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Study on the photoinitiation mechanism of carbazole-based oxime esters (OXEs) as novel photoinitiators for free radical photopolymerization under near UV/visible-light irradiation exposure and the application of 3D printing

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1 **Study on the photoinitiation mechanism of carbazole-based oxime**
2 **esters (OXEs) as novel photoinitiators for free radical**
3 **photopolymerization under near UV/visible-light irradiation**
4 **exposure and the application of 3D printing**

5
6 **Ji Feng**^{a,b}, **Yijun Zhang**^{a,b}, **Di Zhu**^c, **Fabrice Morlet-Savary**^{a,b}, **Michael Schmitt**
7 **^{a,b}, Bernadette Graff**^{a,b}, **Pu Xiao**^{c*}, **Frédéric Dumur**^{d*} and **Jacques Lalevée**^{a,b*}

8 ^a Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France.

9 ^b Université de Strasbourg, France.

10 ^c Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia.

11 ^d Aix Marseille Univ, CNRS, ICR, UMR 7273, F-13397 Marseille, France.

12
13
14 **Abstract:**

15 In this work, twenty-two oxime esters bearing different functional groups and
16 based on carbazole as the chromophore were designed and synthesized as Type I
17 photoinitiators. Interestingly, all structures mentioned in this work have never been
18 reported before (even for their synthesis). These oxime esters were found to have good
19 light absorption properties in the UV-visible range, and especially at 405 nm which is
20 a reference wavelength in photopolymerization. Noticeably, several structures showed
21 better photoinitiation abilities than the benchmark photoinitiator i.e. diphenyl(2,4,6-
22 trimethylbenzoyl)phosphine oxide (TPO), evidencing the interest of these structures. In
23 order to investigate the photoinitiation mechanism of the two series of oxime esters
24 differing by the position of the photocleavable groups, electronic absorption spectra
25 were determined by molecular modeling and density functional theory calculations.
26 Photopolymerization abilities of the different oxime esters and release of CO₂ during
27 the polymerization experiments were determined by Real-Time Fourier Transformed
28 Infrared (RT-FTIR). Active free radicals were characterized by mean of Electron Spin
29 Resonance Spin Trapping (ESR-ST) experiments. On the basis of these different

30 complementary experiments, chemical mechanisms occurring during
31 photopolymerization could be proposed. Experimental results showed that the
32 decarboxylation reaction occurring subsequent to the photocleavage of oxime esters
33 had a beneficial effect on the photoinitiation ability. Finally, 3D printed objects were
34 successfully obtained by using oxime esters exhibiting the best photoinitiating abilities.
35 **Keywords:** Type I photoinitiators; Oxime esters; Photochemical mechanisms; 3D
36 printing; carbazole.

37

38 **1. Introduction:**

39 The development of green and sustainable chemistry processes constitutes the
40 main research directions of future chemistry. Contrarily to the traditional thermal
41 polymerization that is mostly performed in organic solvents ^[1], photopolymerization
42 can be carried out in solvent-free conditions so that emission of volatile organic
43 compounds (VOCs) can be considerably reduced.^[2] From this viewpoint,
44 photopolymerization constitutes a greener and more environmentally friendly
45 polymerization technique than the traditional thermal polymerization ^[3]. Thanks to the
46 abovementioned advantages, photopolymerization has been used in applications such
47 as coatings ^[4], biomedical materials ^[5], food packaging ^[6], 3D printing ^[7-10] and many
48 other research fields, supported by the numerous advantages of photopolymerization
49 such as high efficiency ^[11], energy saving and environmentally friendly conditions ^[12].
50 Nowadays, visible light polymerization is more extensively studied than UV
51 photopolymerization ^[13], visible light photopolymerization offering the possibility to
52 use light sources that are safer for the manipulator than UV light sources ^[14]. As
53 drawback, visible photons are less energetic than UV photons so that visible light
54 polymerization is currently lacking efficient photoinitiators.

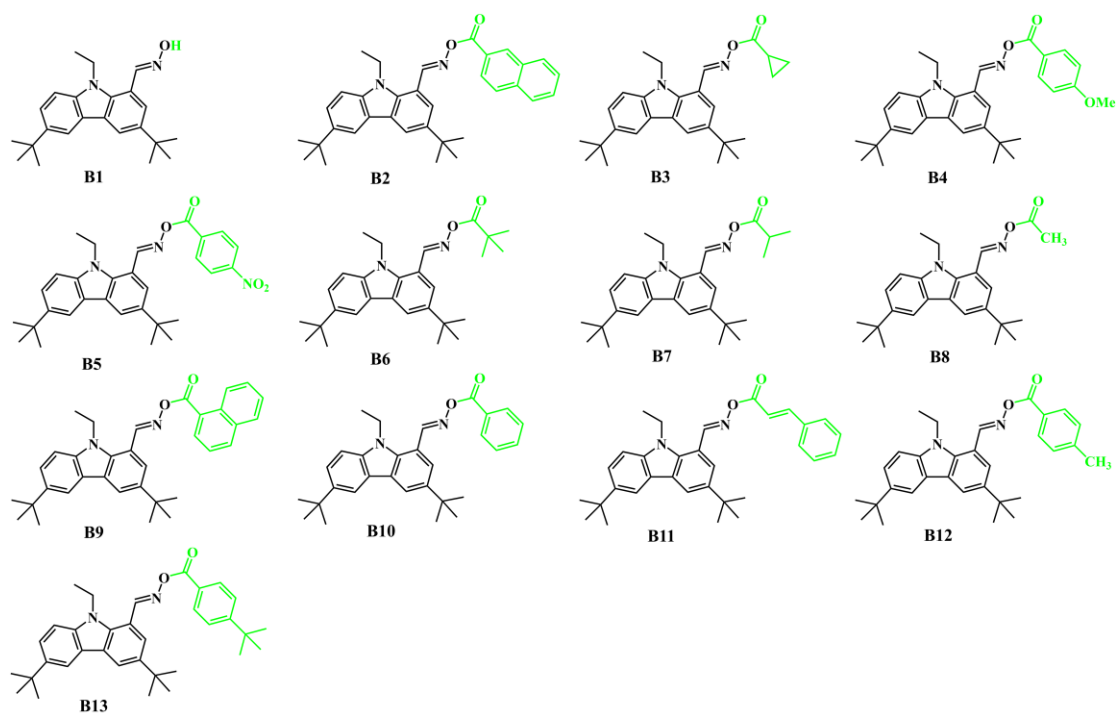
55 In photopolymerization, photoinitiator (PIs) is the key element as it can produce
56 radicals or ions by interacting with light ^[2, 15, 16]. Compared to Type II PIs which can
57 only produce initiating species by mean of a multi-step initiation process involving a
58 bimolecular interaction of the photoinitiator with a co-initiator ^[16], Type I PIs can

59 generate active free radicals without any additives, by homolytic cleavage of a selected
60 chemical bond ^[17]. Considering that the homolytic cleavage is the result of an
61 intramolecular reaction and not from a diffusion-controlled bimolecular interaction
62 which is typically observed with Type II photoinitiators, efficiency of the initiation step
63 is thus less dependent of parameters such as the concentration of the additives/oxygen
64 or the viscosity of the monomers ^[1]. Among all Type I photoinitiators reported in the
65 literature, oxime esters (OXEs) can initiate a polymerization by homolytic cleavage of
66 the N-O bond. Subsequent to the formation of iminyl and acyloxy/aryloxy radicals, a
67 decarboxylation reaction of the acyloxy/aryloxy radicals can occur ^[18], producing
68 active free radicals ^[19] The decarboxylation step is an important step for oxime esters
69 ^[18, 20, 21]. Indeed, by converting acyloxy/aryloxy radicals as alkyl/aryl radicals, no
70 radical recombination with iminyl radicals can occur, additionally the generated carbon
71 centered radicals are more reactive towards monomers. Parallel to this, release of CO₂
72 within the resin contribute to impede oxygen diffusion, enabling to address the oxygen
73 inhibition issue and to improve the monomer conversion. Over the years, various
74 chromophores have been investigated, as exemplified with triphenylamines ^[22], pyrenes,
75 anthracenes ^[23], naphthalenes ^[24], chalcones ^[25], coumarins ^[19], phenothiazines ^[26],
76 fluorophenyls ^[27] and other chromophores. In 2020, Ding and his group ^[27] designed
77 and synthesized OXEs based on the fluorophenyl scaffold and successfully initiated the
78 photopolymerization of tripropylene glycol diacrylate under the irradiation of
79 LED@395 nm with good conversion rates. However, absorptions of these OXEs
80 remained strongly UV-centered. Concerning benchmark OXEs, numerous structures
81 can furnish high monomer conversions. As drawback, their absorptions are centered in
82 the UV range, as exemplified with *O*-benzoyl- α -oxoimine and *O*-acetyloxime for
83 which absorption maxima located at 314 and 335 nm can be respectively determined
84 ^[28]. If high monomer conversions could be obtained with these structures, high-
85 intensity ultraviolet light sources had to be used,^[29] constituting a severe limitation
86 especially in the present context of energy sobriety that is imposed by numerous
87 countries. Alternatives to these high-intensity ultraviolet light sources are thus

88 researched ^[17, 30], and in this field, light emitting diodes (LEDs) have the advantages of
89 being light sources of low cost, exhibiting long operating lifetimes, compactness,
90 robustness and easy availability ^[1, 31]. At present, these relatively cheap devices are
91 more and more used by researchers and now replace the traditional mercury lamps that
92 will be not allowed to be fabricated, imported and exported by the treaty established
93 during the Minamata Convention on Mercury in 2013 ^[32, 33]. However, considering that
94 the absorption spectra (*O*-benzoyl- α -oxoimine OXE 01, $\lambda_{\text{max}} = 326$ nm, *O*-acetyloxime
95 OXE 02, $\lambda_{\text{max}} = 338$ nm) ^[18] of commercial OXEs do not match the emission spectrum
96 of near-UV-visible LEDs (between 365 and 425 nm) ^[28, 33], a great deal of effort remains
97 to be done in order to design the next generation OXEs that can be activated in the near
98 UV/visible range. Therefore, it is very meaningful to design and synthesize new OXEs,
99 and to investigate their photoinitiating abilities at long absorption wavelengths ^[34]. If
100 the absorption properties of photoinitiators is a key parameter governing their
101 reactivities, their solubilities in resins is also important in order the photoinitiator to
102 efficient interact with additives (in the case of Type II photoinitiators), or directly with
103 the monomer (in the case of Type I photoinitiators). With aim at improving the
104 solubility in resins, two distinct strategies can be used. The first one consists in
105 introducing solubilizing chains (generally long alkyl chains) and the second one to
106 introduce functional groups capable to drastically reduce π - π interactions and therefore
107 aggregation. In this field, *tert*-butyl groups, by their tridimensional structures, can
108 easily address the aggregation issue and this strategy is commonly used in Organic
109 Electronics for the design of solution-processed devices or for the design of fluorescent
110 probes. This strategy can also be used in photopolymerization and the two families
111 proposed in this work aim at designing photoinitiators that can be facilely dissolved in
112 resins. This strategy is pertinent, especially, if polyaromatic structures are designed, as
113 done in this work. Noticeably, for the design of the two series of dyes, *N*-ethylcarbazole
114 with its short ethyl chain was selected as the appropriate starting material used for the
115 design of two series of photoinitiators bearing one or two *tert*-butyl groups.

116 In this work, a series of twenty-two OXEs bearing different substituents were

117 successfully synthesized and characterized. Chemical structures of the different OXEs
118 are presented in Figures 1 and 2. Based on carbazole as the chromophore, these OXEs
119 were categorized into two series (B series and C series), differing by the number of *tert*-
120 butyl groups and the position of the photocleavable group. By combining molecular
121 orbital calculation, time dependent density functional theory, free radical
122 photopolymerization (FRP), UV-visible absorption and fluorescence spectroscopy,
123 steady-state photolysis, fluorescence excited state lifetime and electron spin resonance
124 spin trapping (ESR-ST) experiments, photoinitiation abilities of the different OXEs and
125 the mechanisms of polymerization could be established. Finally, as an application, 3D
126 printing experiments were carried out using the best investigated photoinitiator.



127
128

Figure 1. Chemical structures of OXEs B1-B13 (B series).

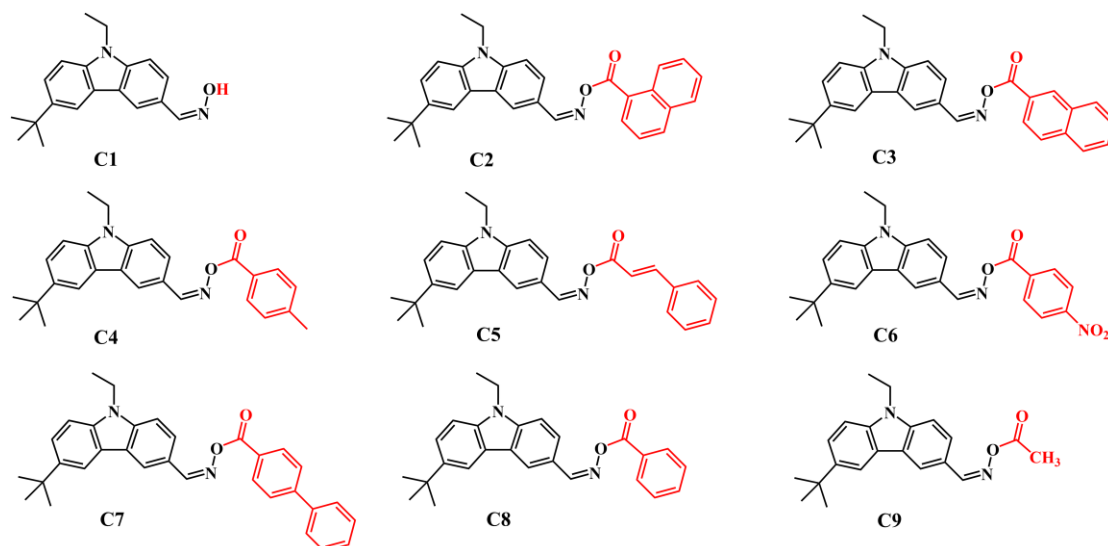


Figure 2. Chemical structures of OXEs C1-C9 (C series).

2. Experimental Section

2.1 Materials

The different OXEs used for photopolymerization have been synthesized by our group (see below part 3.1 and in supporting information). The benchmark monomer i.e. trimethylolpropane triacrylate (TMPTA) used for photopolymerization was purchased from Sartomer (France). The benchmark photoinitiator diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) used for comparison was purchased from Lambson Ltd. (United Kingdom). The colloidal silica suspension (LUDOX-AS-30, 30 wt% suspension in H₂O) was obtained from Sigma-Aldrich. The free radical trapping agent phenyl-*N-tert*-butyl nitron (PBN) used for ESR experiments was obtained from TCI-Europe (France).

2.2 Sample preparation

OXEs and TMPTA were successfully added into a small glass bottle with a stopper and the resulting resin was stirred with a magnetic rotor until the PIs was completely dissolved in the monomer. It was stored in a dark environment before photopolymerization. Here, the weight percentage of OXEs was kept at 0.5 %phr relative to TMPTA. All thin samples were dropped in laminate between two polypropylene films with one drop of resin deposited (See Figure S1(a)). All thick samples were dropped into a circular top with grooves with five drops deposited (See

151 Figure S1(b)).

152 **2.3 Light Absorption Spectrum and Steady-state Photolysis**

153 UV–visible absorption spectra of the different OXEs were measured with a
154 JASCO V730 spectrometer in 5×10^{-5} M solutions in acetonitrile. Steady-state
155 photolysis experiments were carried out by using the same spectrometer. Measurements
156 were performed in acetonitrile under the irradiation of a LED@405 nm (light intensity:
157 110 mW/cm^2). The concentrations of the different OXEs were 5×10^{-5} M.

158 **2.4 Fluorescence Spectrum and Fluorescence Lifetime**

159 Fluorescence spectra of the different OXEs (5×10^{-5} M in acetonitrile) were
160 obtained with a spectrofluorometer JASCO FP-750. When the wavelength of excitation
161 was 367 nm and the impulse width was less than 1.4 ns, the lifetime of fluorescence
162 excited-state of PIs was measured by a detector (Instrument model HORIBA PPD-850).
163 The impulse response function (IRF) of the instrument was calculated through the
164 colloidal silicon dioxide suspension LUDOX.

165 **2.5 Photopolymerization Profiles Obtained by RT-FTIR**

166 Photopolymerization kinetics associated to OXEs were studied by RT-FTIR
167 spectroscopy (JASCO FTIR-4700). The resins were added to a plastic mold (Figure S1)
168 and between two polypropylene films for thick (1.4 mm) and thin (25 microns) samples,
169 respectively. The characteristic peak of the acrylate functional group was continuously
170 detected at about 6150 cm^{-1} (thick samples) and 1650 cm^{-1} (thin samples) by RT-FTIR.
171 The photopolymerization profiles were obtained by the equation:

$$172 \quad \text{Conversion (\%)} = \frac{A_0 - A_t}{A_0} \times 100\%$$

173 Where A_0 is the peak area of the acrylate functional group at 0 s and A_t is the peak
174 area of the acrylate functional group at t s.

175 **2.6 ESR-ST experiments**

176 In order to study the free radicals produced during the photopolymerization
177 process, the ESR-ST was carried out by an X- band spectrometer (Bruker EMXplus).
178 Free radicals were trapped by PBN and observed in a nitrogen atmosphere in *tert*-
179 butylbenzene. The concentration of OXEs was 1×10^{-4} M. All operations were

180 performed at room temperature. In addition, the ESR-ST spectra were simulated by the
181 PEST WINSIM program.

182 **2.7 Computational Procedure**

183 For the molecular modelling data, the N–O bond dissociation energy (BDE) and
184 the triplet state energy (E_T) of OXEs were calculated with the density functional theory
185 (DFT) at the UB3LYP/6-31G* level.

186 **2.8 3D printing experiments**

187 The formulations for 3D printing experiments were 0.5% PIs in TMPTA. Then,
188 direct laser write (DLW) experiments were performed with a laser diode at 405 nm (110
189 mW), and the glass tank used for printing was homemade (about 2 mm thickness). The
190 printed pattern was observed by a digital camera.

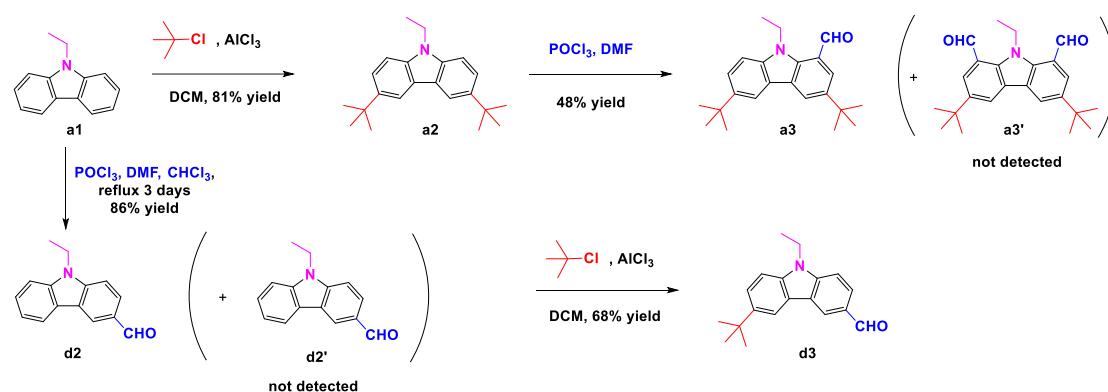
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192 **3. Results and Discussion**

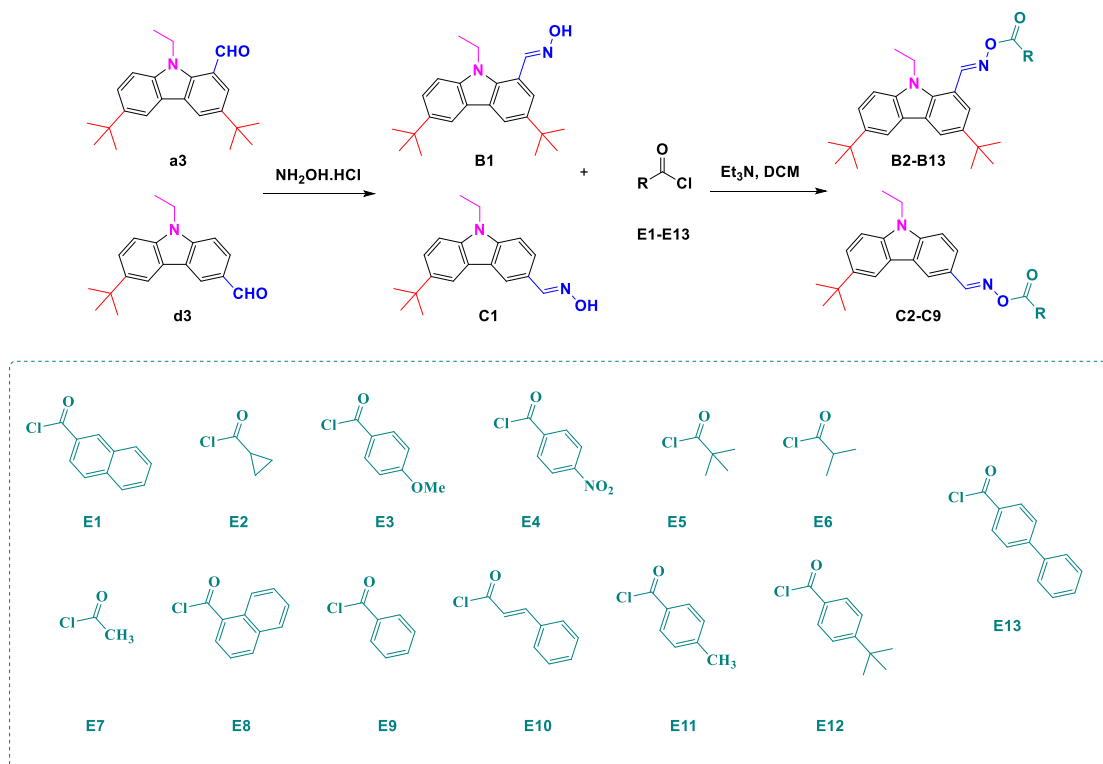
193 **3.1 Synthesis of the OXEs**

194 Syntheses of all OXEs are described in Scheme 1. First, 9-ethyl-9*H*-carbazole (a1)
195 and 3,6-di-*tert*-butyl-9-ethyl-9*H*-carbazole-1-carbaldehyde (a3) used as the starting
196 materials for the synthesis of oxime esters were prepared in two steps. By mean of a
197 Friedel-Craft reaction using 2-methylpropane and aluminum chloride, 3,6-di-*tert*-butyl-
198 9-ethyl-9*H*-carbazole (a2) could be prepared in 81% yield. Then, a2 was converted as
199 3,6-di-*tert*-butyl-9-ethyl-9*H*-carbazole-1-carbaldehyde (a3) by mean of a Vilsmeier-
200 Haack reaction in 48% yield. Interestingly, in the reaction conditions used, no side-
201 products formed and the di(formyl) derivative 3,6-di-*tert*-butyl-9-ethyl-9*H*-carbazole-
202 1,8-dicarbaldehyde (a3') was not detected as structure in the crude reaction mixture.
203 Concerning 6-(*tert*-butyl)-9-ethyl-9*H*-carbazole-3-carbaldehyde (d3), it could be
204 prepared in two steps, first by preparing the aldehyde (d2) that was subjected to a
205 Friedel-Craft reaction with 2-methylpropane, providing the targeted aldehyde (d3) in
206 68% yield (See Scheme 1). Here again, d2 could be obtained without formation of 9-
207 ethyl-9*H*-carbazole-3,6-dicarbaldehyde (d2'), the synthesis of this dialdehyde being
208 only possible in other reaction conditions.

209 Oximes B6 and B7 were prepared in one step using aldehydes a3 and d3, sodium
 210 acetate and hydroxylamine hydrochloride by using mixed solvents (H₂O, MeOH and
 211 THF). The two compounds B1 and C1 could be obtained in quantitative yields.
 212 Specifically, the different oximes B1 and C1 were esterified using the appropriate acid
 213 chloride derivatives E1-E13 and triethylamine as the base (See Scheme 1). All esters
 214 B2-B13 and C2-C9 could be obtained with reaction yields ranging between 66% for
 215 B11 up to 92% for C8 (See Table 1). Detailed synthetic procedures of all OXEs are
 216 given in the Supporting Information. It has to be noticed that all oxime esters reported
 217 in this work have never been previously reported in the literature, evidencing the
 218 interest of these structures. Among the starting aldehydes, even the synthesis of 6-(*tert*-
 219 butyl)-9-ethyl-9*H*-carbazole-3-carbaldehyde (d3) was not reported in the literature.
 220 Only 3,6-di-*tert*-butyl-9-ethyl-9*H*-carbazole-1-carbaldehyde (a3) was mentioned in a
 221 paper devoted to the design of position isomers of bicarbazoles.^[35]



222



223

224

Scheme 1. Synthetic route to the different OXEs B1-B13 and C1-C9.

225

226

Table 1. Reaction yields obtained during the synthesis of the different OXEs.

PIs	Reaction yields (%)	PIs	Reaction yields (%)
B1	quant.	C1	quant.
B2	82	C2	82
B3	71	C3	82
B4	87	C4	74
B5	75	C5	71
B6	77	C6	69
B7	86	C7	88
B8	84	C8	92
B9	74	C9	78
B10	68		
B11	66		
B12	88		
B13	88		

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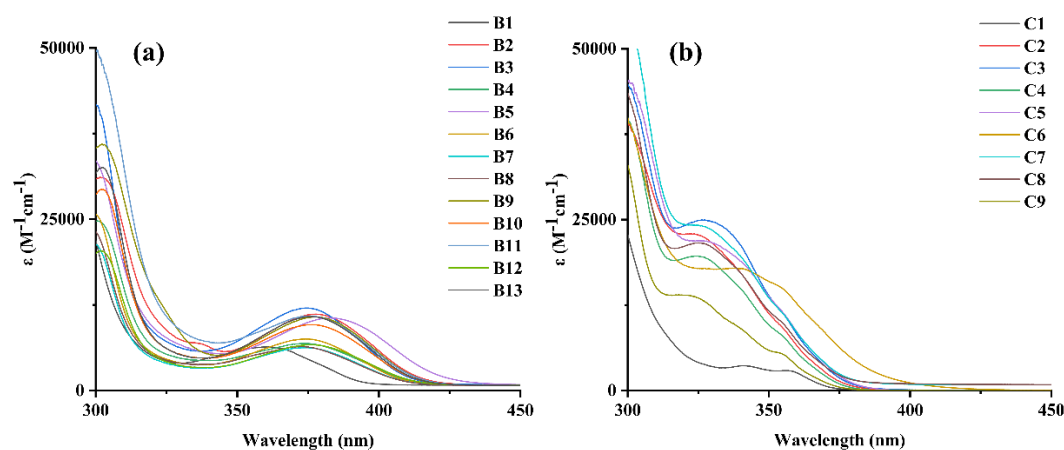
3.2 Light Absorption Properties

229

230

Due to the presence of the tert-butyl group in the two series of Type I photoinitiators, all dyes exhibited a good solution in acetonitrile. UV-visible absorption

231 spectra of the different OXEs were thus studied in acetonitrile as the solvent (See Figure
 232 3). Optical characteristics of OXEs are listed in Table 2. Interestingly, all OXEs have
 233 good solubilities in acetonitrile at room temperature and this remarkable solubility can
 234 be confidently assigned to the presence of tert-butyl groups adversely impacting π - π
 235 stacking interactions (See Figure S2). All OXEs displayed a broad absorption band
 236 extending up to 400-450 nm. The maximum absorption wavelengths (λ_{max}) of B7 and
 237 B8 in series B were 374 and 372 nm respectively. The molar extinction coefficients
 238 (ϵ_{max}) at the λ_{max} were 6260 and 6400 $\text{M}^{-1}\text{cm}^{-1}$, and the molar extinction coefficients
 239 ($\epsilon_{405\text{nm}}$) at λ_{405} were 1830 and 1780 $\text{M}^{-1}\text{cm}^{-1}$, respectively. Compared to compounds B1
 240 and C1 without OXE functional groups, the λ_{max} of OXEs of series B exhibited a red-
 241 shifted absorption, while the λ_{max} of OXEs of series C exhibited a blue-shift. To support
 242 the redshift detected with oxime esters of series B compared to the parent oxime B1, an
 243 electron-withdrawing effect generated by the oxime ester groups was suggested [36]. In
 244 the case of the series C, the substituent is introduced in a none-conjugated position with
 245 regards to the carbazole scaffold, supporting the hypsochromic shift detected for this
 246 series. The above results showed that all OXEs are sensitive to blue light and therefore
 247 are appropriate candidates for photopolymerization experiments done at 405 nm but
 248 more generally for near UV light.



249
 250 **Figure 3. UV-visible absorption spectra of OXEs. (a) OXEs of series B, (b) OXEs**
 251 **of series C in acetonitrile.**

252
 253 **Table 2 Light absorption characteristics of OXEs in acetonitrile**

PIs	ϵ_{max}	$\epsilon_{405\text{nm}}$	PIs	ϵ_{max}	$\epsilon_{405\text{nm}}$
-----	-------------------------	---------------------------	-----	-------------------------	---------------------------

	λ_{\max} (nm)	$(M^{-1}.cm^{-1})$		λ_{\max} (nm)	$(M^{-1}.cm^{-1})$		$(M^{-1}.cm^{-1})$
B1	360	6360	8502	C1	340	3590	60
B2	377	11130	4130	C2	323	22860	15
B3	374	12040	3140	C3	327	24950	60
B4	374	6860	2250	C4	325	19680	0
B5	382	10570	6240	C5	327	21880	0
B6	374	7520	2060	C6	338	17900	790
B7	374	6260	1830	C7	324	24160	890
B8	372	6400	1780	C8	325	21610	950
B9	377	10730	3880	C9	319	13980	0
B10	376	9600	3280				
B11	375	10880	3770				
B12	376	6660	2350				
B13	376	10780	3480				

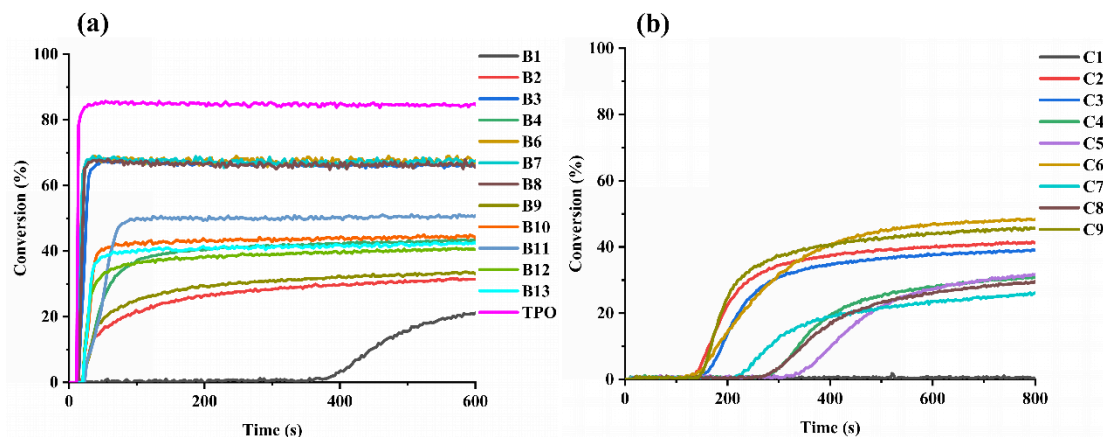
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255 **3.3 Free Radical Photopolymerization**

256 Photoinitiation abilities of the different OXEs and the commercial/benchmark PI
 257 TPO were examined using TMPTA as a trifunctional monomer. RT-FTIR was used as
 258 the appropriate technique to monitor the monomer conversions and thus to establish the
 259 photopolymerization profiles of thin and thick samples when exposed to a 405 nm LED.

260 Photopolymerization profiles of thick samples are presented in Figure 4, and the
 261 final functional acrylate conversions (FCs) of OXEs/TMPTA are listed in Table 3. As
 262 shown in Figure 4, photoinitiation abilities of OXEs of the B series were better than
 263 that of those C series. Among them, B3, B6, B7 and B8 exhibited the highest FCs (68-
 264 69%). The polymerization rates (R_p) are very similar to those of TPO (Figure 4). This
 265 is directly related to the fact that these OXEs comprise alkyl substituents on the oxime
 266 ester moiety, and especially methyl substituents. Indeed, after photocleavage, acetyl
 267 groups are prone to decarboxylation, generating methyl radicals that are well-reported
 268 to be highly reactive radicals^[37]. Photopolymerization profiles of thin samples are
 269 shown in Figure S3. As can be seen in this figure, the B series showed high conversion
 270 rates, some of which were similar to that of TPO (See Figure S3(a)). In the C series, the

271 photopolymerization could be initiated only for four samples, and the FCs of
 272 OXEs/TMPTA were below 55% (See Figure S3(b)).



273
 274 **Figure 4. Photopolymerization profiles of TMPTA in the presence of 0.5 phr**
 275 **OXEs for thick sample (about 1.4 mm) upon exposure to LED@405 nm**
 276 **irradiation. The irradiation starts at $t = 10$ s: (a) OXEs of series B; (b) OXEs of**
 277 **series C.**

278
 279

Table 3. FCs of TMPTA in the presence of OXEs

PIs	FCs (%)	PIs	FCs (%)
B1	21	C2	42
B2	32	C3	39
B3	68	C4	31
B4	44	C5	32
B6	69	C6	48
B7	69	C7	26
B8	68	C8	30
B9	34	C9	46
B10	45	TPO	84
B11	51		
B12	41		
B13	43		

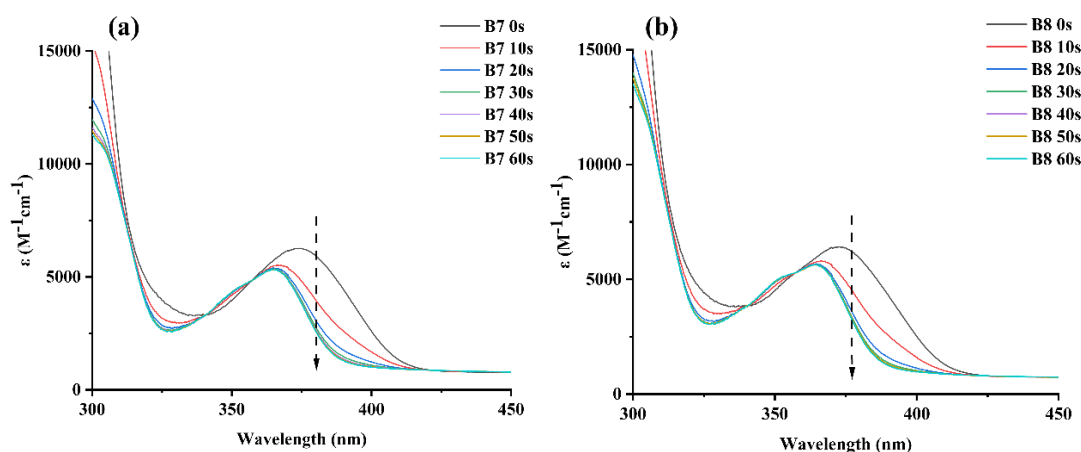
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3.4 Steady-State Photolysis

282 In order to investigate the chemical mechanism of OXEs in photopolymerization,
 283 OXEs were dissolved in acetonitrile and the resulting solutions were exposed to a
 284 LED@405 nm for steady-state photolysis measurements (See Figure 5). Steady-state
 285 photolysis profiles of OXEs are shown in Figures S4 and S5. For B7 and B8, as shown

286 in Figure 5, by increasing the irradiation time of LED@405 nm, the absorption intensity
287 of B7 at $\lambda_{\max} = 374$ nm and that of B8 at $\lambda_{\max} = 372$ nm decreased obviously, and these
288 two compounds were rapidly photolyzed during the first 10 s and photolysis weakens
289 after 60 s of irradiation. Modification of the absorption spectra can be confidently
290 assigned to the homolytic cleavage of the N-O bond in OXEs upon irradiation [5].
291 Conversely, in the case of oximes B1 and C1, (See Figure S4 and S5), after long-time
292 irradiation, absorption intensities at λ_{\max} did not decrease obviously, indicating that no
293 photocleavage occurred with these structures [36].

294 In order to obtain the singlet excited state energy (E_{S1}) of B7, fluorescence
295 emission spectra and UV-visible absorption spectra were recorded in acetonitrile, so
296 that the singlet excited state (E_{S1}) could be obtained from the intersection point between
297 the absorption and the emission spectra (See Figure 6). E_{S1} of the other OXEs are given
298 in Figures S6 and S7. As shown in Table 4, enthalpies of the N-O bond-breaking process
299 of all OXEs ($\Delta H_{\text{cleavage } S1} = \text{BDE (N-O)} - E_{S1}$ and $\Delta H_{\text{cleavage } T1} = \text{BDE (N-O)} - E_{T1}$) [36]
300 from E_{S1} or E_{T1} were calculated. In addition, except for B1 and C1, $\Delta H_{\text{cleavage } S1}$ for all
301 OXEs were negative, indicating that the cleavage of oxime esters can energetically
302 occur from the singlet excited state. Fluorescence lifetimes of OXEs were also
303 measured (See Figure 6 and Figures S8 and S9). Generally, OXEs with short excited
304 state lifetimes exhibited high initiation efficiencies, which is beneficial to the bond
305 breaking process. However, negative $\Delta H_{\text{cleavage } T1}$ values were also calculated so that
306 photocleavage from the triplet excited state can't be ruled out.



307

308

Figure 5. Steady-state photolysis of OXEs under LED@405 nm. (a) B7, (b) B8.

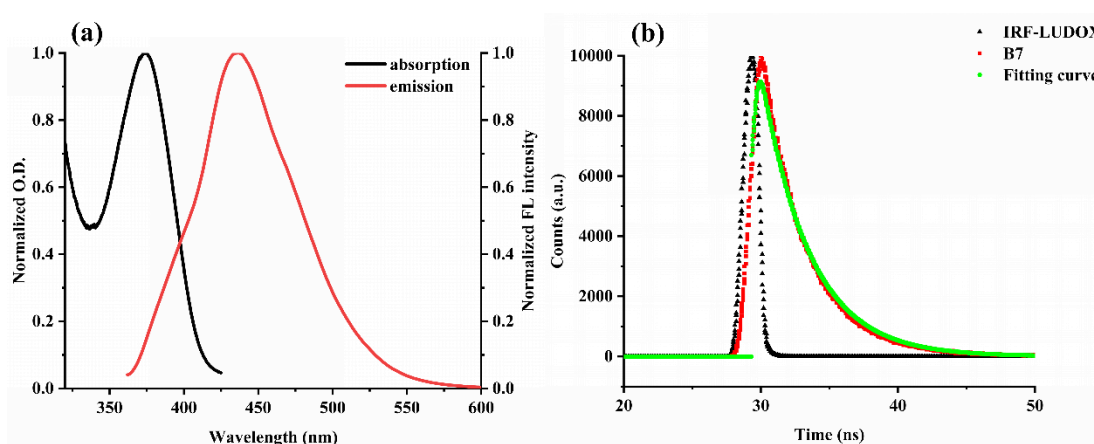
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Table 4. Reference parameters of the OXEs B and C series

PIs	N-O BDE	E_{S1}	$\Delta H_{\text{cleavage } S1}$	E_T	$\Delta H_{\text{cleavage } T1}$
B1	64.74	74.27	-9.53	52.15	12.59
B2	45.49	73.70	-28.21	59.75	-14.26
B3	47.68	72.94	-25.26	53.40	-5.72
B4	44.99	72.57	-27.58	48.72	-3.73
B5	47.62	72.03	-24.41	49.60	-1.98
B6	44.30	72.21	-27.91	48.45	-4.15
B7	47.92	72.03	-24.29	53.86	-5.94
B8	48.44	72.94	-24.50	53.19	-4.75
B9	42.31	72.94	-30.63	57.96	-15.65
B10	42.83	73.70	-30.87	52.42	-9.59
B11	47.75	72.76	-25.01	52.59	-4.84
B12	42.57	73.89	-31.32	52.37	-9.80
B13	42.67	73.89	-31.22	53.10	-10.43
C1	64.55	78.99	-14.44	50.52	14.03
C2	46.54	80.10	-33.56	57.16	-10.62
C3	47.82	78.34	-30.52	59.83	-12.01
C4	47.92	78.99	-31.07	53.15	-5.23
C5	48.90	79.21	-30.31	53.03	-4.13
C6	50.44	78.56	-28.12	58.27	-7.83
C7	48.11	79.43	-31.32	65.26	-17.15
C8	48.22	79.43	-31.21	53.26	-5.04
C9	48.72	80.10	-31.38	53.55	-4.83

311



312

Figure 6. (a) Fluorescence emission spectrum and UV- visible absorption spectrum of B7, (b) fluorescence decay curve of B7.

314

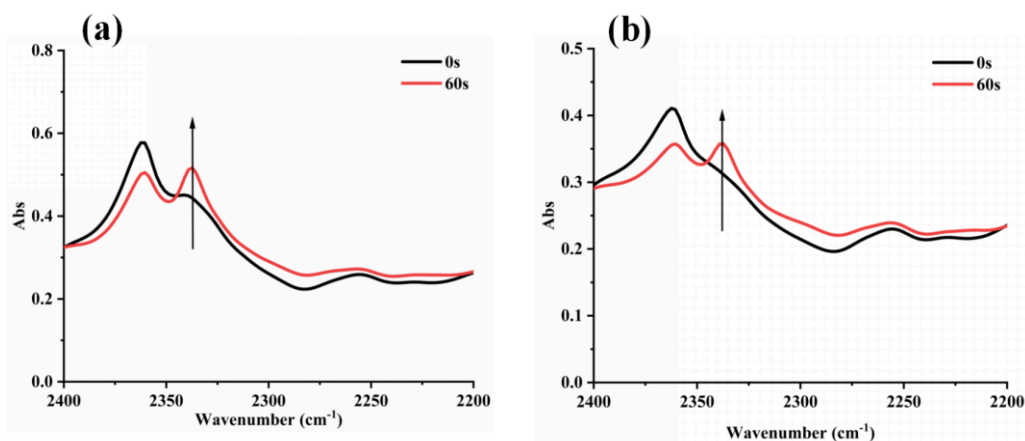
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3.5 Decarboxylation Reaction

317 Occurrence of a decarboxylation reaction (or not) was evidenced by monitoring
318 the production of CO₂ subsequent to the homolytic cleavage of the N-O bond by RT-
319 FTIR. From the Figures 7(a) and (b), in the B7 and B8 systems respectively, a new
320 characteristic peak can be detected at 2337 cm⁻¹ after 60 s of irradiation. For most of
321 the OXE/TMPTA systems, appearance of a new characteristic absorption peak at 2337
322 cm⁻¹ corresponding to CO₂ could be evidenced, but not for all OXEs/TMPTA systems,
323 as shown in Figures S10 and S11. These experimental phenomena can provide evidence
324 of a decarboxylation process. A direct link between polymerization efficiency and CO₂
325 release can be given i.e. efficient OXEs are associated with cleavage processes and
326 decarboxylation reactions.

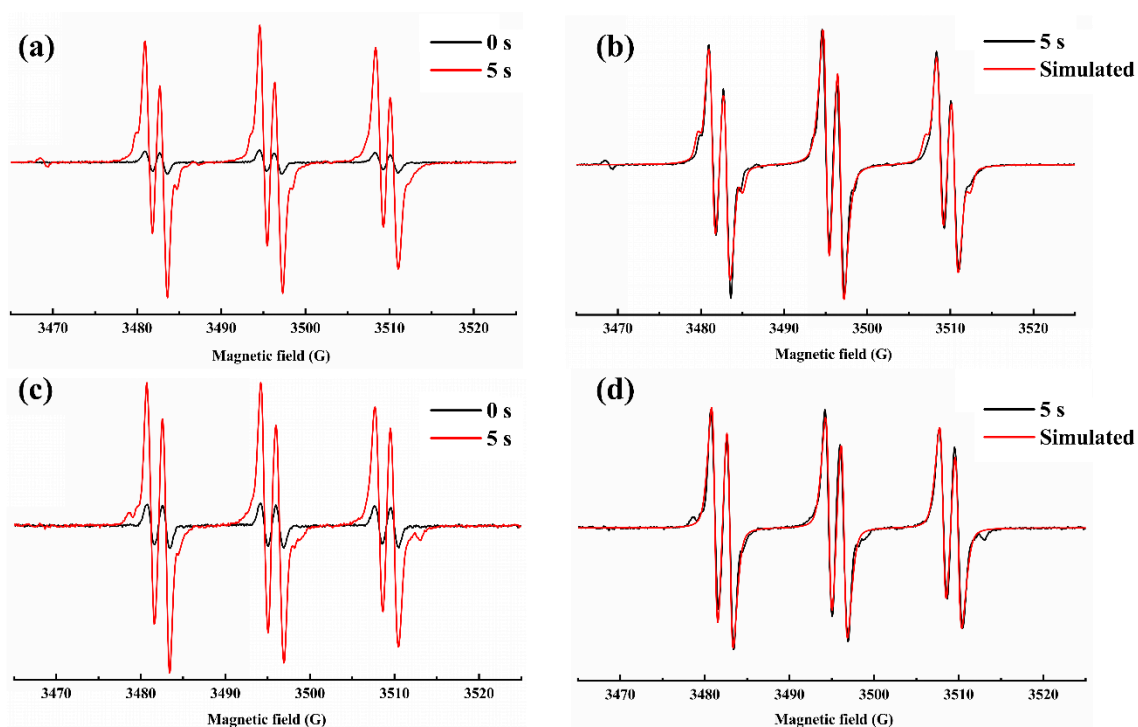
327 On the other hand, the enthalpy for decarboxylation reactions ($\Delta H_{\text{decarboxylation}}$) can
328 also provide evidence for decarboxylation^[37]. In our previous works, the enthalpy of
329 decarboxylation reaction of a series of acyloxyl radicals was reported by our group.
330 According to the previous research of our group^[37], when $\Delta H_{\text{decarboxylation}} < 0$
331 kcal.mol⁻¹, the decarboxylation process is easy to occur (and CO₂ is experimentally
332 observed in RT-FTIR experiments). It thus supports the fact that the decarboxylation of
333 the B8 /TMPTA system is favorable. When $\Delta H_{\text{decarboxylation}} > 0$ kcal.mol⁻¹, the
334 decarboxylation process is unfavorable, so that the formation of CO₂ could not be
335 detected in the RT-FTIR spectra of the B2/TMPTA, B11/TMPTA and B12/TMPTA
336 systems. Occurrence (or not) of a decarboxylation reaction of the acyloxy/aryloxy
337 radicals subsequent to their formations can thus be fully explained and anticipated by
338 theoretical calculations. At the same time, this increase in absorbance can be observed
339 for all systems that generate CO₂ (See Figures S10 and S11).



340
 341 **Figure 7. Infrared spectra of (a) B7/TMPTA and (b) B8/TMPTA at t = 0 and 60**
 342 **s.**

343 3.6 ESR-ST Experiments

344 By homolytic cleavage of oxime esters, active free radicals can be produced,
 345 which constitute the initiating species. To investigate the chemical structures of these
 346 radicals, ESR-ST experiments were carried out on two different systems, namely B7
 347 and B8 (See Figure 8). After irradiation at 405 nm for 5 s, two kinds of free radicals
 348 could be captured by the free radical scavenger PBN in B7 and B8 systems. For the B7
 349 system (See Figures 8a and 8b), the hyperfine coupling constants for one free radical
 350 (97.4%) were $\alpha_N = 13.7$ G and $\alpha_H = 1.7$ G. It may be assigned to the acetyloxy radical
 351 ($\text{CH}_3\text{COO}\cdot$)^[36]. Hyperfine coupling constants for another one free radical (2.6%) were
 352 determined as being $\alpha_N = 13.7$ G and $\alpha_H = 4.8$ G, it may be ethyl radical^[36]. In the B8
 353 system (See Figures 8c and 8d), only one free radical was detected (See Figure 8b) after
 354 5 s of irradiation. Its hyperfine coupling constants were $\alpha_N = 13.5$ G and $\alpha_H = 1.8$ G and
 355 it may be assigned to the acetyloxy radical ($\text{CH}_3\text{COO}\cdot$)^[36]. In addition, the
 356 experimental results obtained by ESR-ST evidenced the formation of acetoxy radicals.
 357 Cleavage of the N-O bond in these different systems is also proved.



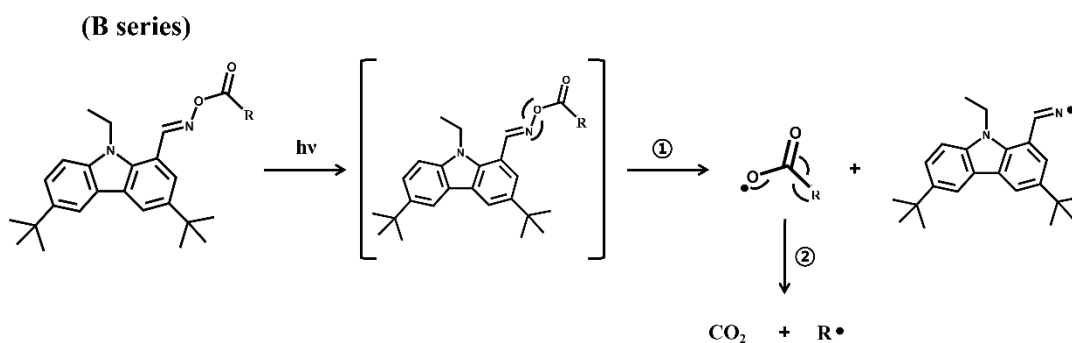
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359 **Figure 8. ESR-ST spectrum of the radical adducts (in tert-butylbenzene). (a) and**
 360 **(b) B7, (c) and (d) B8 under LED@405 nm irradiation.**

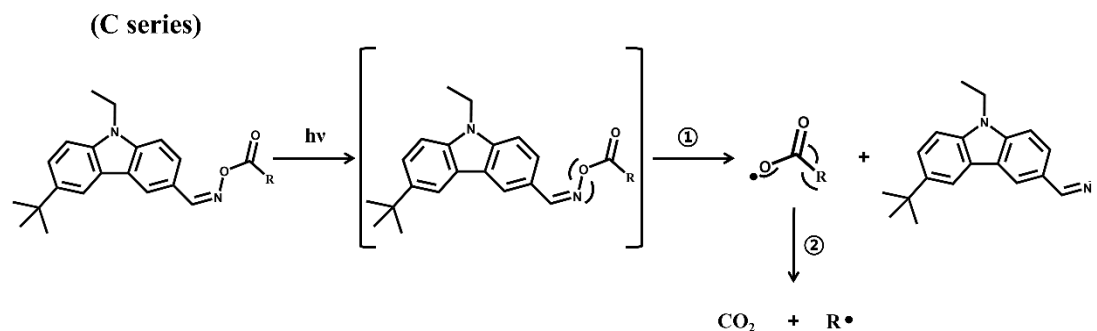
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362 3.7 Photoinitiation Step Mechanisms of OXEs

363 Through the above experimental results, the chemical mechanisms of
 364 photoinitiated polymerization can be proposed and the mechanism is summarized in
 365 Scheme 2. When OXEs were exposed to light, the chromophore was excited from the
 366 ground state to the excited state. The N-O bond of OXEs could cleave homolytically,
 367 producing acyloxy and iminyl radicals (reaction ①). Then, acyloxy radicals can
 368 decarboxylate, producing active radicals that can induce monomer polymerization.
 369 Parallel to this, CO₂ is released (reaction ②).



370

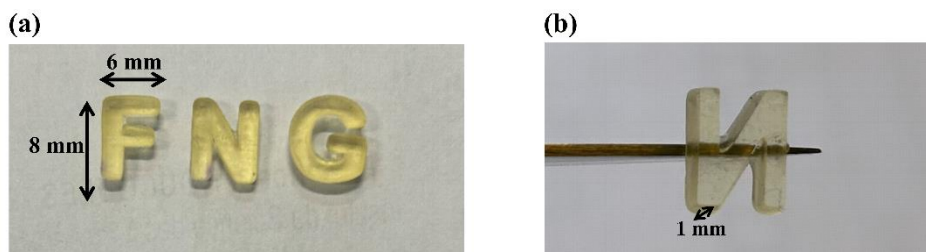


371

372 **Scheme 2. Proposed Photoinitiation Mechanism of B series OXEs and C**
 373 **series OXEs.**

374 **3.8 3D printing experiments**

375 OXEs showed good photoinitiation abilities in photopolymerization of TMPTA.
 376 Taking B8/TMPTA system as an example, applications of this photoinitiating system in
 377 3D printing experiments were tested. As shown in Figure 9, the letter patterns "FNG"
 378 were successfully obtained in 2 minutes by DLW. The letter pattern showed a high
 379 spatial resolution (See Figure 10) and neat edges, which indicates that the printing effect
 380 was good.



381

382

Figure 9. Digital photos of DLW objects using B8/TMPTA.

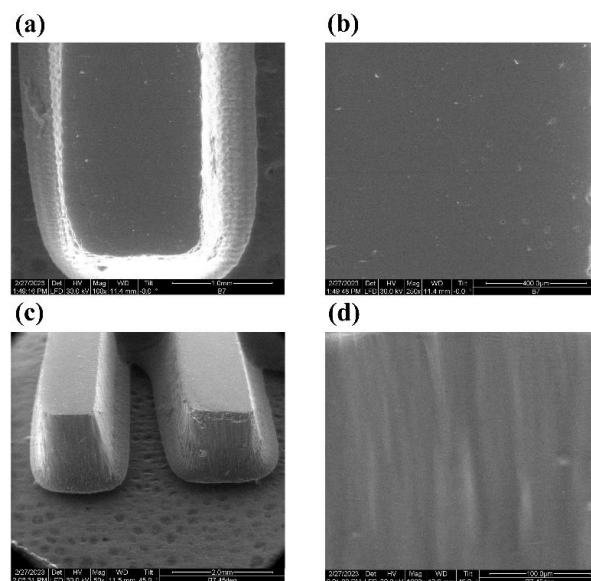


Figure 10. SEM images of surface of DLW objects using B8/TMPTA system.

4. Conclusion

Twenty-two novel OXEs bearing different functional groups (13 in the B series and 9 in the C series) were designed and synthesized for the first time. At room temperature, most OXEs showed good light absorption properties and photolysis under visible light irradiation. The photoinitiation ability was evaluated upon irradiation at 405 nm, and the results showed that some OXEs could initiate the polymerization of TMPTA efficiently. Interestingly, comparison of the photoinitiating abilities of the two series of oxime esters at 405 nm revealed the B series to outperform the C series. It can be concluded that the introduction of the photocleavable group in conjugated position with respect to the carbazole backbone favorably affects the reactivity of the oxime esters. Moreover, the interaction of the group with the chromophore leads to significantly shifted absorption properties depending on the position. Notably, OXE-B7 and OXE-B8 could be efficiently used to manufacture 3D objects with direct Laser write technology due to their high photoinitiating abilities. In addition, investigation of the photoinitiation mechanism of these OXEs showed that the N-O bond could cleave, generating acyloxy and iminyl radicals. By decarboxylation of acyloxy groups, CO₂ could be released and free radicals could be produced. In this study, the good photoinitiation abilities of OXEs were proved by theoretical calculations, RT-FTIR and

404 ESR-ST techniques. This work provides interesting tools for designing new high-
405 performance oxime ester photoinitiators in the future.

406

407 **Conflicts of interest**

408 The authors declare no competing financial interest.

409

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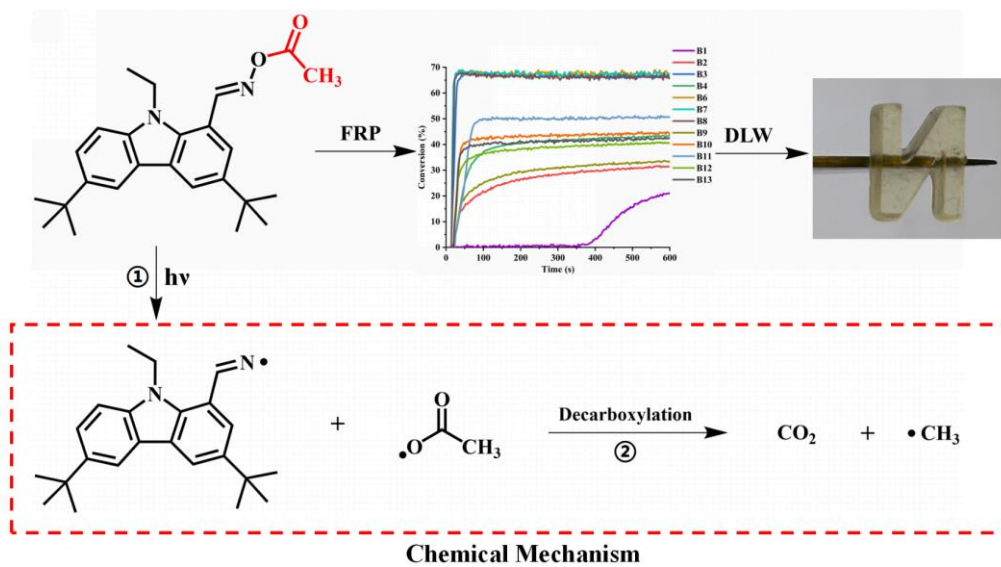
420 **References**

- 421 [1] Y. Li, U. Shaukat, S. Schlögl, T. Xue, J. Li, J. Nie, X. Zhu, *European Polymer*
422 *Journal* **2023**, 182.
- 423 [2] W. Liao, Q. Liao, Y. Xiong, Z. Li, H. Tang, *Journal of Photochemistry and*
424 *Photobiology A: Chemistry* **2023**, 435.
- 425 [3] Z. Tang, Y. Gao, S. Jiang, J. Nie, F. Sun, *Progress in Organic Coatings* **2022**, 170.
- 426 [4] X. Li, Z. Liu, P. Hong, L. Chen, X. Liu, *Progress in Organic Coatings* **2020**, 141.
- 427 [5] X. Guo, W. Wang, D. Wan, M. Jin, *European Polymer Journal* **2021**, 156.
- 428 [6] K. Dietliker, R. Hüsler, J. L. Birbaum, S. Ilg, S. Villeneuve, K. Studer, T. Jung, J.
429 Benkhoff, H. Kura, A. Matsumoto, H. Oka, *Progress in Organic Coatings* **2007**,
430 58, 146.
- 431 [7] A. E. Egorov, A. A. Kostyukov, D. A. Shcherbakov, D. A. Kolymagin, D. A. Chubich,
432 R. P. Matital, M. V. Arsenyev, I. D. Burtsev, M. G. Mestergazi, E. R. Zhiganshina,
433 S. A. Chesnokov, A. G. Vitukhnovsky, V. A. Kuzmin, *Polymers (Basel)* **2022**, 15.
- 434 [8] K. Sun, X. Peng, Z. Gan, W. Chen, X. Li, T. Gong, P. Xiao, *Catalysts* **2022**, 12.
- 435 [9] B. Ozkan, F. Sameni, S. Karmel, D. S. Engström, E. Sabet, *Journal of the European*
436 *Ceramic Society* **2023**, 43, 1649.
- 437 [10] M. Regehly, Y. Garmshausen, M. Reuter, N. F. König, E. Israel, D. P. Kelly, C. Y.
438 Chou, K. Koch, B. Asfari, S. Hecht, *Nature* **2020**, 588, 620.
- 439 [11] W. Liao, M. Jin, *European Polymer Journal* **2023**, 187.
- 440 [12] R. Acosta Ortiz, R. Yanez Macias, J. J. Ku Herrera, A. E. Garcia Valdez, *Polymers*
441 *(Basel)* **2022**, 15.
- 442 [13] M. Mohseni, S. Bastani, X. Allonas, S. Moradian, C. Ley, C. Croutxé-Barghorn,
443 E. Mohajerani, *Progress in Organic Coatings* **2018**, 115, 65.
- 444 [14] P. Xiao, J. Zhang, F. Dumur, M. A. Tehfe, F. Morlet-Savary, B. Graff, D. Gigmes,
445 J. P. Fouassier, J. Lalevée, *Progress in Polymer Science* **2015**, 41, 32.
- 446 [15] J. Radebner, A. Eibel, M. Leypold, C. Gorsche, L. Schuh, R. Fischer, A. Torvisco,
447 D. Neshchadin, R. Geier, N. Moszner, R. Liska, G. Gescheidt, M. Haas, H. Stueger,
448 *Angew Chem Int Ed Engl* **2017**, 56, 3103.
- 449 [16] T.-L. Huang, Y.-C. Chen, *Journal of Photochemistry and Photobiology A:*

- 450 *Chemistry* **2022**, 429.
- 451 [17] Y.-H. Li, Y.-C. Chen, *Polymer Chemistry* **2020**, 11, 1504.
- 452 [18] W. Wang, M. Jin, H. Pan, D. Wan, *Progress in Organic Coatings* **2021**, 151.
- 453 [19] S. Fan, X. Sun, X. He, Y. Pang, Y. Xin, Y. Ding, Y. Zou, *Polymers (Basel)* **2022**,
- 454 14.
- 455 [20] C. Gao, J. Zeng, X. Zhang, Y. Liu, Z. P. Zhan, *Org Lett* **2023**, 25, 3146.
- 456 [21] Y. Miyake, H. Takahashi, N. Akai, K. Shibuya, A. Kawai, *Chemistry Letters* **2014**,
- 457 43, 1275.
- 458 [22] Z.-H. Lee, F. Hammoud, A. Hijazi, B. Graff, J. Lalevée, Y.-C. Chen, *Polymer*
- 459 *Chemistry* **2021**, 12, 1286.
- 460 [23] H. B. Mahmoud Rahal, Sylvain Duval, Bernadette Graff, Tayssir Hamieh,
- 461 Joumana Toufaily, Frédéric Dumur, Jacques Lalevée, *European Polymer Journal*
- 462 **2022**, 177.
- 463 [24] Z. H. Lee, S. C. Yen, F. Hammoud, A. Hijazi, B. Graff, J. Lalevée, Y. C. Chen,
- 464 *Polymers (Basel)* **2022**, 14.
- 465 [25] S. Gong, X. Wu, Q. Liao, S. Deng, J. Hou, K. Tang, Y. Xiong, Z. Li, H. Tang,
- 466 *Green Chemistry* **2023**, 25, 2730.
- 467 [26] X. Ma, R. Gu, L. Yu, W. Han, J. Li, X. Li, T. Wang, *Polymer Chemistry* **2017**, 8,
- 468 6134.
- 469 [27] Y. Ding, S. Jiang, Y. Gao, J. Nie, H. Du, F. Sun, *Macromolecules* **2020**, 53, 5701.
- 470 [28] D. E. Fast, A. Lauer, J. P. Menzel, A.-M. Kelterer, G. Gescheidt, C. Barner-
- 471 Kowollik, *Macromolecules* **2017**, 50, 1815.
- 472 [29] L. Breloy, R. Losantos, D. Sampedro, M. Marazzi, J.-P. Malval, Y. Heo, J. Akimoto,
- 473 Y. Ito, V. Brezová, D.-L. Versace, *Polymer Chemistry* **2020**, 11, 4297.
- 474 [30] Z. Li, X. Zou, F. Shi, R. Liu, Y. Yagci, *Nat Commun* **2019**, 10, 3560.
- 475 [31] Y. Wu, C. Dai, J. Ke, R. Tang, C. Huang, J. Wang, Y. Situ, H. Huang, *Progress in*
- 476 *Organic Coatings* **2023**, 176.
- 477 [32] Y. G. Yijun Zhang, Ludovic Josien, Habiba Nouali, Cyril Vaultot, Angélique
- 478 Simon-Masseron, Jacques Lalevée, *Advanced Materials Technologies* **2021**.

- 479 [33] W. Wang, M. Jin, H. Pan, D. Wan, *Dyes and Pigments* **2021**, 192.
- 480 [34] W. Qiu, M. Li, Y. Yang, Z. Li, K. Dietliker, *Polymer Chemistry* **2020**, 11, 1356.
- 481 [35] S. Kato, H. Noguchi, A. Kobayashi, T. Yoshihara, S. Tobita, Y. Nakamura, *J Org*
482 *Chem* **2012**, 77, 9120.
- 483 [36] Y. Zhang, F. Morlet-Savary, M. Schmitt, B. Graff, A. Rico, M. Ibrahim-Ouali, F.
484 Dumur, J. Lalevée, *Dyes and Pigments* **2023**, 215.
- 485 [37] F. Hammoud, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gignes, F. Dumur,
486 J. Lalevée, *Mater. Chem. Front* **2021**, 5(24). 8361.
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488 TOC graphic:



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