

The Blue-LED-Sensitive Naphthoquinone-Imidazolyl Derivatives as Type II Photoinitiators of Free Radical Photopolymerization

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zation
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Abstract: In this work, new naphthoquinone-based photoinitiators (PIs) were synthesized and ap-15 plied for the first time in free radical photopolymerization. In the presence of acrylate monomers, 16 these PIs displayed excellent photoinitiation capabilities under blue-light (LED@405nm) irradiation 17 in a two-component photoinitiating system where the additive was a common iodonium salt (bis-18 (4-tert-butylphenyl)iodonium hexafluorophosphate - Iod) or a tertiary amine (ethyl 4-dimethylami-19 nobenzoate - EDB). In controlled tests, the polymerization performance of dye4/Iod was equal to or 20 better than that of common commercial Type II photoinitiators (2-isopropylthioxanthone and ben-21 zophenone). Meanwhile, only a trace amount of photoinitiator was required (as low as 0.05%) to 22 initiate the photopolymerization. It is worth noting that some of these compounds can also be used 23 in one-component photoinitiating system (monocomponent Type II behavior) and exhibited high 24 photoinitiation ability. A series of complementary characterization analyses of two new naphtho-25 quinone dyes (i.e. dye 1 and dye 4) with very similar chemical structures were carried out to inves-26 tigate the relevant photochemical mechanism. The results indicated that the interaction between the 27 newly developed PIs and the additives could occur effectively, which can lead to the free radical 28 photopolymerization. Finally, 3D printing experiments using the developed photoinitiating system 29 were carried out by a simple and convenient Direct Laser Write (DLW) technique. 30

 Keywords: Naphthoquinone derivatives; Blue-LED-sensitivity; Photoinitiator; Free radical photo 31

 polymerization; Direct laser write; 3D printing
 32

1. Introduction

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Antiala

In the 21st century, the use of light as an energy source for chemical reactions has been gaining increasing attention.[1-3] Most photochemically involved production processes can effectively 36

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avoid the high energy consumption, which are crucial for practical industrial production. Photopol-37 ymerization, as a representative example of this effort to develop energy-saving reactions, is a low-38 cost green technology in which a photoinitiator is excited by light under mild irradiation conditions 39 and can produce reactive species that are capable to initiate the polymerization of monomers, re-40 sulting in a rapid change of the system from a liquid to a solid state.[4-6] Photopolymerization sys-41 tems are usually composed of photoinitiators, oligomers, monomers, and additives responsible for 42 meeting the specific use requirements of the materials. A photoinitiator directly determines the rate 43 of photopolymerization and besides affects the physical and mechanical properties of the polymer-44 ized materials, so that photoinitiators play a key role in the overall photopolymerization process 45 and thus the photoinitiating system. [7,8] 46

Depending on the type of photoinitiator that are used to initiate the polymerization reaction, the 47 photopolymerization reaction can be mainly divided at the industrial scale into cationic photopol-48 ymerization reaction (CP) and free radical photopolymerization reaction (FRP)[9,10]. For FRPs, 49 most free-radical photoinitiators have a certain sensitivity in the UV and visible regions.[11,12] Un-50 der the irradiation of UV or visible light at a certain wavelength, photoinitiators absorb the light 51 energy and then produce free radicals capable to initiate the polymerization of monomers and to 52 form cross-linked network structures when multifunctional monomers are used.[13,14] Thermo-53 plastics can also be prepared by photopolymerization using monofunctional monomers. FRP tech-54 niques are of great commercial value in the field of photocuring applications since photoinitiated 55 radical polymerization has the advantages of being a relatively rapid reaction under mild irradia-56 tion conditions and to be energy efficient, so that photoresists, printing inks, and curing coatings of 57 different materials have been developed.[15-17] The way in which photoinitiators generate radicals 58 is distinguished by the different structures of photoinitiators, and FRP photoinitiators can be divided into two main categories according to the different mechanisms of generating radicals i.e. 60 Type I and Type II.[18] Upon light irradiation, Type I photoinitiators are directly cleaved to generate 61 initiating radicals, whereas Type II photoinitiators generate radicals through an electron/proton 62 transfer process between hydrogen acceptor (the PI in excited state) and hydrogen donor com-63 pounds (usually called co-initiators).[19-21] 64

Type II initiators are mainly aromatic ketones, such as benzophenone (BP), thianthrone, quinone 65 and their derivatives, etc.[22,23] Among them, BP, thianthrone and their derivatives have good light 66 absorption properties and high initiation efficiency in the UV region, which makes them very pop-67 ular photoinitiators in the field of UV curing.[24-26] Unfortunately, ketyl radicals formed by these 68 photoinitiators after photolysis can initiate chain termination reactions, so that some iodonium salts, 69 bromine substitutes and other additives can be added into the photoinitiating system in order to 70 prevent chain termination reactions by inducing oxidation or bromination reactions with ketyl rad-71 icals.[27,28] In addition, the aryl radicals generated by the reaction of iodonium salts with ketyl 72 radicals can initiate the polymerization reaction. Therefore, these additives can strongly improve 73 the polymerization reaction rate in general. For efficient polymerization reactions, intermolecular 74 hydrogen capture reactions must compete with other side reactions, such as non-reactive quenching 75 of the excited state initiator caused by monomers or oxygen.[29,30] A co-initiator is usually a hy-76 drogen donor that can form reactive radicals after a photochemical reaction. Amines,[31] ethers,[32] 77 sulfides,[33] and mercaptans[34] can be used as hydrogen donors, but amines are the most widely 78 used in light curing because of their low price and their ability to effectively overcome the oxygen 79 inhibition effect.[35] 80

However, amine additives are often toxic. Due to this major drawback, many researchers have de-81 veloped a series of low toxicity, high initiation efficiency photoinitiators that can be used as mono-82 component systems. An effort has also been done in order to expend their scope of application to 83 the visible range so that low-consumption LED sources can be used.[36] For instance, it has been 84 reported [37] that the introduction of acrylic acid and morpholine into the molecular structure of 4-85 methylbenzophenone can lead to a new one-component photoinitiator, MBPAcMP, with a slight 86 redshift of its absorption toward the visible light and exhibiting a molar extinction coefficient of 87 18800 L/mol·cm. The one-component photoinitiating system could act both as a Type II photoiniti-88 ator and a hydrogen donor with a high initiation efficiency and do not require the addition of addi-89 tional co-initiators in the process of initiating monomer polymerization.[38-40] 90

There are numerous studies and reports[41,42] on imidazole-based photoinitiators. Imidazole is a 91 five-membered ring two nitrogen-containing heterocyclic compound which is a popular base in Or-92 ganic Chemistry. The unshared electron pair of the 1-position nitrogen atom in the imidazole ring 93 participates to the conjugation, and the electron density of the nitrogen atom decreases, making the 94 hydrogen on this nitrogen atom easy to leave as a hydrogen ion.[43,44] Hexaalkylbisimidazoles 95 (HABIs) and their derivatives o-Cl-HABI and p-HOH-HABI were effective photoinitiators in thiol-96 alkene reactions. Under UV or short wavelength visible light irradiation, HABI compounds can be 97 interesting for thiol-alkene photopolymerization.[45] However, in contrast, reports on naphthoqui-98 none-based photoinitiators were notably rare. It has been reported [46] that two naphthoquinone 99 derivatives, combined with different additives, were used for the radical and cationic polymeriza-100 tion of trimethylolpropane triacrylate. 101

Markedly, naphthoquinone and its derivatives are widely found in nature, such as chlorophyll qui-102 none, carob quinone and vitamin K, among others.[47] Various derivatives of diazonaphthoquinone 103 were also used as photoresists based on linear phenolic resins, although these compounds were 104 rather old-fashioned photoinitiators. It is based on the generation of nitrogen gas upon illumination, 105 followed by reaction with water (which is usually produced from the substrate) to produce soluble 106 3-carboxyindene.[48] However, it was demonstrated that the diazo group rather than the naphtho-107 quinone group was playing an important role. Therefore, it is extremely interesting and promising 108 to further investigate the photoinitiation ability of naphthoquinones and their corresponding deriv-109 atives. In particular, the combination of imidazole with naphthoquinone to generate a series of 110 naphthoquinone-imidazolyl derivatives can bring a whole new possibility in the research of pho-111 toinitiators 112

In this research, 10 new naphthoquinone-imidazolyl derivatives, which have never been reported 113 before, were synthesized and successfully applied in free radical photoinitiating systems with two 114 different additives, namely bis(4-tert-butylphenyl)iodonium hexafluorophosphate and ethyl 4-di-115 methylaminobenzoate under the light irradiation of a LED@405 nm in air. Noticeably, the possibility 116 to initiate polymerization processes in the absence of additives (i.e. used in one-component Type II 117 photoinitiating system) was studied. Polymerization of trimethylolpropane triacrylate (TMPTA) 118 was monitored using real-time Fourier transform infrared spectroscopy (RT-FTIR). Photochemical 119 mechanism could be elucidated using steady state photolysis and fluorescence quenching experi-120 ments, cyclic voltammetry, fluorescence decay lifetime, and electron spin resonance (ESR) spin cap-121 ture (ESR-ST) experiments. Finally, regular 3D patterns with excellent resolutions were obtained by 122 3D printing with direct laser write (DLW). 123

2. Materials and Methods

2.1. Synthesis of Naphthoquinone-imidazolyl Derivatives

Ten new naphthoquinone-imidazolyl derivatives (See Scheme 1) never reported before in the literature were synthesized according to the procedure described in detail in supporting information (SI). NMR and HRMS characterizations of the different compounds are also given in SI.



Scheme 1. Chemical structures of naphthoquinone-imidazolyl derivatives

2.2. Other Chemical Compounds Used in This Work

The iodonium salt (i.e. *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate, noted Iod or Speedcure 938) and the tertiary amine (ethyl 4-dimethylaminobenzoate, EDB) used in the different photoinitiating system, as well as isopropylthioxanthone (ITX) and benzophenone (BP) used as benchmark Type II PIs in the control experiments, were purchased from Lambson Ltd (Leeds, UK). Trimethylolpropane triacrylate (TMPTA) was obtained from Allnex (Frankfurt am Main, Germany). The above reagents were used without further purification. Chemical structures of the above compounds are shown in Scheme 2.



Scheme 2. Chemical structures of additives and monomer.

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2.3. Photopolymerization Experiments

First, novel naphthoquinone-imidazolyl derivatives were dissolved in TMPTA with Iod or EDB to 144 prepare the photosensitized formulations. The obtained formulations were added dropwise to the 145 pre-prepared molds (8 mm diameter and 4 mm height/thickness) for the photocuring processes. 146 Formulations were exposed to a LED@405 nm ($I_0 = 110 \text{ mW} \cdot \text{cm}^{-2}$) to initiate the free radical polymer-147 ization (FRP) at room temperature under air. During the photopolymerization processes, the IR 148 peak at ~ 6120 cm⁻¹, corresponding to a characteristic peak of TMPTA, was continuously monitored 149 using the real-time FTIR spectroscopy (JASCO FTIR 4100). The polymerization profiles were estab-150 lished using the following equation [13,49]: 151

$$Conversion(\%) = \frac{A_0 - A_t}{A_0} \times 100, \tag{1}$$

where A_0 is the initial peak area before irradiation and A_t is the peak area after irradiation for a given time t.

2.4. Steady state photolysis

Steady state photolysis experiments were monitored by UV-visible absorption spectroscopy (JASCO V730 UV-visible spectrometer). The solutions containing naphthoquinone-imidazolyl derivatives in chloroform were irradiated in a cuvette at room temperature using a LED@405nm.

2.5. Fluorescence quenching and fluorescence lifetime

Fluorescence quenching experiments were performed using a JASCO FP-6200 spectrometer. After159analysis of the fluorescence quenching spectra, the Stern-Volmer coefficients (K_{sv}) could be deter-160mined exactly by calculating the slope values of the Stern-Volmer treatment. [50]. Fluorescence ex-161cited state lifetimes were characterized by a HORIBA PPD-850. Conditions of the experiments were162as follows: The excitation wavelength (λ_{ex}) = 367 nm, the pulse duration < 1.4 ns.</td>163

2.6. Electrochemical measurements

The oxidation (Eox) and reduction (Ered) potentials were determined by electrochemistry as follows. 165 The naphthoquinone-imidazolyl derivatives were co-dissolved with tetrabutylammonium hex-166 afluorophosphate (as the supporting electrolyte) in a mixture of solvents : chloroform/acetonitrile 167 (50%/50% : v/v). The singlet state excitation energy level (E_{s1}) of the PIs were determined from the 168 crossing point of the normalized UV-Vis absorption and fluorescence spectra. The free energy 169 changes from the singlet state (ΔG^{S1}_{Iod} or ΔG^{S1}_{EDB}) for the electron transfer reaction were determined 170 with Eox, Ered, and Es1. The specific calculation formula is detailed in Eqs. (2) and (3).[51] In the same 171 way that Eqs. (4) and (5) show the specific calculations regarding the free energy change from the 172 triplet state (ΔG_{el}). The value of the triplet state energy level (E₁₁) was calculated by molecular mod-173 elling (Gaussian 16 suite of programs). In the literature, the reduction potential of the iodonium salt 174 is -0.7 V,[52] while the oxidation potential of EDB is 1.0 V.[53] 175

$$\Delta G_{\rm Iod}^{\rm S1} = E_{\rm ox} - (-0.7) - E_{\rm S1'} \tag{2}$$

$$\Delta G_{EDB}^{S1} = 1 - (E_{red}) - E_{S1'}$$
(3)

$$\Delta G_{\rm Iod}^{\rm T1} = E_{\rm ox} - (-0.7) - E_{\rm T1'} \tag{4}$$

$$\Delta G_{EDB}^{T1} = 1 - (E_{red}) - E_{T1}$$
(5)

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2.7. Electron spin resonance - spin trapping (ESR-ST)

The test solution was made by dissolving the PI/Iod or PI/EDB in *tert*-butylbenzene (Iod = 2 mg/mL,178EDB = 2 mg/mL and PI = 0.2 mg/mL). After nitrogen saturation at room temperature, the solution179was irradiated using a light source of LED@405nm. N-*tert*-butylbenzonitrone (PBN) was used as a180spin trap (PBN = 2 mg/mL). The free radicals formed can be observed by an X-band spectrometer181(Bruker EMXplus). The ESR spectral simulation was performed by the PES WINSIM software.[50]1822.8. Direct laser write / 3D printing183

The mixed resin solution containing the photoinitiator and formulated in 2.3 was added to the homemade tank (2 mm height). Direct laser write (DLW) experiments were carried out using a laser diode@405 nm under air. The intensity of the laser was 110 mW/cm². The final 3D patterns were observed and photographed using the numerical optical microscope (OLYMPUS DSX-HRSU). 187

3. Results and discussion

3.1. Light absorption properties

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Molar extinction coefficients of the investigated naphthoquinone-imidazolyl derivatives in chloro-190 form were determined by UV-visible spectroscopy (see Figure 1). The specific values corresponding 191 to the spectra are detailed in Table 1. As shown in Figure 1, the maximum absorption wavelengths 192 (λ_{max}) of the different dyes are all in the near UV-visible range (380-444 nm). It ensured to some 193 extent a high sensitivity of all PIs to blue LED light sources. At the maximum absorption wave-194 length, respectively, dye 10 exhibited the highest molar extinction coefficient (ϵ_{max} = 19370 M⁻¹·cm⁻¹) 195 at λ_{max} = 413 nm. It can be confidently assigned to the polyaromaticity of this dye comprising a 5,12-196 dihexyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole moiety. In contrast, dye 4 exhibited the 197 lowest molar extinction coefficient (ε_{max} = 1300 M⁻¹·cm⁻¹) at λ_{max} = 380 nm, despite the similarity of 198 structure with the rest of the dyes. It can be tentatively assigned to the ortho-substitution of the 199 electron donor, inducing an internal torsion to the molecule and adversely affecting the electronic 200 delocalization between the electron donor and the acceptor. At the same time, the molar extinction 201 coefficient at λ = 405 nm was also taken into account. Similar to the results for ε_{max} , dye 10 and dye 202 4 showed the best and worst light absorption properties at 405 nm, with a molar extinction coeffi-203 cient $\epsilon_{\text{@405nm}} = 19000 \text{ M}^{-1} \cdot \text{cm}^{-1}$ of dye 10 and a molar extinction coefficient of $\epsilon_{\text{@405nm}} = 1000 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for 204 dye 4 respectively. 205



Figure 1. UV-visible absorption spectra of the different naphthoquinone-imidazolyl derivatives in 207 chloroform. 208

Table 1. Light absorption properties of the different naphthoquinone-imidazolyl derivatives: max-209 imum absorption wavelengths λ_{max} ; extinction coefficients at λ_{max} (ε_{max}) and extinction coefficients 210 at the emission wavelength of the LED@405 nm(E@405nm) 211

No.	λ _{max} (n m)	ε _{max} (M ⁻¹ ⋅cm ⁻¹)	€@405nm(M ⁻¹ ·cm ⁻¹)
Dye 1	414	1840	1790
Dye 2	430	1850	1540
Dye 3	410	1470	1460
Dye 4	380	1300	1000
Dye 5	444	1930	1250
Dye 6	401	1460	1450
Dye 7	456	1890	1380
Dye 8	405	1600	1600
Dye 9	441	2510	2060
Dye 10	413	19370	19000

3.2. Steady state photolysis of the naphthoquinone-imidazolyl derivatives based photoinitiating systems

In this section, the steady state photolyses of the two-component and three-component systems 214 (dyes/Iod, dyes/EDB, and dyes/Iod/EDB) prepared with the different naphthoquinone-imidazolyl 215 derivatives were studied. Dye 1 and dye 4 were selected as the relevant structures to discuss the PI 216 photolysis behavior.

As shown in Figure 2, when only dye 1 was present in the solution, the absorption peak of dye 1 at 218 414 nm did not change significantly after light irradiation during 100 s, indicating that dye 1 pos-219 sesses a good photostability. In the dye 1/Iod two-component system, dye 1 was hardly consumed 220 during the photolysis process (the absorption peak showed almost no decrease), and the chemical 221

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reaction between dye 1 and Iod was very weak. In contrast, the dye 1/EDB system showed some 222 reactivity. Specifically, dye 1 reacted slowly with EDB (taking 300 s), and the absorption peak 223 showed a really slight redshift at the end of the irradiation. It is noteworthy that in the three-component system of dye 1/Iod/EDB, the reaction rate of dye 1 was greatly enhanced compared with 225 the two-component systems, and the light absorption of dye 1 changed significantly when the irradiation lasted for 20 s. Thus, the interaction of dye 1 with Iod and EDB greatly promoted the comprehensive reaction of the three-component system. 228



Figure 2. UV-vis absorption spectra of dye 1 $(5.5 \times 10^{-5} \text{ M})$: (a) without co-initiators, (b) with Iod229 $(2.92 \times 10^{-2} \text{ M})$, (c) with EDB $(8.14 \times 10^{-2} \text{ M})$, and (d) with both Iod $(2.92 \times 10^{-2} \text{ M})$ and EDB $(8.14 \times 10^{-2} \text{ M})$ 230 $10^{-2} \text{ M})$ under air in chloroform (LED@405 nm).231

Noticeably, as observed for dye 1, no significant photolysis occurred for dye 4 alone under irradiation, and the peak near 320 nm did not change (see Figure 3a). Meanwhile, dye 4 exhibited a more pronounced reactivity in two-component systems. Photolysis reaction of the two-component dye 4/Iod system was relatively more rapid (Figure 3b), since the reaction was completed within 60s. 235 Conversely, chemical reaction between dye 4 and EDB (Figure 3c) could also be detected during the 236 photolysis experiments but required more time to occur. Thus, a clear and obvious photolysis could 237 be detected after 300 s of irradiation. During the photolysis of the final three-component dye 238 4/Iod/EDB system (see Figure 3d), a behavior similar to that observed for the two-component dye 239 4/Iod system was detected. Thus, after 60 s of irradiation, modification of the intensity of the ab-240 sorption peak was no longer detectable. It can be therefore clearly seen that the interactions between 241 the different components in the three-component system were helpful for the enhancement of the 242 photochemical reactivity of the three-component system. Parallel to the photolysis experiments 243 done on dye 4 and dye 10, the steady state photolysis of well-known and benchmark photoinitiators 244 such as ITX and BP were carried out in order these two compounds to be used as reference com-245 pounds. Results of the photolysis experiments are shown in Figure S1 and Figure S2, respectively. 246 Among the two benchmark photoinitiators and as observed for dye 4, ITX could efficiently react 247 with both Iod and EDB, contrarily to BP for which a lower rate of reaction in two-component pho-248 toinitiating systems was detected compared to ITX and dye 4. Under blue light irradiation, ITX had 249 a good photolysis rate in both two- and three-component systems whereas a good photochemical 250 stability was found in solution. These characteristics could also be evidenced for dye 4. Noticeably, 251 the reaction rates of the different ITX and dye 4 systems prepared with Iod and EDB were very 252 similar (100 s, 300 s of photolysis). It therefore demonstrates that dye 4 can compete with the well-253 established ITX in terms of reactivity with iodonium salts and amines under irradiation. 254



(b)





Figure 3. UV-vis absorption spectra of dye 4 (5.5×10^{-5} M) : (a) without co-initiators, (b) with Iod255(2.92×10^{-2} M), (c) with EDB (8.14×10^{-2} M), and (d) with both Iod (2.92×10^{-2} M) and EDB (8.14×10^{-2} M), under air in chloroform (LED@405 nm).256257

3.3. Chemical mechanism of electron transfer reactions

In photopolymerization, efficiency of the photoinitiating system is not only related to the light ab-259 sorption properties of the system but also to other parameters such as their redox processes, excited 260 state lifetimes. To some extent, investigation of their fluorescence quenching and fluorescence life-261 times can give an idea of their chemical reactivity in photopolymerization. Therefore, some param-262 eters such as the electron transfer reactions in the photoinitiating systems, the singlet excited state 263 energy (E_{s1}), the Gibbs free energy change (ΔG), the triplet state energy (calculated at DFT), and the 264 Stern-Volmer coefficients of dye 1 and dye 4 can furnish interesting information on the photoiniti-265 ating systems and the different values were calculated and listed in Table 2. 266

Table 2. Some parameters concerning the electron transfer reactions of dye 1 and dye 4 in chloro 267

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No.	$\mathbf{K}^{\mathrm{sv}_{\mathrm{EDB}}}$	Es1	Ет1	Eox	Ered	$\Delta G^{\rm S1}{}_{\rm Iod}$	$\Delta G^{\rm S1}{}_{\rm EDB}$	
Dye 1	15	2.7 eV		0.33 eV	-0.83 eV	−1.67 eV	–0.87 eV	
Dye 4	25	2.9 eV		0.07 eV	-0.9 eV	-3.67 eV	-1 eV	Commenté [FD2]: What ar the units ? It is not
No.	$\Delta G^{{\rm T1}}{}_{{\rm Iod}}$	$\Delta G^{{\rm T1}_{\rm EDB}}$	Φ_{et}	•				volt?
Dye 1			0.94					
Dye 4			0.96					

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The singlet excited state energy (E_{s1}) was obtained by calculating the intersection of the normalized UV-Vis absorption and fluorescence spectrum of the naphthoquinone-imidazolyl derivatives (see Figure 4). By means of cyclic voltammetry (see Figure S3), the oxidation and reduction potentials of the naphthoquinone-imidazolyl derivatives could be determined. Values of the oxidation potentials vere 0.33 eV and 0.07 eV, and the values of the reduction potentials were –0.83 eV and –0.9 eV, for 274 dye 1 and 4 respectively. The free energy changes of the naphthoquinone-imidazolyl derivatives in 275

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the photoinitiating systems were calculated by the equation given in Section 2. For ΔG^{S1}_{Iod} and ΔG^{S1}_{EDB} with dye 1 and dye 4, their values were negative, which indicated the possibility of electron transfer reactions with Iod and EDB. It is worth noting that the ΔG^{S1}_{Iod} and ΔG^{S1}_{EDB} values of dye 4 were lower than that of dye 1, which theoretically suggested that dye 4 was more likely to react with Iod and EDB compared to dye 1. Calculation of the triplet state energy level Em





Figure 4. Determination of the singlet state energy of (a) dye1 and (b) dye4 in chloroform.

Fluorescence quenching experiments were performed in chloroform for dye 1 and dye 4 (see Figure 282 5). Fluorescence quenching processes for the two-component dye 1/Iod and dye 4/Iod systems were 283 not recorded. Indeed, upon addition of Iod into the solutions of dyes, an intense photoluminescence 284 ascribed to the generation of photoproducts appeared, suggesting a good interaction between the 285 PIs and the additives. Conversely, fluorescence quenching processes of the two-component systems 286 composed with EDB were fully observed and the Stern-Volmer coefficients (Ksv) could be calculated 287 by the slopes of Stern – Volmer treatment. The emission peaks of dye 1 and dye 4 at 540 nm and 510 288 nm respectively decreased continuously with the addition of EDB to the solution. The results 289 showed that the interaction of dye 4 and EDB was effective from the singlet excited state. On this 290 basis, the electron transfer quantum yield (Φ_{et}) in the singlet excited state could be calculated, and 291 the interaction between dye 4 and EDB (Φ_{et} = 0.96) was slightly more efficient than that of dye 1 (Φ_{et} 292 = 0.94). The obtained results were consistent with the free energy change results mentioned above. 293 Finally, fluorescence lifetimes of dye 1 and dye 4 were measured (see Figure S4). Unfortunately, the 294 calculated and analyzed values of dye 1 and dye 4 were shorter than the response time of the appa-295 ratus (1.4 ns). 296



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Figure 5. Fluorescence quenching of (a) dye 1 $(5.6 \times 10^{-5} \text{ M} \text{ in chloroform})$ and (b) dye 4 $(5.6 \times 10^{-5} \text{ M} \text{ in chloroform})$ by amine (EDB). The Stern–Volmer treatment for (c) dye 1/EDB and (b) dye 4/EDB 298

3.4. Free Radical Photopolymerization

Polymerization kinetics of TMPTA in two-component systems under LED@405 nm irradiation 301 could be determined by monitoring the conversion of acrylate functional groups using RT-FTIR. As 302 shown in Figure 6, we first carried out the polymerization tests with the two-component PI/Iod and 303 PI/EDB photoinitiating systems. Both the dye 4/Iod and dye 6/Iod systems showed relatively good 304 photoinitiation performance at room temperature and under air (acrylate functions conversion ~ 305 78%, 72%), especially for the dye 4/Iod system, where the photopolymerization rate was fast (see 306 Figure 6a). In contrast, the two two-component dye/EDB systems furnished lower acrylate conver-307 sions than their two-component dyes/Iod counterparts with a decrease of the monomer conversion 308 of ca. 10% (see Figure 6b). Besides, the two two-component dyes/EDB systems clearly outperformed 309 the dyes/Iod systems in terms of polymerization rate. 310



Figure 6. Photopolymerization profiles of acrylate functions (double bond conversion vs irradiation311time) under air upon exposure to a LED@405nm in the presence of (a) dyes (0.2 wt%)/Iod(2312wt%)/TMPTA; (b) dyes (0.2 wt%)/EDB(2 wt%)/TMPTA; thickness at ~ 2 mm; the irradiation starts313at t = 10 s.314

To further verify our expectation that the interaction of dyes with the additives in three-component 315 system could improve the photoinitiation performance of the resulting systems, dye 4, dye 6 and 316 dye 8 that furnished the best two-component systems were selected to form the three-component 317 systems together with Iod and EDB. As shown in Figure 7, it could be clearly seen from the polymer-318 ization profiles that the polymerization rate of monomers was greatly improved for the three-com-319 ponent dye/Iod/EDB systems compared to the two-component systems based on Iod or EDB. For 320 the dye 6/Iod/EDB and dye 8/Iod/EDB systems, improvement of the initiation ability was more ob-321 vious than for the dye4-based photoinitiating systems. Compared to the two-component systems, 322 the conversions of acrylate functional groups were greatly enhanced while the polymerization rates 323 also increased. To determine the real contribution of the dyes in the three-component photoinitiat-324 ing systems, the monomer conversion was determined for the two-component Iod/EDB system that 325 does not comprise any dye. This experiment was used as a blank control group. The content of Iod 326 and EDB was the same than that used for the abovementioned three-component system. It is worth 327 noting that although the conversion of TMPTA after the photopolymerization reaction (~85%) in the 328 absence of added dyes was slightly higher than that obtained for the three-component systems, 329 besides, the conversion rate of monomers in the dye 4/Iod/EDB system was much faster than that 330 of the blank group. When comparing the time required to "reach the maximum conversion", the 331 blank group without dye required more time than the three-component systems, evidencing the 332 crucial role of the dye in the initiation step. It could be seen that the addition of dyes led to a signif-333 icant increase of the polymerization rate. However, this performance has some drawbacks, notably 334 due to the fact that a faster polymerization rate induces an increase of the polymerization stress.[54] 335 As can be seen from the photographs of the samples obtained after polymerization with the three-336 component systems, the polymerization shrinkage stress caused the samples to rupture, whereas 337 for the samples prepared with the two-component systems, the resulting samples were smooth and 338 homogeneous on the surface and could maintain a good structural integrity. 339



Figure 7. Photopolymerization profiles of TMPTA (double bond conversion vs irradiation time) under air upon exposure to a LED@405nm in the presence of dyes (0.2 wt%)/Iod(2 wt%), dyes (0.2 wt%)/EDB(2 wt%) and dyes (0.2 wt%)/Iod(2 wt%)/EDB(2 wt%); thickness at ~ 2 mm; the irradiation starts at t = 10 s.341

In view of the excellent photoinitiation performance of the dye 4-based systems, we chose ITX and 345 BP as benchmark photoinitiators for comparison (see Figure 8). Surprisingly, in the two-component 346 system with Iod, the initiation ability of dye 4 was similar to that of ITX (see Figure 8a), while the 347 ability of dye 4 when combined with EDB was slightly lower than that of ITX, but still much higher 348 than BP (see Figure 8b). Both dye 4 and ITX were able to maintain a high photoinitiation ability at 349 either 0.05% or 0.1%, while BP was completely ineffective. The low concentration of initiators was 350 more in line with the purpose of environmental protection and green chemistry. Pictures of all sam-351 ples obtained by photopolymerization are detailed in Table S1. 352



Figure 8. Photopolymerization profiles of acrylate functions (double bond conversion vs irradiation353time) under air upon exposure to a LED@405nm in the presence of (a) dye4/Iod(2 wt%)/TMPTA,354ITX/Iod(2 wt%)/TMPTA and benzophenone/Iod(2 wt%)/TMPTA; (b) dye4/EDB(2 wt%)/TMPTA,355ITX/EDB(2 wt%)/TMPTA and benzophenone/EDB(2 wt%)/TMPTA; thickness at ~ 2 mm; the irradiation356ation starts at t = 10 s.357

To further demonstrate the interest of dye 4 as photoinitiator, both ITX and dye 4 were used in onecomponent photoinitiating systems and attempts to initiate the polymerization of TMPTA were carried out. As shown in Figure 9, although the polymerization rate of the monomers was not as fast as that of the two-component photoinitiating systems, the final conversion of the acrylate functional group reached 60% (dye 4 at 300 s). Noticeably, in the same conditions, dye 1 exhibits almost no initiation ability. 363



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Figure 9. Photopolymerization profiles of acrylate functions (double bond conversion vs irradiation time) under air upon exposure to a LED@405nm in the presence of dyes (0.1 wt%)/TMPTA, ITX (0.1 wt%)/TMPTA; thickness at ~ 2 mm; the irradiation starts at t = 10 s

3.5. ESR spin-trapping experiments

As shown in Figure 10a and 10b, the spectra of the dye 4/Iod system before and after irradiation 369 (LED@405 nm) and the simulated spectra after irradiation were given. After 30 s of irradiation, one 370 free radical adduct was successfully detected which could be assigned to a carbon or an oxygen 371 centered radical[55] (values of hyperfine coupling constants: $\alpha_N = 13.50$ G and $\alpha_H = 1.76$ G). For the 372 two-component dye 4/EDB system (see Figure 10c and 10d), after an extended irradiation time, the 373 values of hyperfine coupling constants for one adduct (72.4%) were $\alpha_N = 13.41$ G and $\alpha_H = 1.70$ G 374 which could be assigned to a carbon or oxygen centered radical while another generated radical 375 was aminoalkyl radical ($\alpha_N = 14.16$ G and $\alpha_H = 2.69$ G, 23.3%). The rest could be attributed to the by-376 product of the reaction, which is the oxidation product of PBN [56,57] (PBNox, $\alpha N = 7.93$ G, 4.3%). 377 The one-component photoinitiating system consisting only of dye 4 was also studied. As can be 378 seen from Figure S5, the carbon or oxygen centered radical was also successfully observed (αN = 379 13.49 G and $\alpha_{\rm H}$ = 1.73 G), which fully demonstrated that dye 4 can be used as a photoinitiator for 380 one-component photoinitiating systems for free radical polymerizations. 381



Figure 10. ESR spectra of PIS. (a) dye 4/Iod PIS in acetonitrile (before and after 30 s irradiation); (b)383dye 4/Iod PIS in acetonitrile (experimental and simulated); (c) dye 4/EDB PIS in tert-butylbenzene384(before and after 210 s irradiation); (d) dye 4/EDB PIS in tert-butylbenzene (experimental and simulated).385ulated).386

Therefore, the different ESR experiments do not allow to establish the exact structures of all the generated radicals but unambiguously showed that radicals are generated upon irradiation in full agreement with the photoinitiator behavior of these dyes. 389

3.6 Direct laser write (DLW) experiments (3D printing)

Application of the newly developed photoinitiating systems for 3D printing and the free radical photopolymerization of TMPTA with a laser diode@405 nm as the light source was carried out (see Figure 11). The resulting 3D printed patterns showed clear contours and flat surfaces with a high resolution in the field of view of the electron microscope. It was obvious that the dye 4-based system produced a more regular and better structured product compared to ITX, which reflected the consistently excellent photoinitiation performance of dye 4 (even alone in a monocomponent Type II behavior – Figure 11a). 392 393 394 395 396 396 397 398





(b)

(a)



(**d**)

Figure 11. DLW experiments in TMPTA. Characterization of 3D color patterns by numerical optical399microscopy in the presence of: (a) dye 4/Iod; (b) dye 4/EDB; (c) ITX/Iod; (d) ITX/EDB.400

3.7. Photoinitiation mechanism of free radical polymerization

(c)

According to the analysis of the experimental results depicted above, for the free radical photopolymerization process initiated by the three-component photoinitiator system, the concomitant presence of two different reaction processes could be determined. Thus, for the dye/Iod system, the dye can act as an electron donor for the iodonium salt. Conversely, for the dye/EDB system, the dye reacts as an electron acceptor with the amine acting as an electron donor. The two reactions are shown in Scheme 3 (r1-r3). 402

Dye \rightarrow *Dye (hv)

*Dye + Ar₂I⁺
$$\rightarrow$$
 Dye^{•+} + Ar[•] + Ar-I (r1)

*Dye + EDB
$$\rightarrow$$
 Dye^{•-} + EDB^{•+} \rightarrow Dye-H[•] + EDB_(-H)[•] (r2)

$$Dye-H^{\bullet} + Ar_{2}I^{+} \rightarrow Dye + H^{+} + Ar^{\bullet} + Ar-I \quad (r3)$$

Scheme 3. Proposed chemical mechanism in PIS.

4. Conclusions

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In summary, 10 completely new and never reported naphthoquinone-imidazolyl derivatives were 410 synthesized and successfully applied in free radical photopolymerization. In order to elucidate the 411 relevant photochemical mechanisms, a series of complementary experiments such as steady-state 412 photolysis, cyclic voltammetry, fluorescence quenching, and fluorescence lifetimes were carried 413 out. The generated free radicals from the studied photoinitiating systems were further clarified by 414 ESR experiments. Interestingly, dye 4 demonstrated the best photoinitiation ability among this new 415 series of compounds, both in two-component and in one-component systems. The slight differences 416 in the chemical structures of dye 1 and dye 4 (presence of a methyl group on the imidazole group) 417 resulted in the fact that these two dyes totally behave differently in free radical photopolymeriza-418 tion. By comparing with other commonly used photoinitiators (BP or ITX), dye 4 showed a similar 419 photoinitiating efficiency. In addition, the new photoinitiating systems required only extremely 420 mild and environmentally friendly conditions for the photopolymerization reaction to proceed, and 421 its blue light-sensitive property allowed it to effectively utilize LED light sources. The successful 422 application in 3D printing gave the new naphthoquinone-imidazolyl derivatives a broader prospect 423 for future research in green polymerization processes. 424 Supplementary Materials: Synthesis and characterization (NMR, HRMS data) for all the dyes. Pho-425

tolysis and polymerization date in supporting information figures. 426 427 Author Contributions: Conceptualization, J.L., F.D., M.S., F.M.-S., and P.X.; synthesis of composites, T.B.; validation, all authors; formal analysis, all authors; data curation, all authors; writing-428 original draft preparation, all authors; writing-review and editing, all authors. All authors have 429 read and agreed to the published version of the manuscript. 430 Funding: China Scholarship Council (CSC, No. 202007030005) for Timur Borjigin. 431 Institutional Review Board Statement: Not applicable. 432 Informed Consent Statement: Informed consent was obtained from all subjects involved in the 433 study. 434 Data Availability Statement: Data will be available on request to the authors 435 Acknowledgments: The authors wish to thank the Region Grand Est (France) for the grant "MIPPI-436 4D". This research project is supported by China Scholarship Council (CSC) (No. 202007030005). 437 P.X. acknowledges funding from the Australian Research Council (FT170100301). 438 Conflicts of Interest: The authors declare no conflict of interest. 439 References 440 441 1. Liang, M.; Borjigin, T.; Zhang, Y.; Liu, H.; Liu, B.; Guo, H. Z-Scheme Au@Void@g-C3N4/SnS Yolk-Shell Heterostructures 442 for Superior Photocatalytic CO2 Reduction under Visible Light. ACS Applied Materials & Interfaces 2018, 10, 34123-34131, 443 doi:10.1021/acsami.8b09455 444 2 Borjigin, T.; Schmitt, M.; Morlet-Savary, F.; Xiao, P.; Lalevée, J. Low-Cost and Recyclable Photocatalysts: Metal 445 Oxide/Polymer Composites Applied in the Catalytic Breakdown of Dyes. Photochem 2022, 2, 733-751, 446 doi:https://doi.org/10.3390/photochem203004 447 448

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TOC graphic: