visible absorption. The longest absorption wavelength and corresponding molar extinction
199 coefficient for the four thioxanthone derivatives are gathered in Table 1. Interestingly for the
200 three investigated thioxanthenes TX-2CBZ, TX-2DPA and TX-2PTZ, the lowest energy
201 transition is shifted toward longer wavelengths depending on the electron donating substituent.
202 With the dimethoxydiphenylamine (DPA) substituents, the absorption peak is more shifted than
203 with carbazole (CBZ) or phenothiazine (PTZ) substituents. The emission spectrum of the LED
204 at 405 nm shows a fine overlap with the light absorption of the thioxanthone derivatives (Figure
205 3 inset). Indeed, TX-2CBZ, TX-2DPA, TX-2PTZ and ITX possess molar extinction
206 coefficients at 405 nm around 5900, 2000, 2600 and 1000 L.mol⁻¹.cm⁻¹ respectively. Thus, the
207 three investigated thioxanthone derivatives present a bathochromic shift compared to ITX with
208 higher extinction coefficients. For a better understanding of these light absorption properties,
209 molecular orbital calculations were carried out. The wavelengths determined for the lowest
210 energy transition by theoretical calculations (Table 1) are rather coherent with the experimental
211 ones.



212

213 Figure 3: Absorption spectra of (1) TX-2CBZ, (2) TX-2DPA, (3) TX-2PTZ and (4) ITX in
 214 dichloromethane. The inset is a zoom of the absorption spectra overlaid with (5) the normalized
 215 emission spectra of the used LED at 405 nm.

216

217 Table 1: Absorption properties of the different thioxanthone derivatives.

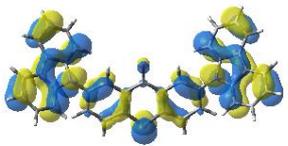
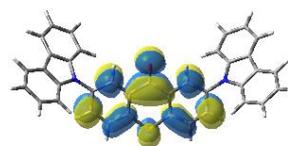
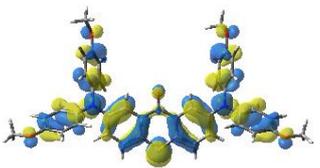
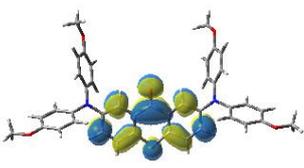
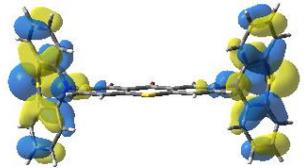
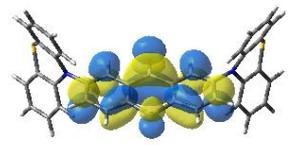
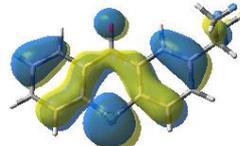
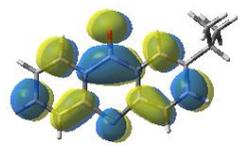
	λ_{\max} (nm)	$\epsilon_{\lambda_{\max}}$ (L.mol ⁻¹ .cm ⁻¹)	$\epsilon_{405\text{nm}}$ (L.mol ⁻¹ .cm ⁻¹)	λ_{\max} calculated (nm)
ITX	386	6.5×10^3	1.0×10^3	340
TX-2CBZ	396	7.9×10^3	5.9×10^3	428
TX-2DPA	478	3.4×10^3	2.0×10^3	470
TX-2PTZ	305; 415 ^a	2.4×10^3	2.6×10^3	335

218 ^a shouldered band

219 The optimised geometries and frontier orbitals, energies of the highest occupied molecular
 220 orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were determined by
 221 theoretical calculations, using density functional theory at uB3LYP/6-31G* level of the theory.
 222 The contour plots of the optimised geometries frontier orbitals are depicted in Figure 4.
 223 Interestingly, for TX-2CBZ, TX-2DPA, TX-2PTZ and ITX, the electronic density of the
 224 LUMO is almost entirely located on the thioxanthone moiety while the substituents are
 225 participating in the HOMO. This complete separation between the frontier orbitals suggests a

226 charge transfer behaviour confirming the D-A-D structure. This charge transfer behaviour is
 227 coherent with the shift of the absorption spectra observed upon modification of the electron
 228 donating groups. Another important parameter for the photochemical reactivity of thioxanthone
 229 is usually the triplet energy level. The computed thioxanthone derivatives triplet state T_1
 230 energies are gathered in Figure 4. The energy of the triplet state decreases in the series $ITX >$
 231 $TX-2CBZ \approx TX-2PTZ > TX-2DPA$.

232

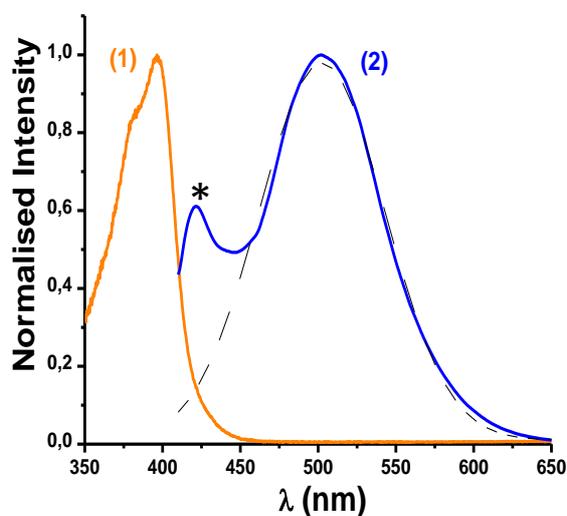
	HOMO	LUMO	E_{T_1} (kcal.mol ⁻¹) ^a
TX-2CBZ			56.38
TX-2DPA			49.27
TX-2PTZ			55.35
ITX			63.83

233 Figure 4: Contour plots of the frontier orbitals determined for the different thioxanthone
 234 derivatives examined in this work and optimised at the B3LYP/6-31G* level of theory and their
 235 calculated T_1 triplet state energy, ^a level ± 3 kcal.mol⁻¹

236 3.2.2. Singlet excited state: Steady state and time resolved fluorescence

237 To assess the properties related to the S_1 singlet excited states of the TX-2CBZ, TX-2DPA, TX-
 238 2PTZ and ITX, a steady state fluorescence analysis in dichloromethane was performed.
 239 Unfortunately, no fluorescence properties are observed for TX-2DPA and TX-2PTZ. This
 240 absence of fluorescence may be associated to a deactivation of the lowest singlet state by a non-
 241 radiative process such as an internal conversion or an intersystem crossing. The excitation and
 242 emission spectra of TX-2CBZ are presented in Figure 5. The fluorescence emission of this
 243 thioxanthone derivative is centred at 502 nm which is consistent with previous results²⁵. The
 244 formation of a fluorescent photoproduct is also observed in Figure 5 with an emission centred
 245 at 420 nm and partially overlapping with the thioxanthone derivative emission peak. This
 246 photoproduct is associated with an impurity since the excitation spectrum at 420 nm does not
 247 fit with the absorption spectrum of TX-2CBZ. In order to evaluate the energy of the first singlet
 248 excited state S_1 , an extrapolation of the shape of the emission peak as a gaussian function (dash

249 line curve) was required. From the crossing point of the absorption and emission spectra, the
250 energy of the first singlet excited state S_1 is estimated to be around $66.9 \text{ kcal.mol}^{-1}$ which is
251 coherent with the $66.6 \text{ kcal.mol}^{-1}$ calculated with molecular modelling of the absorption
252 spectrum. The energetic gap between the triplet state T_1 and the singlet state S_1 of TX-2CBZ is
253 between 5 to 15 kcal.mol^{-1} which is higher than the energy brought by the medium due to
254 thermal agitation³⁰. This last result which come from computational calculation suggests that
255 TX-2CBZ does not present a thermally activated delayed fluorescence (TADF) behaviour but
256 only an extended singlet state lifetime which is in accordance to literature²⁵. However,
257 influence of the solvent which could induce the stabilisation or the destabilisation of TX-2CBZ
258 fundamental and excited states, was not considered here. Thus, the energetic gap between the
259 triplet state T_1 and the singlet state S_1 could be smaller and TX-2CBZ could present a thermally
260 activated delayed fluorescence (TADF) behaviour in other media.

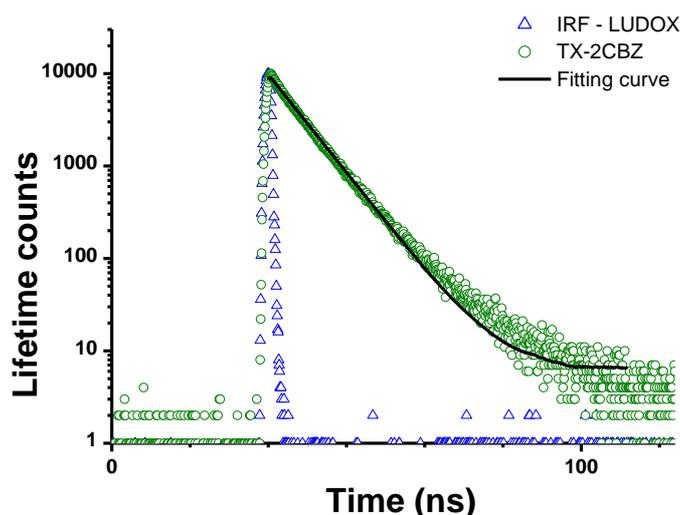


261

262 Figure 5: Fluorescence spectra of TX-2CBZ in dichloromethane under air $[\text{TX-2CBZ}] = 1.4 \times$
263 $10^{-5} \text{ mol.L}^{-1}$ (1) excitation spectrum $\lambda_{\text{em}} = 502 \text{ nm}$, (2) emission spectrum $\lambda_{\text{ex}} = 400 \text{ nm}$, * peak
264 associated with an impurity.

265

266 Analysis by time-correlated single-photon counting (TCSPC) of the S_1 lifetimes shows in
267 Figure 6 the decay profile of the TX-2CBZ fluorescence. From mono-exponential curve fitting
268 of the decay profile, the first singlet state lifetime is assessed at $7 \text{ ns} \pm 1 \text{ ns}$. In comparison, the
269 first singlet state lifetime of ITX is much shorter, inferior to 1.4 ns which is the minimal
270 resolution of the experimental setup; this is in agreement with the singlet state lifetime of 200
271 ps evaluated in the literature in acetonitrile³¹. Fluorescence decay profile of ITX obtained by
272 time-correlated single-photon counting (TCSPC) is presented in Supporting Information Figure
273 S1. The strong elongation of the first singlet state lifetime in TX-2CBZ vs. ITX could be a
274 consequence of the rigidification of the molecule structure by the carbazole substituents.

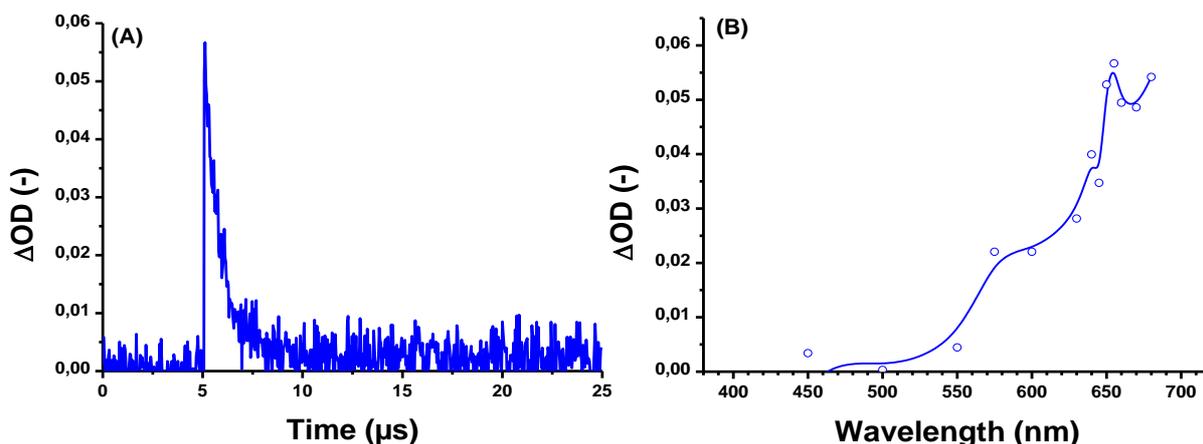


275
 276 Figure 6: Time-correlated single-photon counting of TX-2CBZ in dichloromethane, $\lambda_{\text{ex}} = 367$
 277 nm, $\lambda_{\text{em}} = 502$ nm and $[\text{TX-2CBZ}] = 1.4 \times 10^{-5}$ mol.L $^{-1}$.

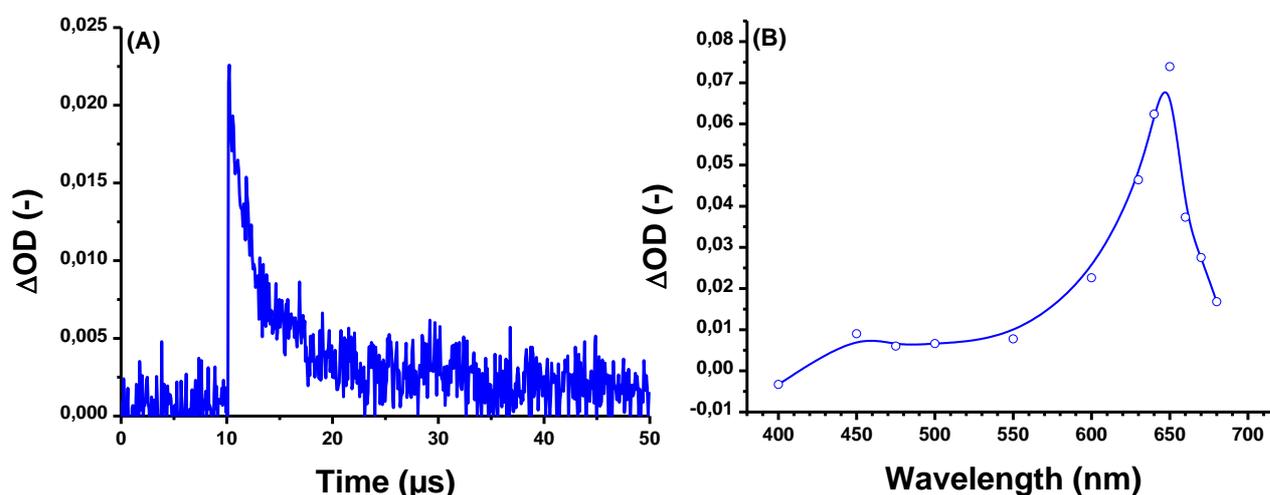
278 In order to fully characterise the reactivity of the singlet state of TX-2CBZ toward amine (EDB)
 279 or iodonium salt (Iod), steady state fluorescence quenching was performed in dichloromethane
 280 by gradually adding EDB or Iod in a TX-2CBZ solution. The Stern-Volmer quenching plots
 281 are presented in Figure S2 in SI. What is significant about these results is the slope of the linear
 282 regression of the Stern-Volmer plot which corresponds to the product of the observed rate
 283 constant of quenching k_q and the singlet lifetime τ_0 . The observed rate constants of quenching
 284 k_q are assessed at 6.5×10^9 and 4.7×10^9 L.mol $^{-1}$.s $^{-1}$ for TX-2CBZ/Iod and TX-2CBZ/EDB
 285 respectively. These constants are very high albeit slightly smaller than the diffusional rate
 286 constant, $k_d = 1.5 \times 10^{10}$ L.mol $^{-1}$.s $^{-1}$.³² Thus, these reactions are really efficient and almost
 287 diffusion-controlled.

288 3.2.3. Triplet excited state: Laser flash photolysis

289 Laser flash photolysis experiments were also carried out on the different thioxanthone
 290 derivatives in order to characterise their triplet state T_1 . Analogously to the fluorescence
 291 analysis, the triplet state of TX-2DPA and TX-2PTZ were not detected in laser flash photolysis
 292 experiments. This result may be explained by either an absence of intersystem crossing or a
 293 triplet excited state lifetime below the resolution of our LFP spectrometer (<10ns) or a non-
 294 radiative deexcitation of the triplet state. The decay traces of the T_1 for TX-2CBZ and ITX are
 295 presented along with their transient absorption spectra recorded 5.12 μs and 10.24 μs after the
 296 acquisition start (laser pulse for $t=5\mu\text{s}$ and $t=10\mu\text{s}$ respectively) in Figure 7 and Figure 8
 297 respectively. The transient spectra of TX-2CBZ and ITX present an absorption from 570 nm to
 298 670 nm which is typically assigned to thioxanthone triplet state^{33 34}. The triplet state lifetime
 299 of TX-2CBZ and ITX in deoxygenated dichloromethane are about 1.0 μs and 5.8 μs . Thus, the
 300 triplet excited state lifetimes of both TX-2CBZ and ITX are of the same order of magnitude.



301
 302 Figure 7: (A) Decay trace of TX-2CBZ recorded at 655 nm under nitrogen in dichloromethane
 303 after laser excitation at 355 nm laser pulse for $t=5\mu\text{s}$ (B) Transient absorption spectrum of TX-
 304 2CBZ recorded after the laser pulse for $t=5.12\mu\text{s}$



305
 306 Figure 8: (A) Decay trace of ITX recorded at 650 nm under nitrogen in dichloromethane after
 307 laser excitation at 355 nm laser pulse for $t=10\mu\text{s}$ (B) Transient absorption spectrum of ITX
 308 recorded after the laser pulse for $t=10.24\mu\text{s}$

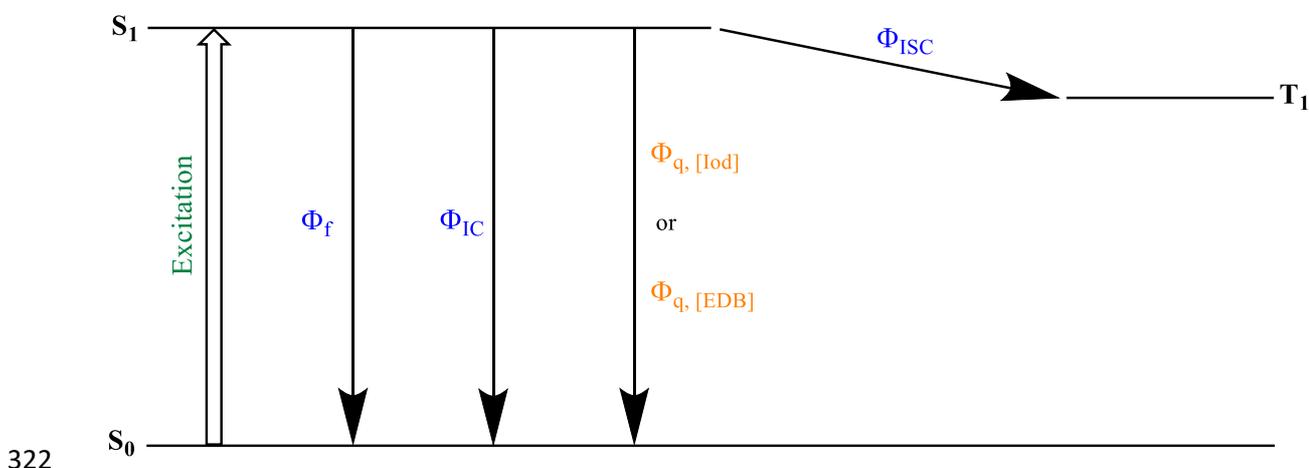
309 In order to fully characterise the reactivity of the triplet state of TX-2CBZ toward amine (EDB)
 310 or iodonium salt (Iod), triplet quenching was performed in dichloromethane by gradually
 311 adding EDB or Iod in a TX-2CBZ solution monitoring the change of triplet state decays. The
 312 Stern-Volmer quenching plots are presented in Figure S3 in SI. The observed rate constant of
 313 quenching k_q are assessed at 7.79×10^8 and 5.44×10^9 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ for TX-2CBZ/Iod and TX-
 314 2CBZ/EDB respectively. Thus, the reactions from TX-2CBZ triplet state are really efficient
 315 and close to the diffusion limit.

316 Since both S_1 and T_1 have a similar reactivity toward the additives (EDB or Iod), we focus on
 317 the different modes of deactivation of the excited state S_1 in order to determine which excited
 318 state is involved in the polymerisation initiating step.

319

3.2.4. Photochemical pathways

320 The different deactivation processes of the first singlet state were characterised through their
321 specific quantum yields (Scheme 2).



323 Scheme 2: Processes from the S_1 excited state: Φ_f , Φ_{IC} , $\Phi_{q,[Iod]}$, $\Phi_{q,[EDB]}$ and Φ_{ISC} represent the
324 fluorescence quantum yield, the internal conversion quantum yield, the quantum yield of
325 quenching by Iod, the quantum yield of quenching by EDB and the intersystem crossing
326 quantum yield.

327 As shown in Scheme 2, the deactivation of the singlet state occurs through the competition
328 between up to four processes: internal conversion (IC), fluorescence (f), intersystem crossing
329 (ISC) and quenching (Q). To simplify the study, TX-2CBZ was first considered in
330 dichloromethane without any quencher. In this case, the quantum yield of the intersystem
331 crossing, fluorescence and internal conversion could be defined by the formulas presented in
332 Equations 1-4³⁵.

333

$$\Phi_{ISC} = \frac{k_{ISC}}{k_{ISC} + k_f + k_{IC}} = k_{ISC}\tau_0 \quad (eq. 1)$$

334

$$\Phi_f = \frac{k_f}{k_{ISC} + k_f + k_{IC}} = k_f\tau_0 \quad (eq. 2)$$

335

$$\Phi_{IC} = \frac{k_{IC}}{k_{ISC} + k_f + k_{IC}} = k_{IC}\tau_0 \quad (eq. 3)$$

336

$$\Phi_{ISC} + \Phi_f + \Phi_{IC} = 1 \quad (eq. 4)$$

337 In these equations, Φ_{ISC} , Φ_f , Φ_{IC} , k_{ISC} , k_f , k_{IC} and τ_0 represent the quantum yield of intersystem
338 crossing, the quantum yield of fluorescence, the quantum yield of internal conversion, the rate
339 constant for intersystem crossing, the rate constant of fluorescence, the rate constant for internal
340 conversion $S_1 \rightarrow S_0$ and the singlet lifetime in the absence of any quencher, respectively.

341 The quantum yield of the intersystem crossing was evaluated through laser flash photolysis
342 experiments. The quantum yield of intersystem crossing was determined from the transient

343 yields of triplet 1-methylnaphthlene produced when it was added as a quencher. Benzophenone
344 was used as standard due to his well-known intersystem crossing quantum yield $\Phi_{ISC}=1$ ³². The
345 decay trace of TX-2CBZ and benzophenone in presence of 1-methylnaphthalene are presented
346 in Figure S4 in SI. The intersystem crossing quantum yield of TX-2CBZ is about 0.60 ± 0.03 .

347 To complete this assessment, the quantum yield of fluorescence was determined by comparing
348 the integrated areas beneath the fluorescence emission spectra of TX-2CBZ with that of a
349 standard. The emission spectra were recorded with the same acquisition condition. Quinine
350 sulphate in H_2SO_4 0.1M was used as a standard with a fluorescence quantum yield $\Phi_f=0.54$ ³⁶.
351 Variation of the integrated fluorescence intensity vs absorbance at the excitation wavelength is
352 presented in Supporting Information Figure S5. The fluorescence quantum yield of TX-2CBZ
353 is assessed at 0.03. Since the intersystem crossing quantum yield of TX-2CBZ is about 0.60, in
354 absence of quenching reaction, the internal conversion quantum yield could be inferred from
355 the intersystem crossing quantum yield and the fluorescence quantum yield of TX-2CBZ and
356 is assessed at 0.37.

357 Thus, the deactivation of the singlet excited state while omitting the quenching reactions seems
358 to be a competition between internal conversion and intersystem crossing. However, in
359 presence of the additives of the two-component initiating system, Iod or EDB, the quenching
360 reaction could not be neglected. The singlet quenching quantum yields were derived from the
361 observed rate constant of quenching k_q using Equation 5. The quenching quantum yield is about
362 0.65 and 0.77 for system TX-2CBZ/Iod and TX-2CBZ/EDB respectively. Using the Equation
363 6 with a quencher concentration in accordance with the conditions of the polymerisation
364 experiments, the influence of the quenching on the quantum yield Φ_f , Φ_{IC} and Φ_{ISC} was
365 determined. These recalculated quantum yields are $\Phi_{q,[Iod]} = 0.65$, $\Phi_{f,[Iod]} = 0.01$,
366 $\Phi_{IC,[Iod]} = 0.13$ and $\Phi_{ISC,[Iod]} = 0.21$ in presence of Iod (Figure S7 in SI), and in presence of
367 EDB, $\Phi_{q,[EDB]} = 0.77$, $\Phi_{f,[EDB]} < 0.01$, $\Phi_{IC,[EDB]} = 0.09$ and $\Phi_{ISC,[EDB]} = 0.14$. In presence
368 of either additive the quenching of TX-2CBZ became the main deactivation mode of the first
369 singlet excited state.

$$370 \quad \Phi_{q,[Q]} = \frac{k_q \tau_0 [Q]}{1 + k_q \tau_0 [Q]} \quad (eq. 5)$$

371 In this equation, $\Phi_{q,[Q]}$, k_q , $[Q]$ and τ_0 represent the quenching quantum yield, the observed
372 rate constant of quenching, the quencher concentration and the singlet lifetime, respectively.

$$373 \quad \frac{\Phi_X}{\Phi_{X,[Q]}} = 1 + k_q \tau_0 [Q] \quad (eq. 6)$$

374 In this equation, $\Phi_{X,[Q]}$, Φ_X , k_q , $[Q]$ and τ_0 represent the quantum yield in presence or absence
375 of a quencher Q (where X stands for either ISC, f or IC), the observed rate constant of
376 quenching, the quencher concentration and the singlet lifetime, respectively.

377 All the thioxanthone derivatives possess absorption properties making them interesting
378 candidates for the photoinitiation under visible light. The reactivity of TX-2CBZ with Iod or
379 EDB occurs through the first singlet excited state while for isopropylthioxanthone this
380 reactivity usually occurs through the first triplet excited state³⁷. Since the properties of the

381 thioxanthone derivatives have been assessed, we focus on their use as photoinitiating systems
382 for the polymerisation of various monomers.

383 3.3. Polymerisation

384 3.3.1. Free radical polymerisation in TMPTA

385 Thioxanthone derivatives were investigated as photoinitiators for the free radical
386 polymerisation of TMPTA upon LED irradiation at 405 nm to produce either 25 µm thick
387 samples in laminate or 1.4 mm thick samples under air.

388 TX-2CBZ, TX-2DPA and TX-2PTZ were tested as type II photoinitiators with an amine (EDB)
389 and comparisons were established with a benchmark commercial initiator, 2-
390 isopropylthioxanthone (ITX). After the irradiation of the EDB/thioxanthone derivative system,
391 a reaction took place between the excited state of the thioxanthone derivative and EDB.
392 Provided that these derivatives react as unsubstituted thioxanthone (TX), an electron transfer
393 from EDB ground state to thioxanthone excited state followed by a rapid proton transfer will
394 occurred as stated in reaction r1-r2³⁸. The polymerisation profiles of TMPTA in presence of a
395 photoinitiator/EDB system are presented in Figure 9. Among the tested thioxanthone
396 derivatives, only ITX and TX-2CBZ allow the formation of a polymer with a tack-free surface.
397 For the polymerisation of 25 µm thick samples (Figure 9A), only ITX and TX-2CBZ systems
398 show a high efficiency and fast kinetics while TX-2DPA and TX-2PTZ systems demonstrate a
399 low efficiency and slow kinetics. The final C=C double bond conversions are 53%, 36%, 19%
400 and 7% for ITX, TX-2CBZ, TX-2DPA and TX-2PTZ respectively. The same trend in the
401 polymerisation efficiency is observed for 1.4 mm thick samples (Figure 9B). However, a very
402 high efficiency and fast kinetics were observed for ITX/EDB and TX-2CBZ/EDB (final
403 conversion = 83% and 84% respectively). These results suggested that the thioxanthone
404 derivatives react similarly to the reference ITX. Moreover, the poor efficiency of TX-2DPA
405 and TX-2PTZ are in accordance with the non-measurable singlet/triplet state lifetime
406 suggesting probably mainly internal conversion as a deactivation pathway of the S1 excited
407 state with a slow reaction with Iod or EDB.



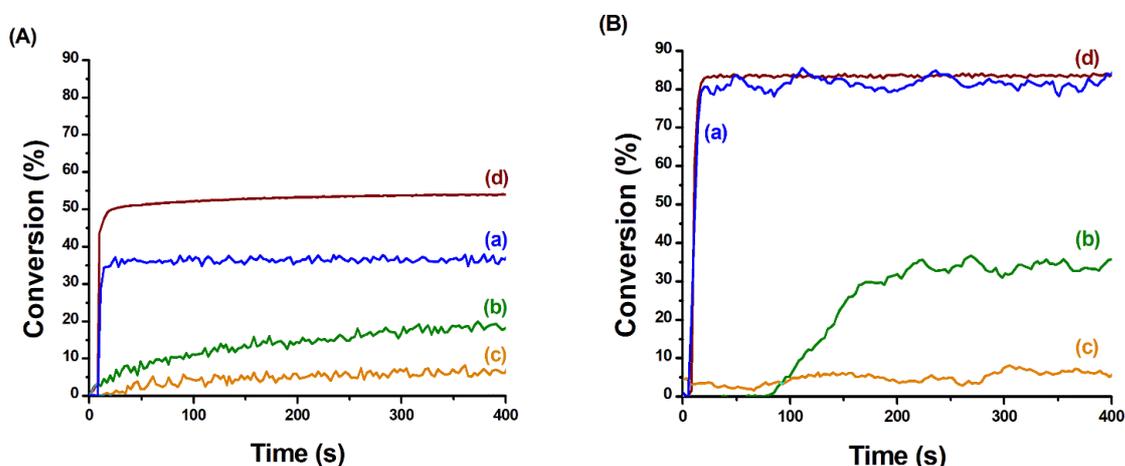
409 TX-2CBZ, TX-2DPA and TX-2PTZ were also tested as photoinitiator with an iodonium salt
410 (Iod). For the sake of comparison, polymerisation was also performed with the standard system
411 ITX/Iod. The thioxanthone derivative/Iod interaction corresponds to an electron transfer
412 reaction which leads to an aryl radical Ar[•] as presented in reactions r3-r4³⁹. The polymerisation
413 profiles of TMPTA in presence of a photoinitiator/Iod system are presented in Figure 10. For
414 the polymerisation of 25 µm thick sample (Figure 10A), the efficiency trend of thioxanthone
415 derivative as photoinitiator respects the following order: ITX > TX-2CBZ > TX-2PTZ > TX-
416 2DPA. The final C=C double bond conversions are 63%, 46%, 38% and 23% respectively and
417 a polymer with a tack-free surface is only obtained with ITX, TX-2CBZ and TX-2PTZ. Similar
418 results in terms of the polymerisation efficiency are obtained for 1.4 mm thick samples (Figure
419 10B). Among the tested thioxanthone derivatives, only ITX allows to obtain a polymer with a
420 tack-free surface while TX-2CBZ and TX-2PTZ allow to synthesize a polymer with a close to
421 tack-free surface. The final C=C double bond conversions are 74%, 78%, 51% and 25% with
422 ITX/Iod, TX-2CBZ/Iod, TX-2PTZ/Iod and TX-2DPA/Iod respectively. Since the incertitude
423 on the conversion was of 3% in these conditions, the efficiency trend of thioxanthone
424 derivatives as photoinitiators respects the following order: TX-2CBZ ≈ ITX > TX-2PTZ > TX-

425 2DPA. This last order of reactivity is in accordance with the one of the triplet state energy found
 426 by molecular modelling.



427

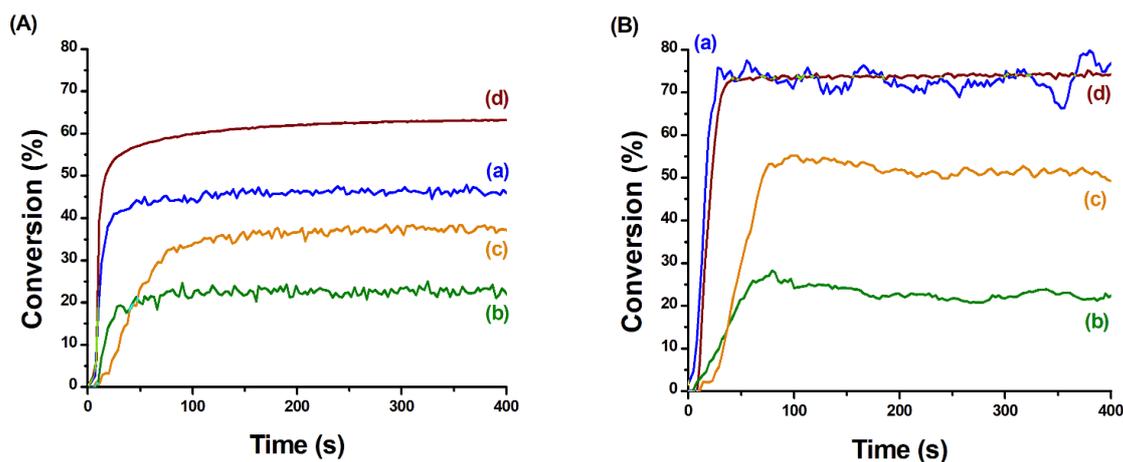
428 Among the investigated thioxanthone derivatives used for the free radical polymerisation of
 429 TMPTA, TX-2CBZ appears as an interesting photoinitiator. Indeed, in initiating system with
 430 either the amine EDB or the iodonium salt Iod, TX-2CBZ exhibits performances slightly lower
 431 or similar than the standard photoinitiator ITX but for a lower weight percentage in the
 432 formulation as the comparison was given for similar absorption properties at 405nm. When the
 433 same molar percentage is used in the formulation, the same performances are observed as
 434 showed in Figure S6 in SI.



435

436 Figure 9: Polymerisation profiles (acrylate function conversion vs irradiation time) of TMPTA
 437 upon irradiation with a LED at 405 nm, irradiation starts at 10 s, 50 mW.cm⁻²; (A) sample
 438 thickness = 25 µm and (B) sample thickness = 1.4 mm. Photoinitiating systems: (curve a) TX-
 439 2CBZ/EDB (0.07/1.9 w/wt%), (curve b) TX-2DPA/EDB (0.22/1.9 w/wt%), (curve c) TX-
 440 2PTZ/EDB (0.17/2.0 w/wt%) and (curve d) ITX/EDB (0.19/2.0 w/wt%)

441



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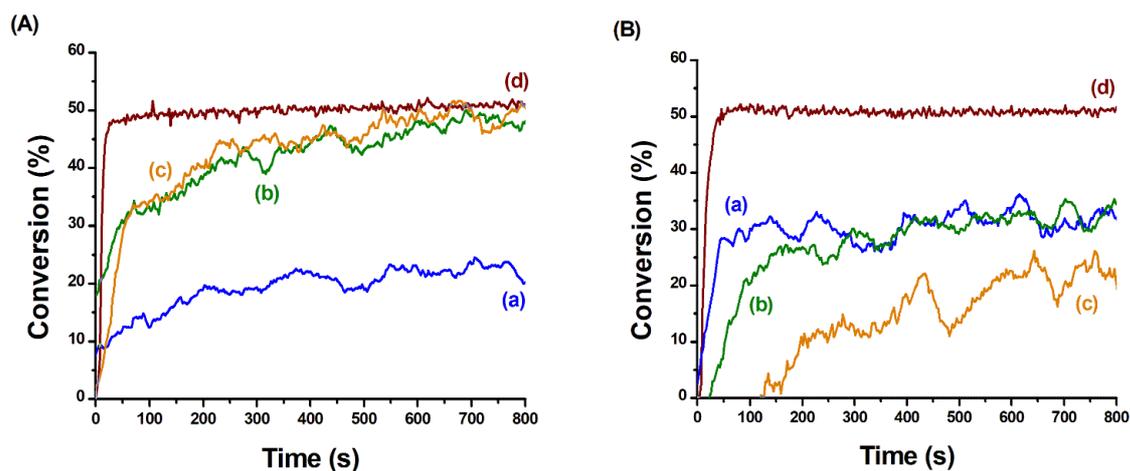
443 Figure 10: Polymerisation profiles (acrylate function conversion vs irradiation time) of TMPTA
 444 upon irradiation with a LED at 405 nm, irradiation starts at 10 s, 50 mW.cm⁻²; (A) sample
 445 thickness = 25 µm and (B) sample thickness = 1.4 mm. Photoinitiating systems: (curve a) TX-
 446 2CBZ/Iod (0.07/1.9 w/wt%), (curve b) TX-2DPA/Iod (0.22/2.0 w/wt%), (curve c) TX-
 447 2PTZ/Iod (0.18/2.0 w/wt%) and (curve d) ITX/Iod (0.19/2.0 w/wt%)

448

3.3.2. Cationic polymerisation in EPOX

449 Thioxanthone derivatives were also investigated as photosensitizers with an iodonium salt (Iod)
 450 for the cationic polymerisation of EPOX upon LED irradiation at 405 nm to produce either 25
 451 µm thick or 1.4 mm thick samples under air. For the sake of comparison, polymerisation was
 452 also performed with the standard system ITX/Iod. After the irradiation of the system
 453 thioxanthone derivative/Iod, a reaction took place as described previously in reaction r3 and r4.
 454 An electron transfer reaction from the excited thioxanthone derivative to Iod occurs and lead to
 455 the formation of an aryl radical Ar[•] and a radical cation TX^{•+} which can initiate the cationic
 456 polymerisation³⁹. The polymerisation profiles of EPOX in presence of a photoinitiator/Iod
 457 system are presented in the Figure 11. Among the tested thioxanthone derivatives, only ITX
 458 allows to obtain a polymer with a tack-free surface. For the polymerisation of 25 µm thick
 459 sample (Figure 11A), the different systems show an average to low efficiency with a fast kinetic
 460 for ITX and slower kinetics for the others compounds. The efficiency trend of thioxanthone
 461 derivative as photoinitiator respects the following order: ITX > TX-2DPA = TX-2PTZ > TX-
 462 2CBZ. The final epoxide function conversions are 59%, 51%, 53% and 22% respectively. The
 463 same polymerisation efficiency and kinetics are observed for 1.4 mm thick samples (Figure
 464 11B). However, the efficiency trend of thioxanthone derivative as photoinitiator respects the
 465 following order: ITX > TX-2CBZ = TX-2DPA > TX-2PTZ. The final epoxide function
 466 conversions are 51%, 35%, 34% and 22% respectively. The low performance of the new
 467 thioxanthone systems could be attributed to the low reactivity of the radical cation toward the
 468 monomer.

469 Unfortunately, among the investigated thioxanthone derivatives for the cationic polymerisation
 470 of EPOX, no photoinitiator appears as efficient as ITX. The introduction of amines such as
 471 EDB which possess labile hydrogens might improve the polymerisation efficiency by a free
 472 radical promoted polymerisation process i.e. the aminoalkyl radicals generated in r2 can be
 473 oxidized to generate additional cations^{6 40}. Another possibility to improve the epoxide function
 474 conversion is the synthesis of interpenetrated polymer networks.



475

476 Figure 11: Polymerisation profiles (epoxide function conversion vs irradiation time) of EPOX
 477 upon irradiation with a LED at 405 nm, irradiation starts at 10 s, 50 mW.cm⁻²; (A) sample
 478 thickness = 25 μm and (B) sample thickness = 1.4 mm. Photoinitiating systems: (curve a) TX-
 479 2CBZ/Iod (0.07/1.8 w/wt%), (curve b) TX-2DPA/Iod (0.22/1.9 w/wt%), (curve c) TX-
 480 2PTZ/Iod (0.17/2.0 w/wt%) and (curve d) ITX/Iod (0.19/2.0 w/wt%)

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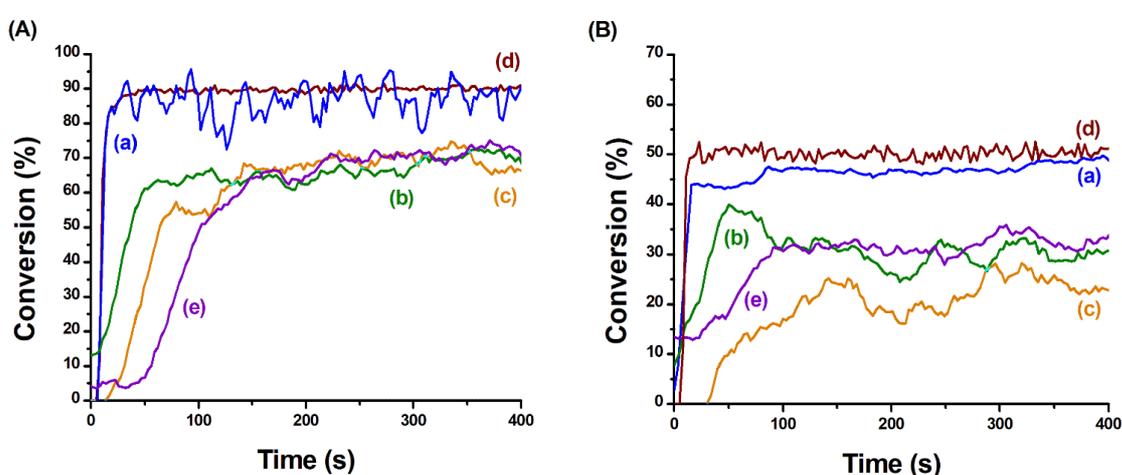
3.3.3. IPN synthesis: hybrid polymerisation in TMPTA/EPOX blend

482 Thioxanthone derivatives were investigated as photoinitiators with an iodonium salt (Iod) and
 483 an amine (EDB) for the polymerisation of a TMPTA/EPOX blend (50/50 w/wt%) upon LED
 484 irradiation at 405 nm to produce 1.4 mm thick samples under air (Figure 12). This three-
 485 component system initiates concomitantly the free radical and the cationic polymerisation to
 486 obtain two chemically different interlaced polymer networks which are not covalently bonded.
 487 For the sake of comparison and to assess the thioxanthone derivative benefits, polymerisation
 488 was also performed with two standard systems i.e. ITX/Iod/EDB and Iod/EDB. Indeed, upon
 489 irradiation, iodonium salt Iod and amine EDB could form a charge transfer complex (CTC)
 490 which might initiate the polymerisation^{41 42}. The different systems show a high efficiency
 491 toward the free radical polymerisation and an average efficiency toward the cationic
 492 polymerisation. Among the tested three-component systems, only those with ITX or TX-2CBZ
 493 allow to obtain a polymer with a tack-free surface. The efficiency trend of thioxanthone
 494 derivatives in a three-component system respects the following order for both radical and
 495 cationic polymerisation: ITX ≈ TX-2CBZ > CTC Iod/EDB = TX-2DPA = TX-2PTZ. The final
 496 C=C double bond conversions are 90%, 87%, 72%, 72% and 72% respectively. The final
 497 epoxide function conversions are 51%, 48%, 33%, 32% and 22% respectively. In terms of
 498 kinetic, all thioxanthone derivatives induce an increase in the polymerisation speed compared
 499 to the control sample containing only Iod and EDB. However, a stronger effect is obtained with
 500 ITX and TX-2CBZ for both radical and cationic polymerisations.

501 The synthesis of interpenetrated polymer networks using a TMPTA/EPOX blend reveals a
 502 performance increase for all the investigated systems compared to those used in the free radical
 503 polymerisation of TMPTA. In comparison with the two-component systems investigated for
 504 the cationic polymerisation of EPOX, only the three-component system, for IPN synthesis,
 505 based on TX-2CBZ shows a significant performance increase in both final epoxide function
 506 conversion and kinetics. All these improvements can be related to the use of a three-component
 507 initiating system. They could also be linked to the synergy between the free radical
 508 polymerisation and cationic polymerisation during the IPN synthesis. Indeed, under irradiation,

509 while the radical polymerisation process is at first inhibited by the oxygen in the medium, the
510 cationic polymerisation immediately begins which increases the medium viscosity limiting the
511 diffusional oxygen replenishment. The cationic monomer also acts as a diluting agent for the
512 radical polymer network allowing to achieve a higher conversion. Moreover, the exothermicity
513 of the radical polymerisation process tends to boost the cationic polymerisation which is
514 temperature sensitive.

515 Among the investigated thioxanthone derivatives used for the synthesis of interpenetrated
516 polymer networks in TMPTA/EPOX blend, TX-2CBZ appears as an interesting photoinitiator
517 which exhibits similar performances than ITX but for a lower content due to its better light
518 absorption properties. However, depending on the application in which the polymer is used,
519 other parameters than the photoinitiating system efficiency and kinetics need to be considered
520 such as the polymer colour.



521
522 Figure 12: Polymerisation profiles (A) (acrylate function conversion vs irradiation time) and
523 (B) (epoxide function conversion vs irradiation time) of TMPTA/EPOX blend (50/50 w/wt%)
524 upon irradiation with a LED at 405 nm, sample thickness = 1.4 mm, irradiation starts at 10 s,
525 50 mW.cm⁻². Photoinitiating systems: (curve a) TX-2CBZ/Iod/EDB (0.07/2.0/2.0 w/w/wt%),
526 (curve b) TX-2DPA/Iod/EDB (0.23/2.0/2.0 w/w/wt%), (curve c) TX-2PTZ/Iod/EDB
527 (0.16/2.0/2.0 w/w/wt%), (curve d) ITX/Iod/EDB (0.18/1.9/1.9 w/w/wt%) and (curve e)
528 Iod/EDB (2.0/2.0 w/wt%)

529 530 3.4. Valorisation of the photoinitiating systems containing TX-2CBZ

531 To determine to what extent TX-2CBZ could be used in an application as photoinitiator, three
532 current concerns were looked upon: the polymer final colour, the photoinitiator migration after
533 polymerisation and its use in photosensitive resin for laser writing.

534 3.4.1. Polymer colorimetric analysis

535 To determine to what extent TX-2CBZ could be an alternative to ITX, a colorimetric analysis
536 of the polymerised 1.4 mm thick samples was performed. The results are presented in Table 2
537 as CIE L* a* b* parameters. The CIE L* a* b* is a uniform colour space where each colour is
538 represented by three coordinates. L* characterises the brightness with black and white

539 corresponding to value 0 and 100 respectively. a^* indicates the red/green coordinate with
 540 positive value for red and negative for green. b^* indicates the yellow/blue coordinate with
 541 positive value for yellow and negative for blue. Considering the samples prepared with ITX
 542 initiating systems as standard, the colour variation generated by the change of photoinitiator
 543 could be assessed by a simple subtraction. While using TX-2CBZ in a concentration to have
 544 the same optical density at 405 nm before polymerisation as the standard, no significant colour
 545 variation has been detected. Since TX-2CBZ possesses higher molar extinction coefficients in
 546 the visible range, the concentration of TX-2CBZ to achieve the same final colour of the polymer
 547 is lower which is an advantage for the synthesis of colourless polymers while potentially
 548 lowering the safety issue (photoinitiator release).

549

550 Table 2: L^* a^* b^* parameters of 1.4 mm thick polymer samples obtained thanks to ITX or TX-
 551 2CBZ initiating systems

Initiating system and Monomer	L^*	a^*	b^*
TX-2CBZ / Iod in TMPTA	52	0	2
TX-2CBZ / EDB in TMPTA	54	0	4
TX-2CBZ / Iod in EPOX	59	0	4
TX-2CBZ / Iod / EDB in TMPTA/EPOX	74	-1	8
ITX / Iod in TMPTA	49	0	2
ITX / EDB in TMPTA	54	-2	6
ITX / Iod in EPOX	57	0	4
ITX / Iod / EDB in TMPTA/EPOX	62	-2	8

552

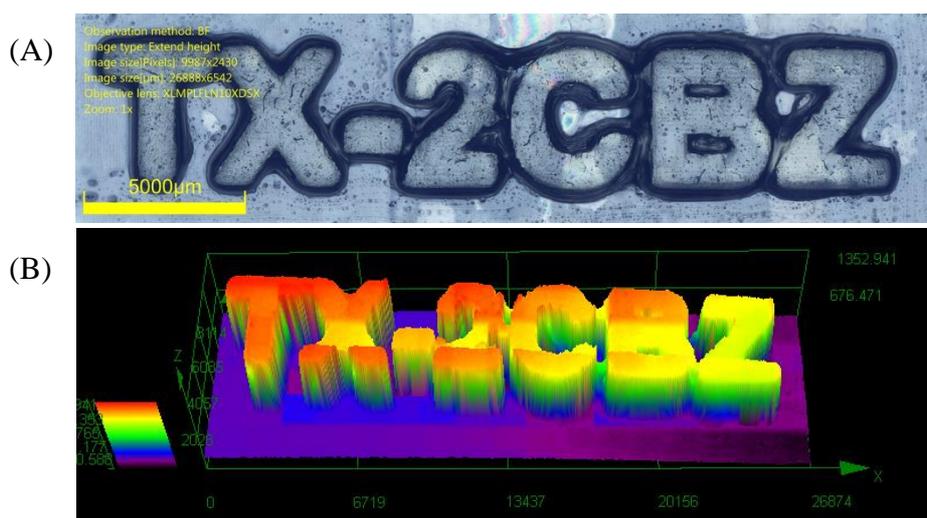
553 **3.4.2. Photoinitiator migration**

554 The migration of the photoinitiator after polymerisation is an important topic when selecting a
 555 photoinitiator. Indeed, the potential release of photoinitiator may affect the end-use of the
 556 polymeric material due to safety issue, in particular for applications related to graphic arts,
 557 medicine or food. To assess the migration of the photoinitiator, for either TX-2CBZ or ITX, an
 558 experiment with 1.4 mm thick IPN samples was performed. The polymers were synthesised
 559 from a TMPTA-EPOX blend with a three-component photoinitiating system containing either
 560 TX-2CBZ or ITX. After an immersion of the sample in acetonitrile for 1h35, the photoinitiator
 561 content in the liquid medium was measured by UV-visible absorption spectroscopy and
 562 compared with the theoretical amount in the sample. No migration of TX-2CBZ was detected
 563 while around 7% of ITX (molar percentage) could be extracted. Due to the higher molecular

564 weight of TX-2CBZ compared to that of ITX (542.65 vs. 254.30 $\text{g}\cdot\text{mol}^{-1}$), these results could
565 be expected. Indeed, higher molar mass tends to limit the diffusion phenomenon in the
566 polymeric material and consequently the migration. Thus, TX-2CBZ, with a similar efficiency
567 as ITX and a lower migration, is an interested photoinitiator and a potential alternative to ITX.

568 3.4.3. Photosensitive resin for laser writing experiments

569 Laser writing experiment for IPN synthesis using the three-component photoinitiator system,
570 TX-2CBZ/Iod/EDB, in a TMPTA/EPOX blend was performed under air. The sample
571 successfully obtained was analysed by numerical optical microscopy, the 2D and 3D images of
572 the sample are presented in Figure 13. The three-dimensional pattern (TX-2CBZ) was
573 characterized through a profilometric observation to assess the sample thickness H and the
574 spatial resolution r . As expected, efficient photopolymerisation processes occurred in the
575 irradiated area and did not spread out which highlight a good spatial control of the processes.
576 Optical microscopy revealed that the printed sample has a controlled thickness of 1 mm (H)
577 and a spatial resolution of around 70 μm (r) which is slightly higher than the size of the laser
578 beam ($50\mu\text{m}$). A shrinkage study of the 3D printed sample using Archimede's principle showed
579 a low shrinkage percentage of 1.7% .



580

581 Figure 13 Optical microscopy of the three-dimensional pattern obtained from TX-
582 2CBZ/Iod/EDB (0.07/2.0/2.0 w/w/wt%) in a TMPTA/EPOX blend (50/50 w/wt%) (A) 2D
583 panorama, (B) 3D panorama

584 **4. Conclusion**

585 In the present paper, thioxanthone derivatives are studied in details as potential photoinitiators.
586 The reactivity and efficiency of thioxanthone derivatives have been compared with 2-
587 isopropylthioxanthone (ITX) for the free radical polymerisation of TMPTA and the cationic
588 polymerisation of EPOX to produce 25 μm and 1.4 mm thick samples upon LED irradiation at
589 405 nm. Similarly, their efficiency toward IPN synthesis were evaluated. The reported data
590 reveal an interesting photoinitiator, 2,7-Dicarbazole-9H-thioxanthen-9-one (TX-2CBZ), which
591 tends to have similar or slightly lower performances than the standard photoinitiator (ITX) but
592 with the advantage of a lower content due to better light absorption properties. The chemical
593 mechanisms were characterised thanks to absorption spectroscopy, fluorescence spectroscopy,
594 laser flash photolysis and molecular modelling. Interestingly, TX-2CBZ presents an extended
595 singlet state S_1 lifetime compared to thioxanthone which may explain why TX-2CBZ excited
596 state S_1 is the main photoactivated species involved in the photoinitiating systems. TX-2DPA
597 and TX-2PTZ were not highly reactive and their excited states S_1 and T_1 cannot be detected
598 and therefore their S_1 deexcitation are probably governed by internal conversion. The use of a
599 photosensitive resin containing TX-2CBZ for laser writing has been efficiently tested with low
600 shrinkage. TX-2CBZ, with a similar performance for initiating polymerisation as ITX and a
601 lower migration, is an interested photoinitiator. Further work needs to be done to establish
602 whether this photoinitiator is an alternative to ITX in particular in terms of cytotoxicity of the
603 photoinitiating system and the cost of production at an industrial scale.

604

605 **Acknowledgement**

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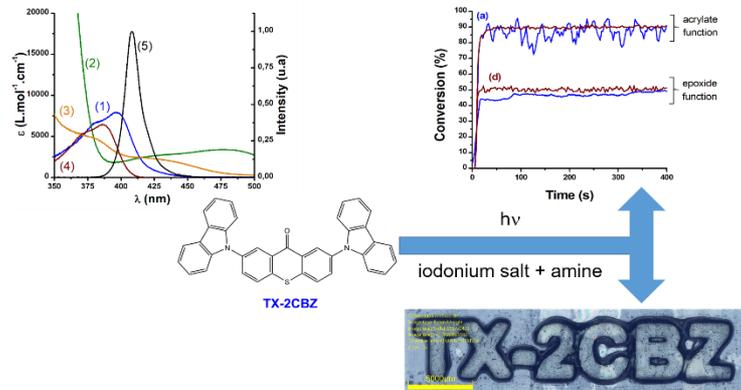
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