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Recent Advances on Anthraquinone-based Photoinitiators of Polymerization

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Abstract

The design of photoinitiating systems activable in the visible range and under low light intensity is an active research field supported by the vast applications of photopolymerization. In the search for dyes that can exhibit panchromatic absorptions, anthraquinone has been identified as a promising scaffold. Over the years, numerous modifications have been carried out on this scaffold by molecular engineering, enabling to design water-soluble, panchromatic or photobleachable dyes. In this review, an overview of the recent advances concerning photopolymerization with anthraquinone-based photoinitiating systems is given.

Keywords

Photoinitiator; visible light; photopolymerization; LED; anthraquinone; natural compound; water-soluble

1. Introduction

During the past decades, photopolymerization has been the focus of intense research efforts, resulting from the wide of applications using photopolymerization.[1–5] Notably, photopolymerization is commonly used for applications ranging from solvent-free paints, microelectronics, adhesives, dentistry, coatings and varnishes, and 3D and 4D printing to name but a few.[4,6–18] This intense research activity is also supported by the recent safety concerns raised by the use of UV light in industry. Notably, UV light can cause skin cancers and eye damages. Ozone can also be produced by UV light, constituting another drawback of UV photopolymerization. However, nowadays, the main concern that will end UV photopolymerization is the high energy consumption combined with the elevated costs of the UV irradiation setups. Considering that in the coming years, energy sobriety will be the main focus of numerous countries, this historical polymerization technique is now totally disconnected with the present preoccupation of our societies. Shift of the irradiation wavelength from the UV range towards the visible range exhibit several advantages. Notably, a higher light penetration can be achieved in the visible range, rendering visible light photopolymerization more attractive than UV photopolymerization. Indeed, use of UV photopolymerization was restricted to the polymerization of thin films and coatings. By polymerizing under visible light, a light penetration ranging between a few millimetres up to

a few centimetres can be obtained, enabling to polymerize thick samples and samples containing fillers (See Figure 1).[19]

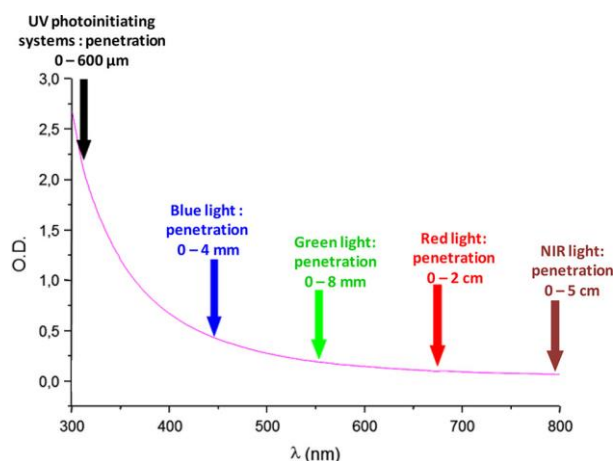


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm.
Reprinted with permission from Ref.[19]

As other advantages, an excellent spatial and temporal control of the polymerization process can be obtained, what cannot be achieved by the classical thermal polymerization in solution. However, if numerous advantages can be cited for visible light photopolymerization, the disadvantages can't be denied. Thus, visible light photoinitiators strongly absorb in the visible range, providing an undesired colour to the final coating. A lack of reactivity can also be mentioned. Indeed, visible light photons are less energetic than UV photons so that a reduction of the monomer conversions is often observed. Additionally, with aim at using energy-saving polymerization conditions, light-emitting diodes (LEDs) are now commonly used for photopolymerization. As the main advantages, these devices are cheap, compact and exhibit long operating lifetimes. Ideally, highly reactive photoinitiating systems could even be activated with daylight or sunlight.[20] However, availability of sunlight photoinitiators is still scarce in the literature. Face to these considerations, the search for dyes capable to bleach is still an active research field, only few visible light photoinitiating systems exhibiting this highly researched property.[21] With aim at developing highly reactive photoinitiating systems, an extensive screening has been developed during the last decades. A wide range of structures have been examined, as exemplified by dihydroanthraquinones,[22] *N*-heterocyclic carbene boranes,[3] curcumin,[23–26] benzylidene ketones,[27–34] cyclohexanones,[35–38] perovskites,[39,40] iron complexes,[41–48] diketopyrrolopyrroles,[49–51] viologen derivatives,[52–54] naphthoquinones,[55] porphyrins,[56–58] dithienophospholes,[59,60] thiophene derivatives,[61] 2,3-diphenylquinoxaline derivatives,[62,63] benzophenones,[64–71] carbazoles,[72–87] silyl glyoximides,[88] Bodipy,[89–94] imidazole derivatives,[95] truxene derivatives,[96] cyanines,[97–103] naphthalimides,[104–122] Schiff bases,[123] triphenylamines,[124,125] anthracene,[126] metal organic framework (MOFs),[41,127,128] furan derivatives,[129] benzylidene ketones,[27,28] push-pull dyes,[42,130–144] perylenes,[145–148] quinoxalines,[62,149–161] pyrenes,[162–170] polyoxometalates,[171–173] chromones and flavones,[174–176] pyridinium salts,[177,178] phenothiazines,[179–189] coumarins,[190–203] camphorquinones,[204,205] iodonium salts,[89,104,206–214] iridium complexes,[215–222] thioxanthenes,[89,223–237] chalcones,[14,238–253] gold complexes,[254]

copper complexes,[255–272] helicenes,[273,274] zinc complexes,[275] squaraines, [276–280] pyrrole derivatives,[281,282] conjugated polymers,[283] acridones,[284,285] acridine-1,8-diones,[286–288] bisacylphenylphosphine oxide,[289] and phenazines.[290] Among structures that have been investigated for the design of photoinitiators, anthraquinone can be cited as a scaffold that was under-investigated compared to other structures. Besides, anthraquinone was extensively used for the design of various semi-conductors, chromophores and light-emitting materials for organic electronics.[291–294] Anthraquinone was also employed for the design of various laxatives, antimicrobial and anti-inflammatory agents.[295–297] As far as photopolymerization is concerned, the first report mentioning the use of anthraquinone as photoinitiator of polymerization was reported as soon as 1957 by Tordoff and coworkers.[298] In this pioneering work, the polymerization of acrylamide in aqueous solution sensitized by hydrogen peroxide and 9,10-anthraquinone-2,6-disulfonic acid disodium salt was examined. Besides, upon irradiation with a 366 nm light, the reaction proved to be too complex to be controlled. In 1960, Hermans and coworkers examined the grafting of various monomers on the cellulose backbone using 9,10-anthraquinone-2,6-disulfonic acid disodium salt as the photosensitizer.[299] Noticeably, presence of oxygen was determined as enhancing the grafting efficiency on cellulose, resulting from the in-situ formation of hydroperoxyl radicals. A systematic study was proposed in 1968 by Anwaruddin and coworkers in which 9,10-anthraquinone-2,6-disulfonic acid disodium salt, 9,10-anthraquinone-2,7-disulfonic acid disodium salt and 9,10-anthraquinone-2-sulfonic acid sodium salt were used as photosensitizers for the aqueous polymerization of acrylamide under inert atmosphere.[300] Interestingly, addition of sodium chloride in water totally suppressed the induction time, which varied between 2 and 3 hours without NaCl. A photoinduced electron transfer between the chlorine anion and the excited anthraquinone derivative was proposed as the initiating step. A similar reduction of the inhibition time could be demonstrated using 9,10-anthraquinone-2,7-disulfonic acid disodium salt and ferric chloride during the photoinduced grafting of methyl methacrylate (MMA) on cellulose.[301] However, this approach proved to be ineffective to form hydrogels with poly(*N*-isopropylacrylamide).[302] By using the water-soluble two-component 9,10-anthraquinone-2-sulfonic acid sodium salt/(4-benzoylbenzyl) trimethylammonium chloride system, grafting of acrylamide and *N*-isopropylacrylamide on polyethylene was obtained, enabling an efficient surface modification.[303] Thus, the hydrophobic nature of the poly(ethylene) surface could be converted as a hydrophilic one. Photocrosslinking of polyethylene was also investigated by Kachan and coworkers in 1986 and investigation of the photochemical mechanism with 9,10-anthraquinone as the photoinitiator revealed photocrosslinking to occur during photoreduction of the dye.[304] In 1975, Taylor and coworkers reported the photopolymerization of methyl methacrylate (MMA) in THF under aerobic and anaerobic conditions using anthraquinone and 2-*tert*-butylanthraquinone.[305] Photolysis experiments done in THF as the solvent revealed the mechanism to involve a hydrogen abstraction from THF by the excited anthraquinone, generating THF radicals (THF•). A similar mechanism of hydrogen abstraction was also evidenced with other solvents such as cyclohexane or isopropanol,[306] but also with triethylamine, generating α -aminoalkyl radicals.[307] Extractability of photoinitiators can drastically limit the potential use of polymers and this issue was examined with the design of

anthraquinone-based macrophotoinitiators.[308,309] By introducing an acrylamide group on anthraquinone, the anthraquinone chromophore could serve as a photosensitizer for its own polymerization using lauroyl peroxide. In the presence of MMA, copolymer could be prepared with different 2-substituted amido and acryloxy-anthraquinones.[310] By use of water-soluble co-monomers such as acrylamide, 2-acrylamido-2-methylpropane sulphonic acid and 2-acryloxyethyl trimethylammonium iodide, water-soluble copolymers comprising anthraquinone units could be obtained.[311] By the presence of crosslinkable groups on anthraquinones, grafting of anthraquinones onto nylon-6,6-polymer could also be successfully obtained.[312,313] Positions of the lowest singlet excited state π - π^* relative to the triplet $n\pi^*$ state was determined as playing an important role in photopolymerization.[314,315] Thus, without amine, all anthraquinone derivatives bearing electron-withdrawing groups proved to be more reactive than those bearing electron-donating groups. A different situation was found in the presence of amine. In this case, halogenated anthraquinones proved to be more reactive than the others. Anthraquinones were not only used for initiating the polymerization of acrylates and epoxides. The polymerization of styrene was notably examined in 2009 by Sakurai and coworkers with a series of 1-(arylmethoxy)-9,10-anthraquinones.[316] Here again, a strong influence of the substitution pattern of anthraquinones was evidenced during the polymerization of styrene, and better monomer conversions were obtained for the naphthalene-substituted anthraquinones compared to the phenyl-substituted ones. Hybrid polymerizations of styrene and epoxides was also examined in this work and could be possible due to the concomitant formation of arylmethyloxy radicals and arylmethyl carbocations. Photodegradation of polymers was also another major concern of polymerists and the photodegradation of poly(styrene) was notably examined.[317–319] Use of anthraquinone as a photosensitizer capable to initiate the crosslinking of alkali-soluble polymers bearing double bonds from both acrylate and maleic acid monoester groups was also examined. By using trimethylolpropane trimethacrylate (TMPTMA) as a diluent monomer, hydrogels containing up to 85% water could be prepared.[320] Finally, investigations of anthraquinones as photosensitizers was not limited to one-photon polymerization and the first examples of two-photon photosensitizers based on anthraquinone were reported in 2007 by Kawata and coworkers.[321] In order to get a large two-photon absorption cross-section, an oligo(phenylene-vinylene)-type structure was used for the design of the two photosensitizers, enabling to get two-photon absorption cross-sections of 1635GM and 995GM at 800 nm. The design of pressure sensitive adhesives using an anthraquinone-based photoinitiator was also recently reported in the literature. Influence of the photoinitiator concentration, the UV dose used for polymerization, and the rate of crosslinking was determined as impacting the mechanical properties of the pressure-sensitive adhesives.[322]

In this review, the different anthraquinone derivatives that have been developed since 2010 are presented. A wide range of structures have been proposed in light of the rich history concerning the design of anthraquinone-based photoinitiators. Notably, metal complexes, phthalocyanine, water-soluble dyes or biosourced anthraquinones have been investigated for photopolymerization. In these different works, comparisons have been established to evidence the interest of these structures.

2. Anthraquinone-based photoinitiators of polymerization

2.1. Biosourced anthraquinones.

Investigations of natural dyes as photoinitiators of polymerization is an active research field, supported by the fact that these dyes are often abundant and exhibit only a low toxicity.[323] In this field, one of the most popular natural dye in photopolymerization is undoubtedly curcumin which was at the basis of numerous photoinitiating systems.[23–26,324–326] By polymerizing polymethacrylates, biocompatible polymers could be obtained, the resulting polymers being not toxic for fibroblast HS-26 cells.[23] 9,10-Anthraquinone derivatives can also be extracted from numerous plants and four derivatives, namely 1,8-dihydroxyanthraquinone (18-DHAQ, chrysazine), 1,2-dihydroxyanthraquinone (12-DHAQ), 1,4-dihydroxyanthraquinone (14-DHAQ, quinizarin) and 1,5-dihydroxyanthraquinone (15-DHAQ) were tested as photoinitiators for the free radical photopolymerization (FRP) of multifunctional monomers, reversible addition-fragmentation chain transfer (RAFT) polymerization of monofunctional monomers and the cationic polymerization of epoxides (See Figure 2).[22] Notably, chrysazine and hypericin can be both extracted from a flowering plant named *Hypericum* genus. Hypericin is notably used in the photodynamical therapy of cancer[327] and chrysazine as a laxative.[328] On their sides, 12-DHAQ, 14-DHAQ (quinizarin) also exhibit biological activities as anticancer drugs by their remarkable abilities to bind to DNA.[329] Concerning 15-DHAQ, this molecule is used since 1916 as an antipsoriasis drug.[330]

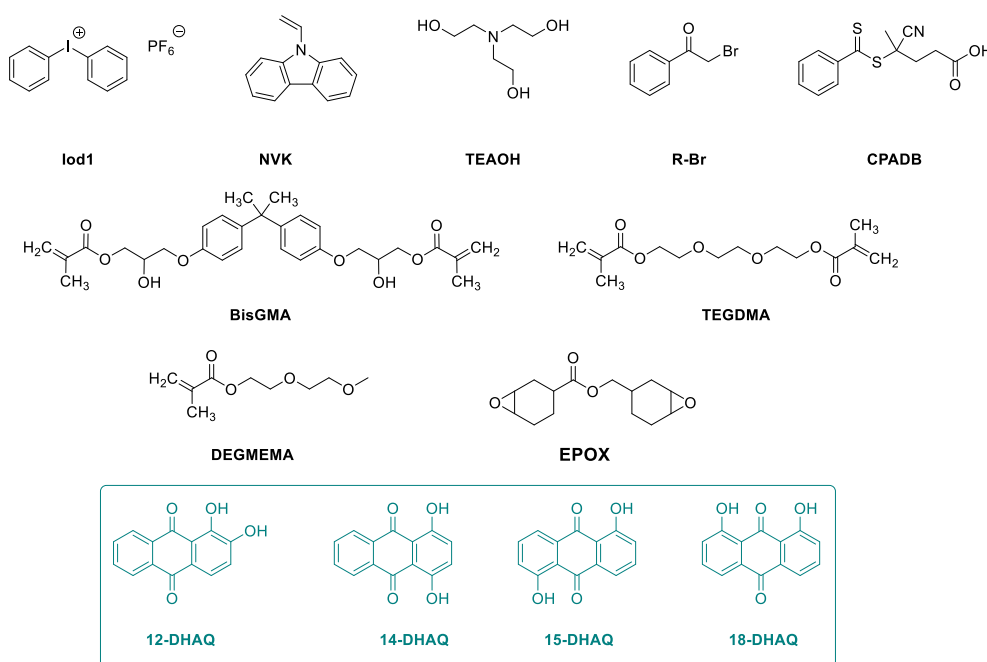


Figure 2. Chemical structures of 12-DHAQ, 14-DHAQ, 15-DHAQ, 18-DHAQ, different monomers and additives.

In 2016, Xiao and coworkers investigated the four dyes as blue light sensitive photoinitiators. Indeed, as shown in the Figure 3 and Table 1, UV-visible absorption spectra in acetonitrile revealed 15-DHAQ and 18-DHAQ to absorb at the same positions, in the 350-500

nm range whereas a redshift of the absorption was detected for 14-DHAQ (375-550 nm range). In the case of 12-DHAQ, its absorption spectrum could not be acquired in acetonitrile due to its insolubility. It therefore clearly evidenced the crucial influence of the substitution pattern on the solubilities of dyes but also on their absorption properties.

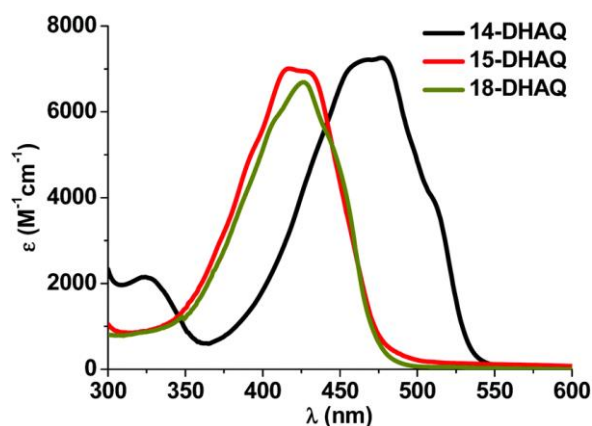


Figure 3. UV-visible absorption spectra of three dihydroxyanthraquinones **14-DHAQ**, **15-DHAQ**, **18-DHAQ** recorded in acetonitrile. Reproduced with permission from Ref. [22].

Table 1. Light absorption properties of the studied anthraquinone derivatives: absorption maxima λ_{\max} , extinction coefficients at λ_{\max} and at the maximum emission wavelengths of the different LED bulbs

| compounds | λ_{\max} (nm) | ϵ_{\max} ($M^{-1}\cdot cm^{-1}$) | $\epsilon_{455\text{ nm}}$ ($M^{-1}\cdot cm^{-1}$) | $\epsilon_{518\text{ nm}}$ ($M^{-1}\cdot cm^{-1}$) |
|-----------|-----------------------|---|--|--|
| 14-DHAQ | 477 | 7200 | 7000 | 3000 |
| 15-DHAQ | 417 | 7000 | 3500 | 150 |
| 18-DHAQ | 426 | 6700 | 3900 | 50 |

Theoretical calculations done on the different dyes revealed the electronic distribution to be totally different between dyes (See Figure 4). Thus, the highest occupied molecular orbital (HOMO) was determined to be located onto the polyphenol moieties whereas the lowest unoccupied molecular orbital (LUMO) was centered onto the quinone moiety. Especially, the two hydroxy groups of 14-DHAQ contribute to the HOMO orbital, supporting its redshifted absorption compared to 15-DHAQ and 18-DHAQ for which a weaker contribution to the HOMO orbital was found.

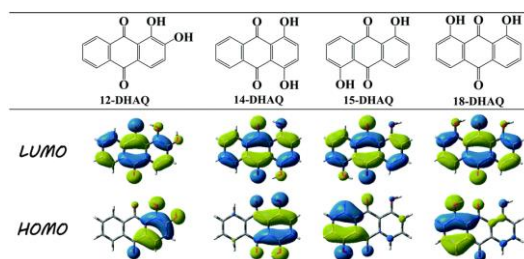


Figure 4. Contour plots of the HOMO and LUMO energy levels of dihydroxyanthraquinone using DFT at the UB3LYP/6-31G* level. Reproduced with permission from Ref. [22].

In order to investigate their photoinitiating abilities during the FRP of a blend of multifunctional methacrylate monomers i.e. bisphenol A-glycidyl methacrylate (BisGMA)/triethyleneglycol dimethacrylate (TEGDMA), two different three-component systems were examined. First, by using the three-component dye/Iod/NVK (0.5%/2%/3%, wt%) system (where Iod and NVK respectively stand for diphenyliodonium hexafluorophosphate and *N*-vinylcarbazole), the highest monomer conversion was obtained with 18-DHAQ, furnishing 56% conversion after 300 s of irradiation at 455 nm with a LED. This value is close to that obtained with the second three-component dye/TEAOH/R-Br (0.5%/2%/3%, wt%) system (where TEAOH and R-Br respectively stand for triethanolamine and phenacyl bromide) for which a conversion of 55% was determined. Following 18-DHAQ in terms of reactivity, 14-DHAQ was the second most efficient photoinitiator of the series (40 and 48% for the dye/Iod/NVK (0.5%/2%/3%, wt%) system and dye/TEAOH/R-Br (0.5%/2%/3%, wt%) system respectively) (See Figure 5). Comparison with camphorquinone (CQ) which a benchmark photoinitiator revealed 18-DHAQ to outperform camphorquinone, irrespective of the photoinitiating system used. Interestingly, photopolymerization experiments could be successfully done at 518 nm with 14-DHAQ and 18-DHAQ, despite the weak molar extinction coefficient of 18-DHAQ at 518 nm (See Figure 6).

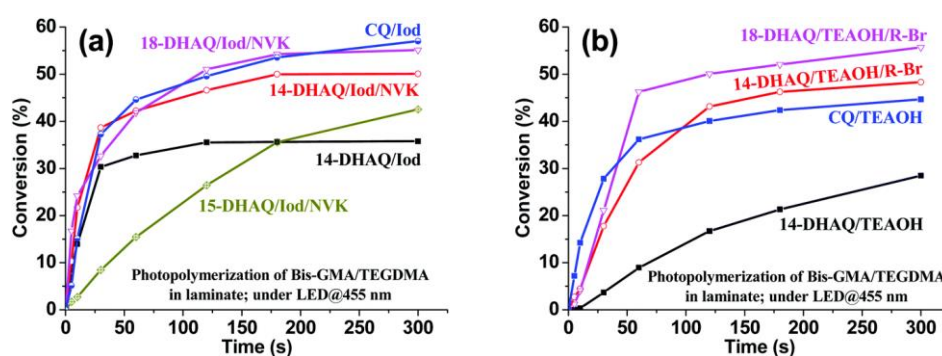


Figure 5. Monomer conversions obtained during the FRP of Bis-GMA/TEGDMA blend (70%/30%, w/w) in laminate in the presence of (a) dye/Iod/NVK (0.5%/2%/3%, wt%) and CQ/Iod (0.5%/2%, wt%) as the reference. (b) Dye/TEAOH/R-Br (0.5%/2%/3%, wt%) and CQ/TEAOH (0.5%/2%, wt%) as the reference, irradiation at 455 nm. Reproduced with permission from ref. [22]

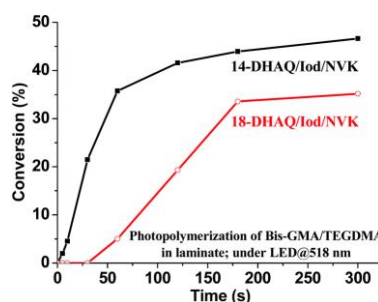
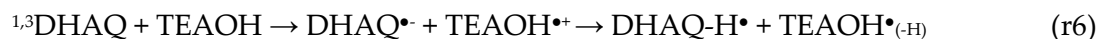
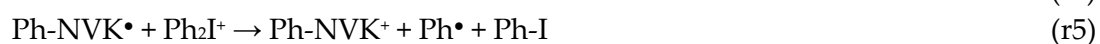
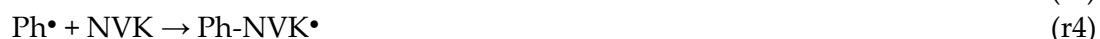


Figure 6. Monomer conversions obtained during the FRP of Bis-GMA/TEGDMA blend (70%/30%, w/w) in laminate in the presence of dye/Iod/NVK (0.5%/2%/3%, wt%), irradiation at 518 nm. Reproduced with permission from ref. [22]

To support the remarkable photoinitiating abilities of 14-DHAQ and 18-DHAQ, photochemical mechanism was investigated by mean of complementary techniques including photolysis experiments, electron spin resonance (ESR) experiments and cyclic voltammetry. The following mechanism was proposed by the authors. Thus, upon photoexcitation of the dye, a photoinduced electron transfer between the excited dye and the iodonium salt can occur (see r2 and r3, Scheme 1), producing initiating aryl radicals (Ph•) by decomposition of the unstable iodine radical. Reactivity of the aryl radicals can be improved upon introduction of NVK, generating the highly reactive Ph-NVK• (see r4). Parallel to this, cations can also be formed by equation (r5), enabling to initiate the cationic polymerization of epoxides. In the case of the second photoinitiating system, a different mechanism takes place, based on a photoinduced electron transfer followed by a hydrogen abstraction process, enabling to generate DHAQ-H• and TEAOH•(-H) radicals (See equation r6). By reaction with phenacyl bromide, initiating radicals R• can be formed (See equation r7). Noticeably, no direct correlation between the molar extinction coefficient and the monomer conversion could be evidenced, 15-DHAQ and 18-DHAQ exhibiting similar absorption properties, but also the lowest and the highest monomer conversions. Therefore, it was concluded that other parameters such as the solubility in resins, the rate constant of electron transfer were governing the polymerization efficiency. Occurrence of a back electron transfer between 15-DHAQ and TEAOH or Iod was suggested as a plausible explanation supporting the lower polymerization efficiency of this dye.



Scheme 1. Chemical mechanism involved with the first (eq. r1-r5) and the second (eq. r6-r7) three-component photoinitiating systems.

Interestingly, promising results were obtained during photoRAFT experiments with a monofunctional monomer. By using di(ethylene glycol) methyl ether methacrylate (DEGMEMA) as the monomer and 4-cyanopentanoic acid dithiobenzoate (CPADB) as the RAFT agent, polymers of controlled size could be obtained ($M_n = 7500$ g/mol, $D = 1.14$) after four hours of irradiation at 455 nm using the three-component 18-DHAQ/Iod/CPADB (0.2%/0.8%/1% w/w/w) system. In the absence of the RAFT agent, a lower control of the polymerization process was obtained and a higher polydispersity was determined ($M_n = 31100$ g/mol, $D = 1.75$). Finally, the possibility of initiating the cationic polymerization of epoxides was examined during the CP of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX). Here again, the trend of reactivity previously established was confirmed, with 18-DHAQ outperforming the other dyes (See Figure 7).

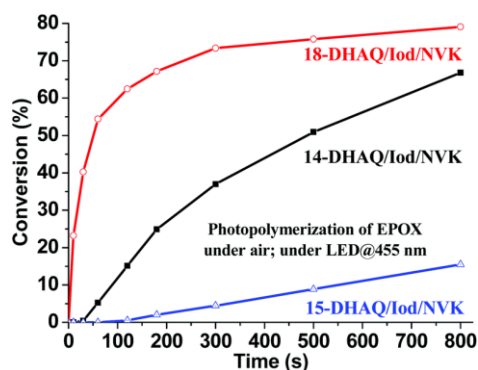


Figure 7. Monomer conversions obtained during the CP of EPOX using different three-component photoinitiating systems. Reproduced with permission from ref. [22]

In 2020, Versace and coworkers revisited quinizarin (i.e. 18-DHAQ) in the context of crosslinkable photoinitiators.[331] Two polymerizable groups were introduced, namely an epoxide and an allyl group (See Figure 8). In 2022, the methacrylated version Q1Ac and Q2Ac were proposed by the same authors.[332] Parallel to quinizarin, Versace and coworkers also developed the photopolymerizable version of purpurin (1,2,4-trihydroxyanthraquinone, 124-THAQ) and introduced one or three allyl groups (PmA and PA respectively).[333] It has to be noticed that the introduction of polymerizable units on anthraquinones has previously been reported in the literature by Ritter and coworkers in 2013.[334] In that work, by copolymerizing blue, green and red-absorbing dyes, copolymers with broad absorption could be obtained.

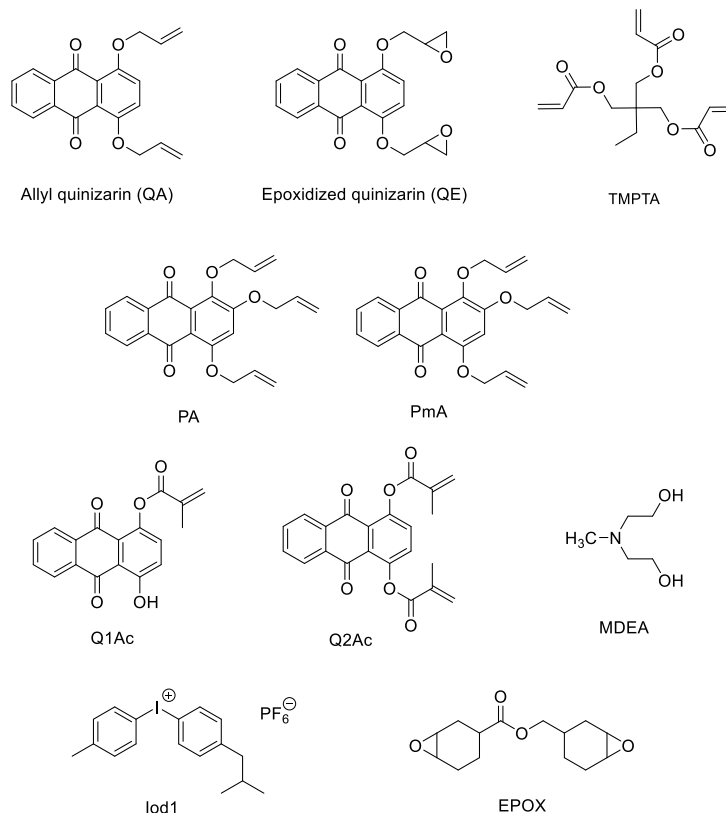


Figure 8. Chemical structures of crosslinkable quinizarin derivatives QA and QE.

Noticeably, upon alkylation of the phenol groups, a significant blueshift of the absorption maxima was found for ZA and ZE in acetonitrile ($\lambda_{\max} = 415$ and 407 nm respectively) compared to the parent structure quinizarin (QZ) ($\lambda_{\max} = 477$ nm) (See Figure 9). Molar extinction coefficients of 6000 and $5530 \text{ M}^{-1} \cdot \text{cm}^{-1}$ were also determined for the two dyes, greatly higher than that of camphorquinone ($66 \text{ M}^{-1} \cdot \text{cm}^{-1}$ at 466 nm). Based on their absorptions, polymerization experiments could be carried out at 405 , 455 and 470 nm.

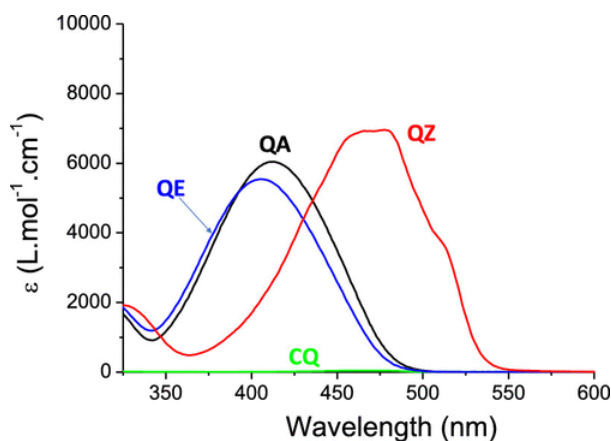


Figure 9. UV-visible absorption spectra of QA, QE and quinizarin (QZ) in acetonitrile. Reproduced with permission of Ref. [331]

During the CP of EPOX, the higher photoinitiating ability of the quinizarin derivatives (ZA and ZE) compared to the parent structure was demonstrated. Thus, if no monomer conversion could be detected with QZ and camphorquinone with the two-component dye/Iod1 system (where Iod1 stands for 4-(2-methylpropyl)phenyliodonium hexafluorophosphate), irrespective of the irradiation conditions, a conversion of 76% could be evidenced with ZA after 800 s of irradiation with a Xe lamp, higher than that obtained with ZE (57%). For all the other irradiation conditions, ZE greatly outperformed ZA in terms of monomer conversion (See Table 2). The same trend of reactivity was demonstrated during the FRP of TMPTA. If ZA could outperform ZE upon irradiation with a Xe lamp, a different situation was found with LEDs of narrower emission. Noticeably, good monomer conversions could be obtained with two different two-component systems based on MDEA or Iod1. However, a higher polymerization efficiency was determined with Iod1, evidencing the higher reactivity of the oxidative pathway. Here again, all photoinitiating systems based on QZ were less efficient than those based on ZA and ZE, attributable to the presence of phenolic groups on QZ acting as termination agents quenching the chain growth but also to the ability of phenols to act as inhibitors of polymerization.[335,336]

Table 2. EPOX and TMPTA conversions obtained with the two-component dye/Iod1 (0.5%/2.0%, wt%) or the two-component dye/MDEA (0.5%/2%, wt%) systems upon irradiation at different wavelengths for 800 s.

| EPOX conversion under air | | | | |
|---------------------------|------------|------------|------------|------------|
| | Xenon lamp | LED@405 nm | LED@455 nm | LED@470 nm |

| | | | | |
|------------------------------|------------|------------|------------|------------|
| CQ/Iod1 | n.p. | n.p. | n.p. | n.p. |
| QZ/Iod1 | n.p. | n.p. | n.p. | n.p. |
| QA/Iod1 | 76% | 56% | 43% | 52% |
| QE/Iod1 | 57% | 72% | 58% | 50% |
| TMPTA conversion in laminate | | | | |
| | Xenon lamp | LED@405 nm | LED@455 nm | LED@470 nm |
| CQ/MDEA | 39 | - | 40 | 44 |
| QZ/MDEA | 30 | 37 | 28 | 12 |
| QA/MDEA | 55 | 69 | 54 | 44 |
| QE/MDEA | 57 | 57 | 55 | 50 |
| CQ/Iod1 | 45 | - | 50 | 32 |
| QZ/Iod1 | n.p. | 15 | n.p. | n.p. |
| QA/Iod1 | 70 | 77 | 65 | 50 |
| QE/Iod1 | 75 | 80 | 66 | 36 |

n.p. no polymerization.

Finally, the concomitant polymerization of TMPTA and EPOX was examined, enabling to access to interpenetrated polymer networks (IPNs). Due to oxygen inhibition, higher TMPTA conversions were obtained in laminate than under air.[337] Conversely, due to the higher polymerization rate of TMPTA, a decrease of the EPOX conversion was determined in laminate compared to that determined under air (See Table 3).

Table 3. Monomer conversions obtained during the photopolymerization of an EPOX/TMPTA (50/50 w/w) blend upon irradiation at 455 nm for 800 s.

| QA/Iod (0.5/2.0%, w/w) | | QE/Iod (0.5/2.0%, w/w) | |
|------------------------|----|------------------------|----|
| under air | 72 | 48 | 49 |
| in laminate | 52 | 76 | 39 |

The most interesting result of this study concerned the antibacterial properties provided to IPNs by the presence of quinizarin derivatives. Indeed, the design of antibacterial materials is an active research field.[338] Due to the presence of the dyes within the polymer films, singlet oxygen could be produced at the surface of the irradiated films, enabling to provide antibacterial properties to the polymer films. Indeed, singlet oxygen formed by photosensitization with quinizarin can oxidize the olefinic double bonds of bacteria, leading to their deaths.[339,340]

Inspired by the photoinitiating abilities of natural anthraquinones, a series of three poly(hydroxy)anthraquinones was investigated by Xiao and coworkers, differing by the number of hydroxy groups but also by the substituent positions (See Figure 10).[341]

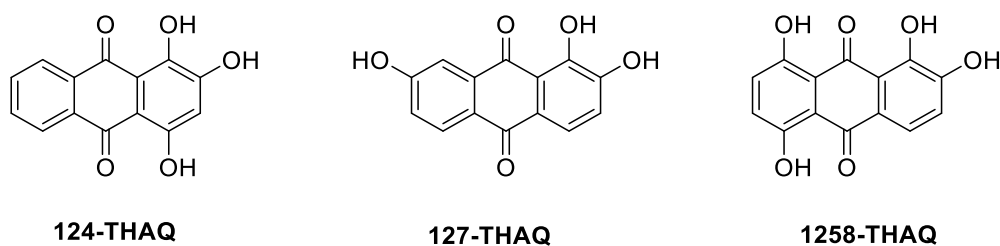


Figure 10. Chemical structures of different poly(hydroxy)anthraquinones.

In this series, 1,2,4-trihydroxyanthraquinone (124-THAQ, purpurin) is also a natural product that can be extracted from the roots of a madder plant (*Rubia cordifolia*), a plant which is of the same family from which quinizarin (1,4-dihydroxyanthraquinone) is extracted (*Rubia tinctorum*). For comparison, other non-natural poly(hydroxy)anthraquinone were investigated, namely 1,2,7-trihydroxyanthraquinone (127-THAQ, anthrapurpurin) and 1,2,5,8-tetrahydroxyanthraquinone (1258-THAQ, quinalizarin). In this series of dyes, all anthraquinones bearing hydroxy groups in *para*-position exhibited the most redshifted absorptions. Thus, 124-THAQ and 1258-THAQ exhibited absorption maxima at 477 and 480 nm contrarily to 411 nm for 127-THAQ that does not comprise two hydroxy groups in *para*-position to each other (See Figure 11). Based on their absorptions, polymerization experiments could be carried out at 518 nm (i.e. with green light) with all dyes.

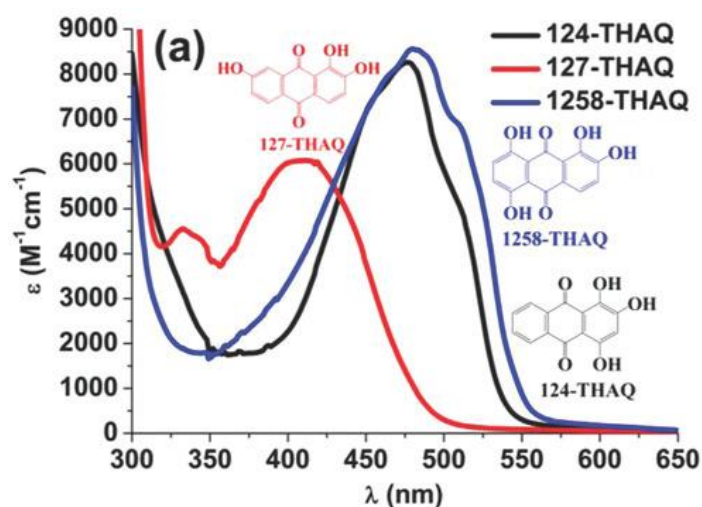


Figure 11. UV-visible absorption spectra of different poly(hydroxy)anthraquinones in acetonitrile. Reproduced with permission of Ref.[341]

Fluorescence quenching experiments done with Iod revealed the photobleaching to be very fast for 124-THAQ and 127-THAQ whereas almost no quenching was detected with 1258-THAQ, indicative of an inefficient electron transfer. A lower reactivity during FRP experiments can be thus anticipated for 1258-THAQ. During steady state photolysis experiments done in acetonitrile, if a decrease of the light absorption was detected for the two-component 124-THAQ and 1258-THAQ/Iod systems, no modification of the absorption properties was detected for the two-component system based on 127-THAQ, demonstrating

the non-reactivity of this system. Based on the fluorescence and steady state photolysis experiments, the following order of reactivity could be established: 124-THAQ, then 1258-THAQ and 127-THAQ. This trend of reactivity determined in solution was confirmed during the FRP experiments. Thus, during the FRP of a BisGMA/TEGDMA blend, monomer conversions of 41% could be determined with the two-component 124-THAQ/Iod (0.5%/2%, w/w) system, consistent with the aforementioned higher photochemical reactivity of 124-THAQ compared to the other dyes (36% with 1258-THAQ and no monomer conversion with 127-THAQ).

2.2. Amino-substituted anthraquinones.

Natural anthraquinones are mainly substituted with hydroxy groups and their photoinitiating abilities have been clearly demonstrated in the different aforementioned works. Inspired by these results, a series of amino-substituted anthraquinones was designed and examined as photoinitiators of polymerization. A series of three amino-substituted anthraquinones (DB1, DB3 and OBN) was reported in 2013 by Lalevée and coworkers (See Figure 12).[342] In this series of commercially dyes, various applications have been reported. Notably, aside from photopolymerization disperse blue 1 (DB1) and disperse blue 3 (DB3) are primarily used in hair colour formulations whereas oil blue N (OBN) is used for staining fatty substances in animal tissues. As the main interest of introducing amino groups on anthraquinones, absorptions at long wavelengths can be obtained. As shown in the Figure 13, DB1, DB2 and OBN exhibited absorption maxima located at 635 nm, therefore significantly red-shifted compared to that of the hydroxy-substituted quinizarin (477 nm). Benefiting from this redshifted absorption, polymerization experiments could be performed at 536 nm with a laser diode and at 630 nm with a LED.

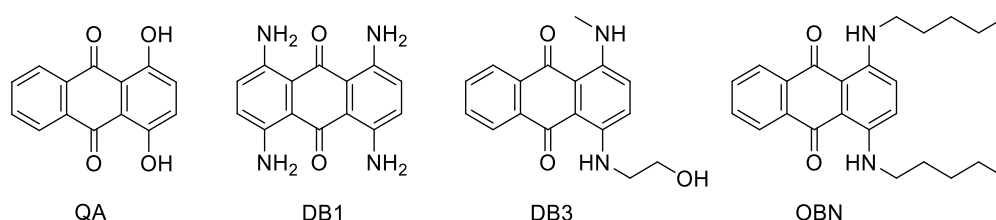


Figure 12. Chemical structures of different amino-substituted anthraquinones.

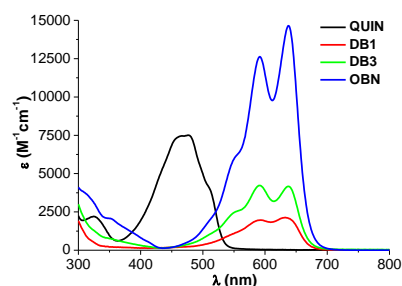


Figure 13. UV-visible absorption spectra of different amino-substituted anthraquinones recorded in acetonitrile. Reproduced with permission of Ref.[342]

Thiol-ene photopolymerization experiments done with trimethylolpropane *tris*(3-mercaptopropionate) (trithiol)/DVE (57%/43% w/w) blend revealed the two-component OBN/Iod (0.5%/2%, w/w) system to be remarkably performant upon irradiation with a laser diode (98% DVE conversion) or with a LED (68% conversion). However, a low trithiol conversion could also be determined (35 and 20% conversions), evidencing that DVE was also polymerizing with mean of a cationic process in competition with the thiol-ene polymerization (See Figure 14).

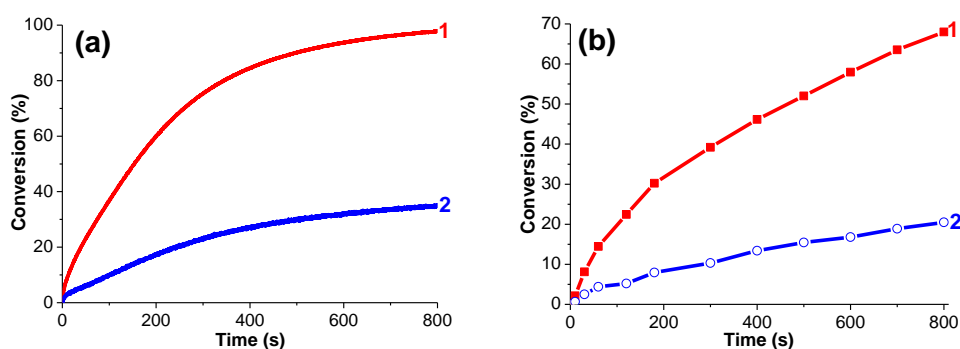
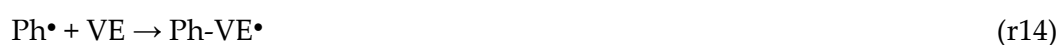
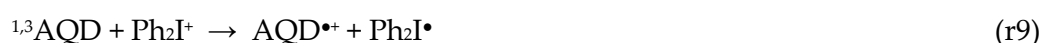


Figure 14. Polymerization profiles obtained during the thiol-ene polymerization of a Trithiol/DVE-3 (57%/43%, w/w) blend in laminate using the two-component OBN/Iod (0.5%/2%, w/w) system upon irradiation with (a) Laser diode at 635 nm (b) LED at 630 nm. Red curve: DVE-3 conversion, blue curve: trithiol conversion. Reproduced with permission of Ref.[342]

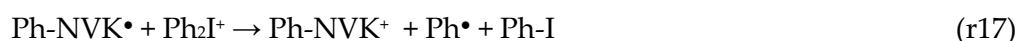
The two competing mechanisms are depicted in the Scheme 2, in equations r8-r15.



Scheme 2. Photochemical mechanisms involved in the thiol-ene polymerization and the cationic polymerization of DVE-3.

Cationic polymerization of EPOX with the different two-component dyes/Iod (0.5%/2% w/w) system revealed QA, DB1 and DB3 to be ineffective. Upon introduction of *N*-vinylcarbazole (NVK) to the photoinitiating system (3 wt%), only low EPOX conversions were obtained after 800 s of irradiation with a halogen lamp. Thus, conversions of 28, 38 and 59% were respectively obtained with the three-component OBN/Iod/NVK (0.5%/2%/3% w/w/w)

systems. The same trend of reactivity was confirmed during the FRP of TMPTA, OBN outperforming DB1 and DB3. For comparison, no polymerization could be detected with QA due to the insufficient absorption at these wavelengths, irrespective of the photoinitiating systems (See Table 4). To support the higher reactivity of the photoinitiating systems in the presence of NVK, the formation of Ph-NVK• radicals exhibiting a higher reactivity than the Ph• radicals was proposed (See Scheme 3).



Scheme 3. Mechanism of radical and cation generation occurring upon addition of NVK to the formulation.

Table 4. EPOX or TMPTA final conversions obtained upon exposure to the halogen lamp and the laser diode at 635 nm in the presence of anthraquinone derivative based PISs.

| PISs | Halogen lamp | | Laser diode at 635 nm | |
|----------------------------|-------------------|--------------------|-----------------------|--------------------|
| | EPOX ^a | TMPTA ^b | EPOX ^a | TMPTA ^b |
| Iod | 0 | | 0 | - |
| QA/Iod (0.5%/2%) | 0 | | - | - |
| QA/Iod/NVK (0.5%/2%/3%) | 0 | | - | - |
| DB1/Iod (0.5%/2%) | 0 | | - | - |
| DB1/Iod/NVK (0.5%/2%/3%) | 28% | | - | - |
| DB3/Iod (0.5%/2%) | 0 | | - | - |
| DB3/Iod/NVK (0.5%/2%/3%) | 38% | | - | - |
| OBN/Iod (0.5%/2%) | 53% | | 12% | 10% |
| OBN/Iod/NVK (0.5%/2%/3%) | 59% | | 24% | 13% |
| OBN/MDEA (0.5%/2%) | - | | 27% | 22% |
| OBN/MDEA/R-Br (0.5%/2%/3%) | - | | 28% | 25% |
| OBN (2%) | - | | 22% | 6% |
| OBN/R-Br (2%/3%) | - | | 25% | 8% |

^a photopolymerization under air for 800 s; ^b photopolymerization in laminate for 400 s.

If the polymerization efficiency is the focus of numerous studies, an interesting work done by Versace and coworkers on diaminoanthraquinone also focused on an application for the final polymers. In the present case, the design of antifouling and biocide coatings were examined.[343] In this work, 2,6-diaminoanthraquinone (AQD) was examined as a photoinitiator of polymerization in combination with Iod and benzyl alcohol for the cationic polymerization of epoxides (See Figure 15).

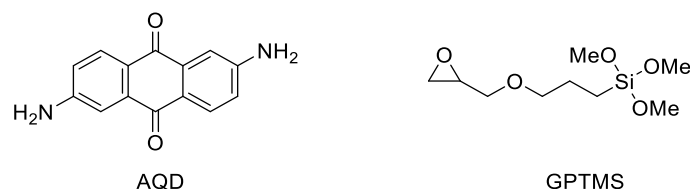
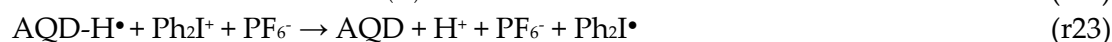
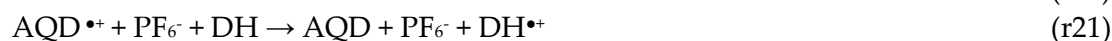
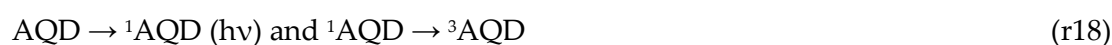


Figure 15. Chemical structure of AQD.

By electron spin resonance spin-trapping (ESR ST) experiments, a mechanism of hydrogen abstraction between AQD and benzyl alcohol (DH) could be evidenced, occurring directly from the excited dye or by mean of the phenyl radicals (See Scheme 4, equations r18-r24). As a result of this, HPF_6 and D^+ cations could be generated, improving the polymerization efficiency.



Scheme 4. Mechanism involved in the cationic polymerization of epoxides.

Due to the in-situ liberation of protic acid, 3-glycidyloxypropyltrimethoxysilane (GPTMS) could be hydrolyzed, enabling the formation of Si-O-Si bond between silane groups and thus the formation of a silica network concomitant to the formation of the polymer. By the presence of the GPTMS coating, anti-adhesion properties but also a biocide activity could be demonstrated for the epoxy-based polymers against Gram-negative bacteria (*E. coli*) and Gram-positive bacteria (*S. aureus*). Conversely, control experiments done for epoxy-based polymers not containing GPTMS coating did not exhibit any antibacterial or anti-adhesion properties.

On his side, Xiao and coworkers investigated a series of diamino-substituted anthraquinones (AHAQ, 14-DAAQ and 15-DAAQ) differing from AQD by the substitution pattern (See Figure 16).[344]

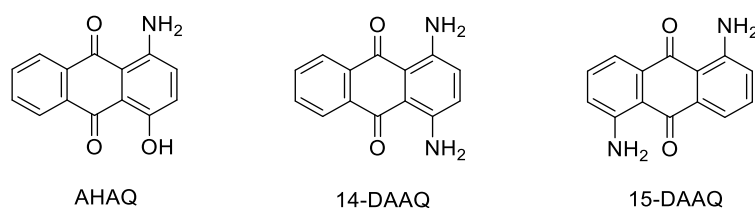


Figure 16. Chemical structures of AHAQ, 14-DAAQ and 15-DAAQ.

Here again, a strong influence of the substitution pattern could be evidenced, the absorption maxima varying from 479 nm for 15-DAAQ to 544 nm for 14-DAAQ and 522 nm

for AHAQ. As previously observed, the most redshifted absorption was found for 14-DAAQ bearing two amino groups in *para*-position from each other (See Figure 17).

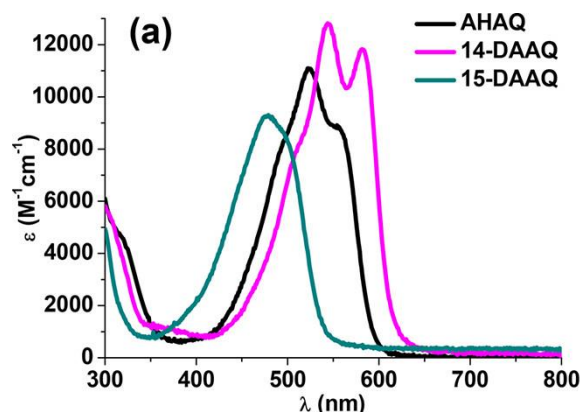


Figure 17. UV-visible absorption spectra of AHAQ, 14-DAAQ and 15-DAAQ in acetonitrile. Reproduced with permission of Ref. [344]

Photopolymerization experiments done at 455, 518, 594 and 636 nm evidenced the perfect adequation between absorption and reactivity. Thus, if a higher polymerization ability was found for 15-DAAQ at 455 and 518 nm, 14-DAAQ outperformed 15-DAAQ at 594 and 636 nm due to a better adequation of its absorption spectrum with the emission of the light sources.

Functionalization of the amino groups of anthraquinone by different structures was also investigated as a tool enabling to improve the solubility of dyes in resins, finely tune the absorption properties of anthraquinones but also to improve the free radical efficiency. Indeed, if OBN proved to be an efficient photoinitiator to promote the CP of EPOX in combination with Iod and NVK, the ability to initiate the FRP of TMPTA remained low. In 2019, Xiao and coworkers examined a series of diaminoanthraquinones bearing different groups as versatile multicolor photoinitiators activable under blue, green and red LED irradiations (See Figure 18), and capable to promote FRP, CP and even thiol-ene polymerizations.[345,346] As previously observed for DB1, DB3 and OBN, an absorption centered in the 500-700 nm range could be determined for SB36, SB68 and SG3 (See Figure 19). Absorption maxima at 638, 606 and 635 nm could be measured for SB36, SB68 and SG3, close to that of OBN (638 nm). It was thus determined that the functionalization of the amino groups of anthraquinone did not significantly affect the position of the absorption maxima.

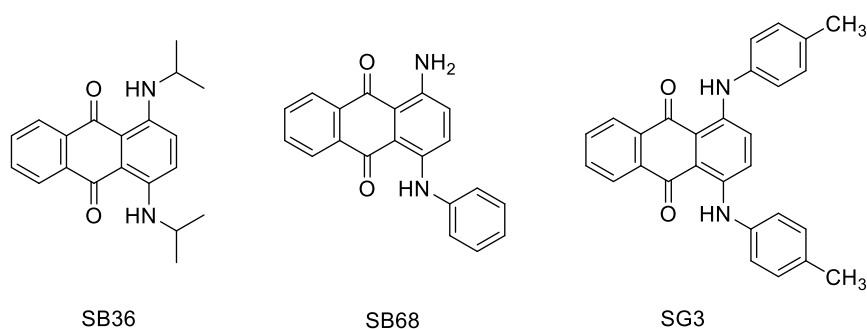


Figure 18. Chemical structures of SB36, SB68 and SG3.

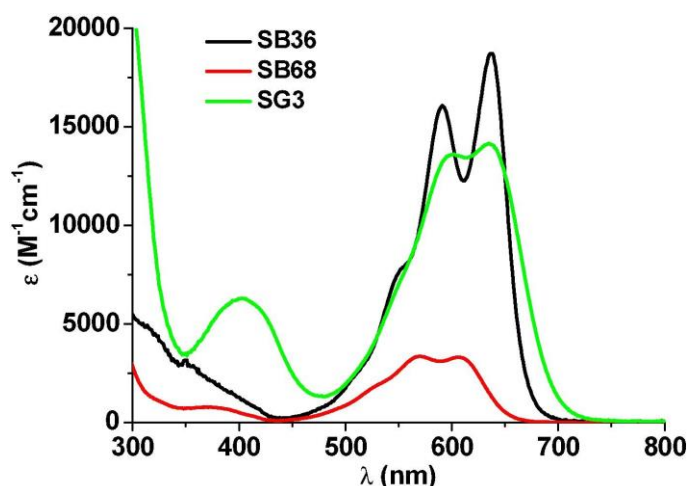


Figure 19. UV-visible absorption spectra of SB36, SB68 and SG3 in acetonitrile. Reproduced with permission of Ref.[345]

Noticeably, cationic polymerization of EPOX revealed the newly designed anthraquinone derivatives to give lower monomer conversions than OBN in three-component dye/Iod/NVK (0.5%/2%/3%, w/w/w) systems, except SB36 that could compete with OBN (56% conversion vs. 62% conversion with OBN (See Figure 20). To support this result, the higher reactivity of OBN^{•+} compared to SB36^{•+} was proposed. Noticeably, an improvement of the EPOX conversion could be obtained with OBN upon irradiation with a LED at 636 nm (62% conversion) compared to a laser diode at 635 nm (54% conversion) and this unexpected result was assigned to a better overlap of the absorption spectrum of OBN with the emission of LED compared to the laser diode. Investigation of SB36 during the FRP of TMPTA with the three-component SB36/Iod/NVK (0.5%/2%/3% w/w/w) systems revealed the TMPTA conversion to be lower than that obtained with OBN (18% conversions after 300 s of irradiation at 636 nm vs. 28% for OBN). Besides, by modifying the additives and by using the three-component dye/TEAOH/R-Cl system (where R-Cl stands for 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine), the conversion could be increased up to 42% in the same irradiation conditions.

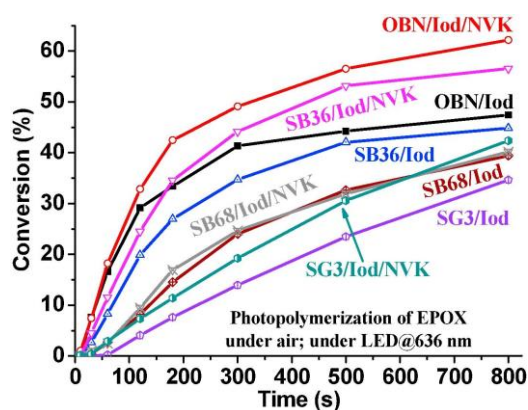


Figure 20. Polymerization profiles obtained during the CP of EPOX using different three-component AAQs/Iod(/NVK) (0.5%/2%/3%, w/w/w) systems upon irradiation with a LED at 636 nm. Reproduced with permission of Ref.[345].

Considering the high reactivity of SB36, thiol-ene polymerization with this dye was also studied with a wide range of monomers.[346] Finally, a series of mono-amino substituted anthraquinones (AAQ, MAAQ, and BAAQ) was studied by the same authors (See Figure 21).[347,348] As observed for the disubstituted ones, the CP of EPOX or the FRP of TMPTA could be efficiently promoted upon irradiation at shorter wavelengths compared to that used for the disubstituted ones (455 nm vs 635 nm), due to blue-shifted absorptions standing in the 350-600 nm range.

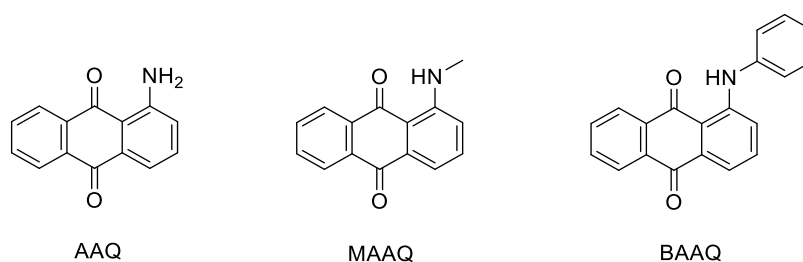


Figure 21. Chemical structures of AAQ, MAAQ and BAAQ.

2.3. Water-soluble anthraquinones.

The design of water-soluble photoinitiators constitutes one of the main challenges of the coming decades.[349] Indeed, with aim at developing polymerization processes more respectful from the environment, polymerization in water offers the possibility to polymerize in safer conditions. In order to provide water solubility, different approaches can be used. The first one consists in the chemical modification of water insoluble dyes. However, the main drawback of this approach is the number of synthetic steps that are required in order to access to the desired structures. With aim at developing water soluble dyes without extensive synthetic steps, an efficient strategy consisted in forming charge transfer complexes with a water-soluble molecule and in this field, the electron-donating triethanolamine has been extensively studied.[247,349] Encapsulation of organic dyes in cavities such as cyclodextrins or cucurbiturils constitutes another efficient strategy enabling to minimize the synthetic steps.[111,118] This strategy is notably based on a host-guest interaction between a hydrophobic cavity and a water-insoluble dye. In 2014, Duan and coworkers proposed a water soluble two-photon polymerization (TPP) initiator, namely 2,7-bis(2-(4-pentaneoxyphenyl)vinyl)anthraquinone (N) with a C_{2v} symmetry[350] whose structure was strongly inspired by his previous works done in 2007 on the same scaffold.[321] As the main difference, two pentoxy chains were introduced on N to improve the solubility in organic solvent but also improve its hydrophobicity (See Figure 22). In the present case, 2-hydroxypropyl- β -cyclodextrins (2-Hp- β -CDs) was used as the host for N, producing the water-soluble supramolecular structure WI. Upon encapsulation of N in 2-Hp- β -CDs, a blueshift of the absorption was detected, shifting from 328 nm in chloroform to 290 nm in water. A long tail extending up to 600 nm for WI was found, making this dye an interesting

photoinitiator under visible light. Examination of their optical properties in chloroform for N and water for WI revealed the two-absorption cross-section δ_{TPA} values to be of 600 GM at 820 nm and 300 GM at 770 nm respectively. Especially, for WI, a δ_{TPA} value of 200 GM at 780 nm could be determined in water, greatly higher than that of commercial photoinitiators.[351]

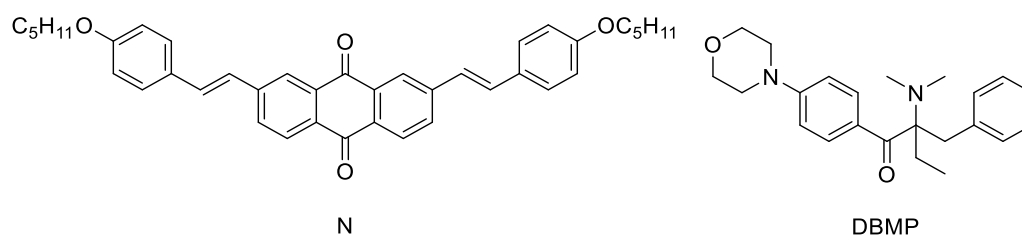


Figure 22. Chemical structure of N and DBMP.

Two-photon polymerization experiments done on poly(ethylene glycol) diacrylate (PEGDA) in water using WI as the initiator and 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (DBMP) as the photosensitizer revealed the threshold energy to be of 8.6 mW at the scanning rate of 10 $\mu\text{m/s}$. This value increased to 10.2 mW at the scanning rate of 50 $\mu\text{m/s}$. As shown in the Figure 23, smooth and continuous lines could be obtained while using 0.03 wt% of WI.

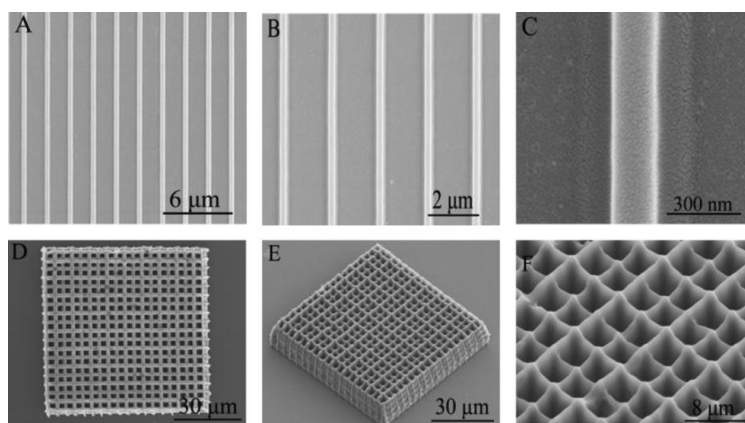


Figure 23. SEM images of TPP microfabrications using WI as the initiator. Reproduced with permission of Ref. [350]

2.4. Anthraquinone-based phthalocyanines

The design of panchromatic photoinitiators is an active research field supported by the fact that such photoinitiators are easier to excite with light than dyes exhibiting a narrower absorption.[49,89,120,229,264,277,285] Indeed, these dyes can be excited at different wavelengths while maintaining an excellent monomer conversion. Considering that anthraquinone exhibits an absorption centered in the 300-450 nm range, absorption spectra of anthraquinone could be extended by its covalent linkage to phthalocyanine.[352] Choice of phthalocyanine was also motivated by the ability of phthalocyanine to reduce oxygen inhibition during FRP experiments upon irradiation in the B band of phthalocyanines with a UV light.[353] Despite the wide range of phthalocyanines reported in the literature, use of phthalocyanines as photoinitiators remains scarce and attributable to the low solubility of

these structures.[354,355] In 2020, the functionalization of a zinc phthalocyanine (Zn-Pc) by peripheral anthraquinone units was examined by Versace and coworkers (See Figure 24).[352]

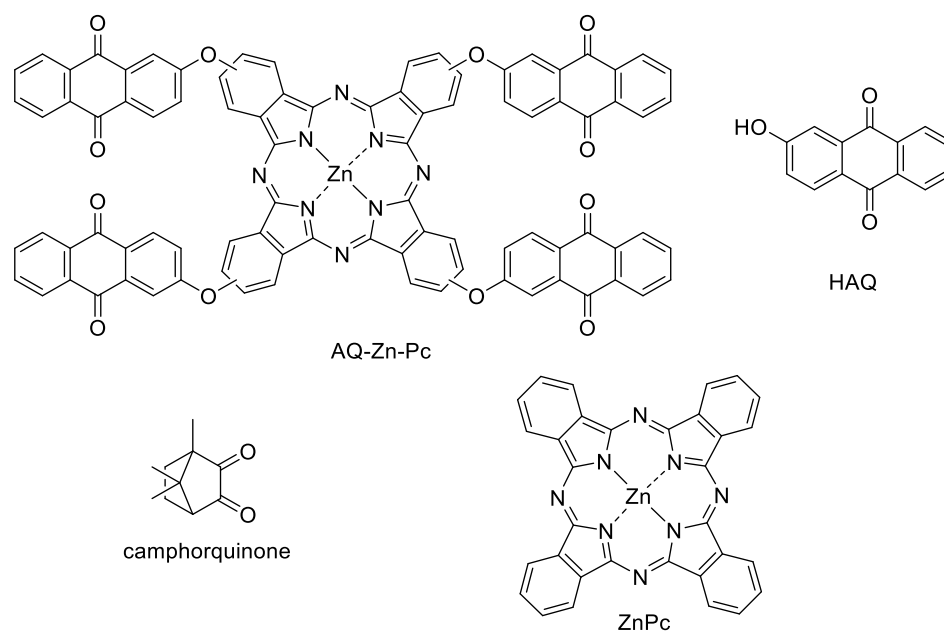


Figure 24. Chemical structures of AQ-Zn-Pc, ZnPc, HAQ and camphorquinone.

By attaching four anthraquinone units onto the phthalocyanine core, AQ-Zn-Pc could exhibit a molar extinction coefficient of $44\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ at 342 nm and $38\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ at 650 nm respectively in DMSO (See Figure 25), greatly higher than that of anthraquinone ($6\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ at 325 nm). Considering the broad absorption of AQ-Zn-Pc, photopolymerization experiments could be carried out at 385 , 405 , 455 and 470 nm with LEDs.

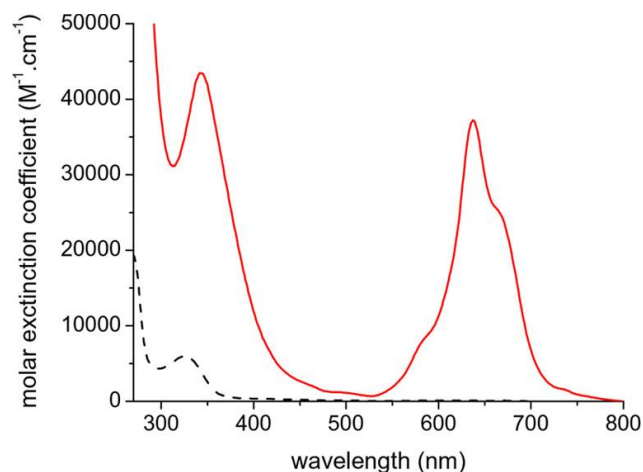


Figure 25. UV-visible absorption spectra of AQ-Zn-Pc in DMSO (red line) and anthraquinone (black line). Reproduced with permission of Ref.[352]

Among the different two-component systems used for the FRP of TMPTA, almost similar monomer conversions were obtained with the two-component AQ-Zn-PC/TT system (where TT stands for trimethylolpropane *tris*(3-mercaptopropionate)), the well-established AQ-Zn-PC/Iod2 system (where Iod2 stands for *bis*(4-methylphenyl)iodonium hexafluorophosphate) and the two-component AQ-Zn-PC /MDEA system (See Tables 5, 6 and

7). Especially, the highest monomer conversions were obtained at 385 and 405 nm, due to the high molar extinction coefficient of AQ-Zn-PC in the 300-400 nm range. Interest of the anthraquinone-phthalocyanine combination was demonstrated by comparing the photoinitiating abilities of AQ, HAQ and ZnPc. Thus, if the anthraquinone-phthalocyanine combination was capable to initiate a polymerization in the 385-530 nm range, this ability was considerably reduced for AQ, HAQ and ZnPC, the dyes considered separately being only able to initiate a polymerization between 385 and 405 nm.

Table 5. TMPTA conversions obtained in laminate using different two-component dye/TT (0.25%/5% w/w) photoinitiating systems based on AQ-Zn-Pc, AQ, CQ, 2-hydroxyanthraquinone (HAQ) and ZnPc upon irradiation with different LEDs and a Xenon lamp for 800 s.

| | 385 nm | 405 nm | 455 nm | 470 nm | 530 nm | Xe lamp |
|-------------|--------|--------|--------|--------|--------|---------|
| AQ-Zn-Pc/TT | 40% | 45% | 21% | 15% | 18% | 20% |
| AQ/TT | 50% | 33% | np | np | np | 27% |
| CQ/TT | | 40% | 39% | | | 40% |
| HAQ/TT | 50% | 60% | 33% | 10% | np | 40% |
| ZnPc/TT | 22% | 35% | np | np | np | np |

np: no polymerization

Table 6. TMPTA conversions obtained in laminate using different two-component dye/MDEA (0.25%/5% w/w) photoinitiating systems based on AQ-Zn-Pc, AQ, CQ, 2-hydroxyanthraquinone (HAQ) and ZnPc upon irradiation with different LEDs and a Xenon lamp for 800 s.

| | 385 nm | 405 nm | 455 nm | 470 nm | 530 nm | Xe lamp |
|---------------|--------|--------|--------|--------|--------|---------|
| AQ-Zn-Pc/MDEA | 50% | 50% | 25% | 20% | 20% | 50% |
| AQ/ MDEA | 50% | 40% | np | np | np | 42% |
| CQ/ MDEA | | 55% | 50% | | | 40% |
| HAQ/ MDEA | 45% | 55% | 25% | np | np | 30% |
| ZnPc/ MDEA | 7% | 21% | np | np | np | np |

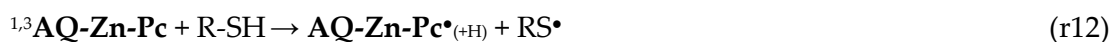
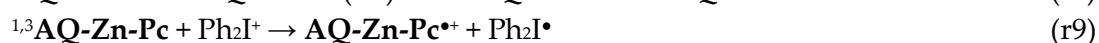
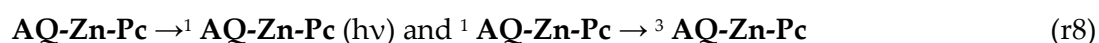
np: no polymerization

Table 7. TMPTA conversions obtained in laminate using different two-component dye/Iod2 (0.25%/5% w/w) photoinitiating systems based on AQ-Zn-Pc, AQ, CQ, 2-hydroxyanthraquinone (HAQ) and ZnPc upon irradiation with different LEDs and a Xenon lamp for 800 s.

| | 385 nm | 405 nm | 455 nm | 470 nm | 530 nm | Xe lamp |
|----------------|--------|--------|--------|--------|--------|---------|
| AQ-Zn-Pc/ Iod2 | 42% | 44% | 20% | 20% | 20% | 45% |
| AQ/ Iod2 | 55% | 59% | np | np | np | 34% |
| CQ/ Iod2 | | 40% | 50% | | | 38% |
| HAQ/ Iod2 | 60% | 60% | np | np | np | np |
| ZnPc/ Iod2 | np | 25% | np | np | np | np |

np: no polymerization

Comparison with reference systems based on camphorquinone revealed camphorquinone to outperform AQ-Zn-Pc at 455 nm due to the lack of absorption of AQ-Zn-Pc at this wavelength. Conversely, at 405 nm, similar monomer conversions were obtained with AQ-Zn-Pc and CQ. Besides, interest for AQ-Zn-Pc as photoinitiators still exists, polymerization experiments being possible at five different wavelengths. By combining the photolysis, fluorescence quenching and EPR experiments, the photochemical mechanism involved in the three different conditions could be established and are detailed in the Scheme 5.



Scheme 5. Chemical mechanism involved with the three two-component systems comprising AQ-Zn-Pc as the photoinitiator.

2.5. Anthraquinone-based metal complexes

Oxygen inhibition and extractability of photoinitiators are two major drawbacks numerous photoinitiating systems are facing. An interesting study was notably recently devoted to investigate the migratability of a series of 14 benchmark photoinitiators in food.[356] With aim at addressing these two drawbacks, a series of zirconium-based complexes was proposed by Allonas and coworkers, bearing benzophenone or anthraquinone-based ligands (See Figure 26).[357]

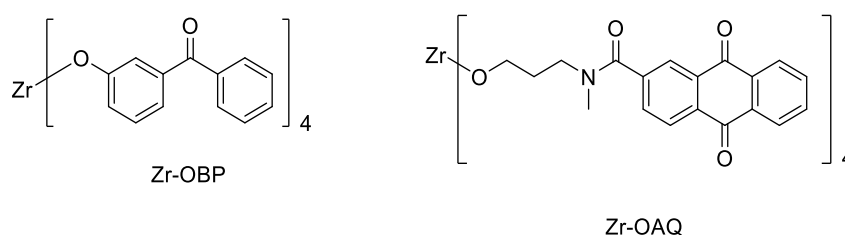


Figure 26. Chemical structures of zirconium-based complexes.

In terms of absorption properties, formation of the metal complexes contributed to improve the molar extinction coefficients, compared to the ligands considered alone. In the case of Zr-OAQ, a fourfold enhancement of the molar extinction coefficient can be evidenced, compared to the ligand AQ-N-OH ($32400 \text{ M}^{-1} \cdot \text{cm}^{-1}$ vs. $7400 \text{ M}^{-1} \cdot \text{cm}^{-1}$ for AQ-N-OH). Noticeably, a similar absorption maximum was found between the metal complex and the free ligand (388 nm). A different situation was found for Zr-OBP for which a blue shift by ca. 35 nm was found

between the ligand and the corresponding metal complex (325 nm vs 360 nm for BP-OH). Photopolymerization tests done on a bisphenol A diacrylate/1-6-hexanediol diacrylate (HDDA) blend (80/20) using the two-component dye/EDB systems revealed the two ligands to furnish low monomer conversions at low photoinitiator content. This issue could be addressed by increasing the concentration up to 2 mol%, enabling to get a final conversion around 60% with BP-OH and only 50% with AQ-N-OH, due to its low solubility in monomers. By using the corresponding complexes as photosensitizers, a significant increase of the monomer conversion could be detected, attributable to the simultaneous presence of four benzophenone and anthraquinone units capable to react with EDB (See Figure 27). By determining the depth conversion profile of the different samples, a significant reduction of the inhibited layer was determined for all samples polymerized with Zr-OAQ. The higher polymerization rates of the inhibited layer were assigned in the case of metal complexes used as photoinitiators to the ability of zirconium complexes to convert peroxy radicals as initiating radicals. This ability was notably previously demonstrated with a type I photoinitiator, namely diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO).[358] By ligand exchange with peroxy radicals, new initiating radicals could be produced according to the mechanism depicted in the Scheme 6.[358]

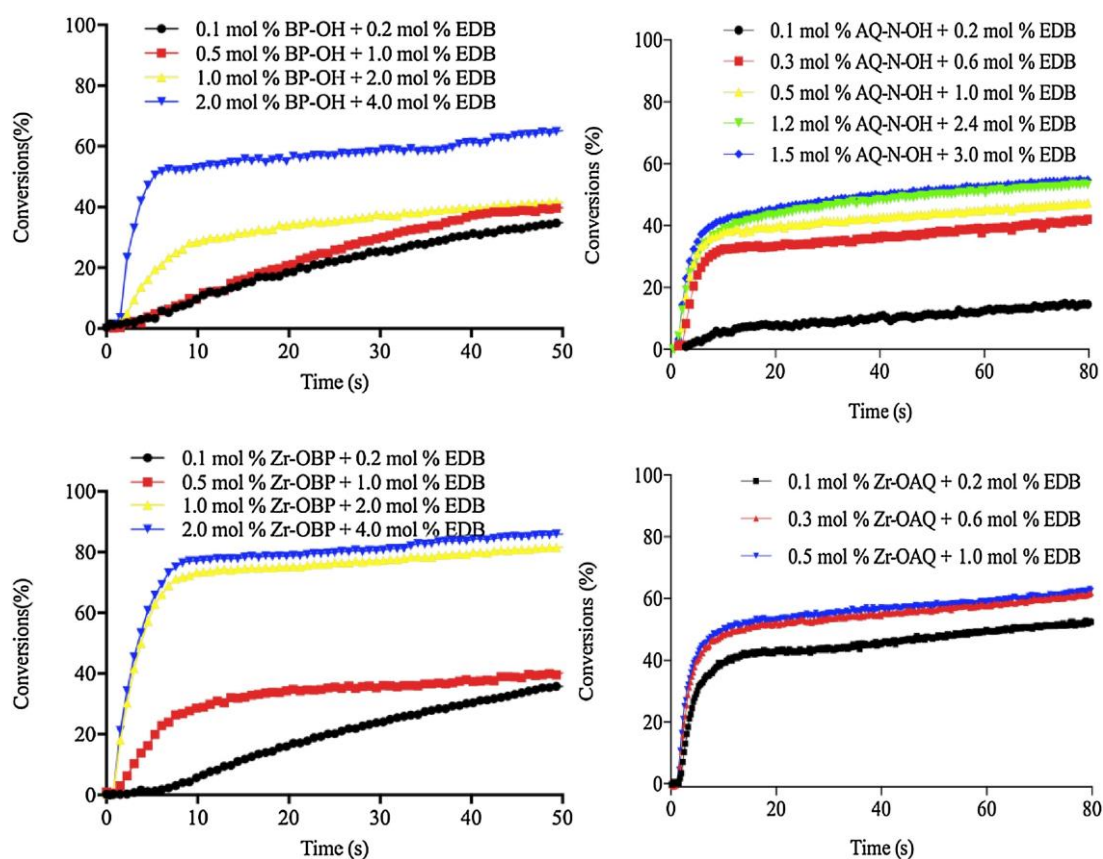
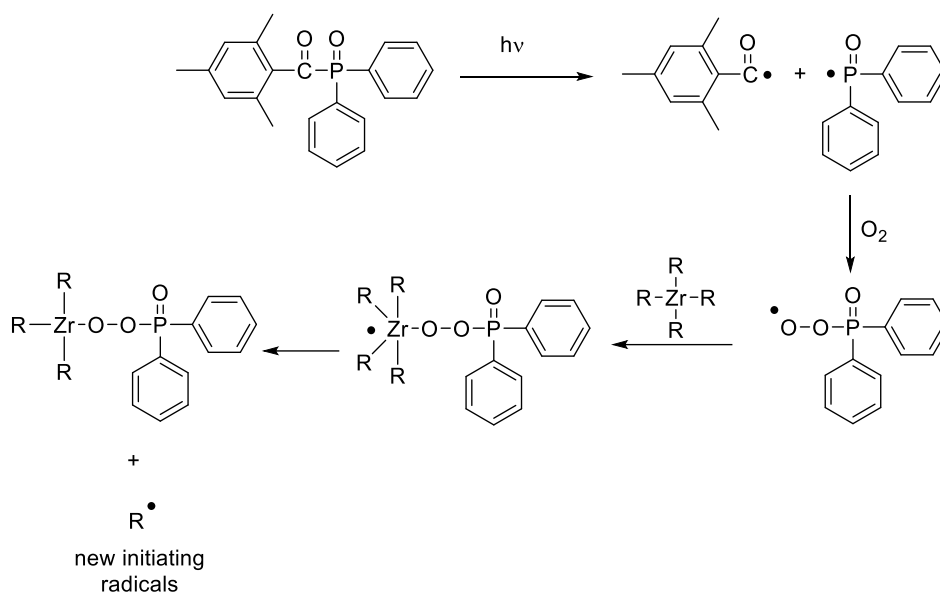


Figure 27. polymerization profiles obtained with different two-component dye/EDB systems upon irradiation by a UV light. Reproduced with permission of Ref. [357]



Scheme 6. mechanism enabling to overcome oxygen inhibition with zirconium complexes.

As shown in the Figure 28, an increase of the monomer conversion by going far from the surface could be evidenced.

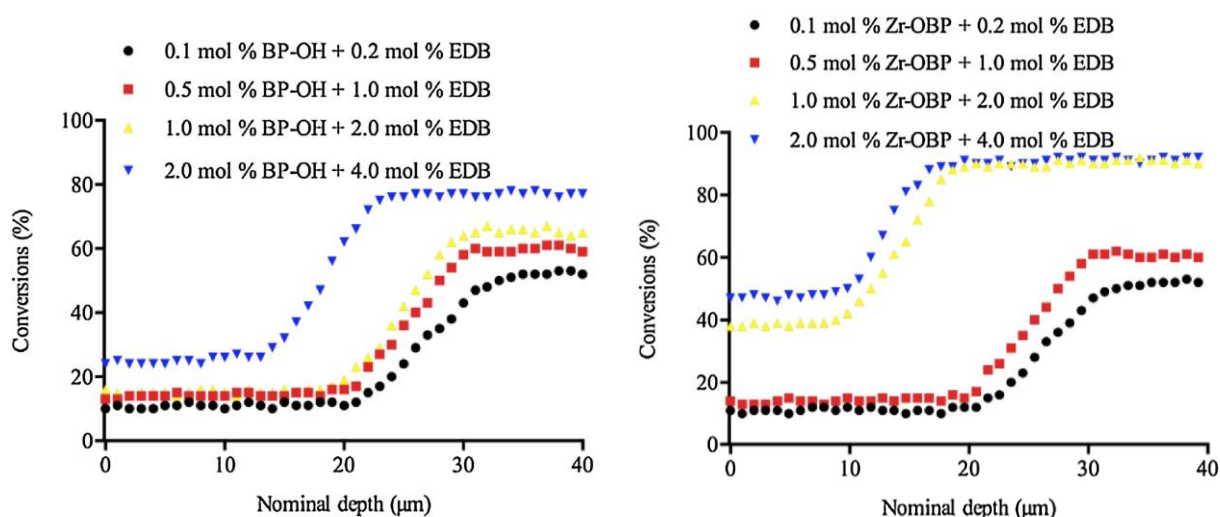


Figure 28. Monomer conversion determined as a function of the distance from the surface of the samples exposed to air. Reproduced with permission of Ref. [357]

2.6. Anthraquinone derivatives as monocomponent photoinitiating systems

As stated above, all anthraquinone derivatives have been investigated in combination with different additives, anthraquinones considered alone being unable to initiate any polymerization processes. This point was addressed in 2021 with the development of Q3 and Q4 that could act as monocomponent photoinitiators (See Figure 29).[359] Their photoinitiating abilities were notably examined with the previously reported allyl quinizarin QA and Q3 bearing allyl groups. Interestingly, Q4 exhibited an absorption maximum at 368

nm ($\epsilon = 5893 \text{ M}^{-1}\cdot\text{cm}^{-1}$), with a tail extending up to 450 nm. Compared to QA and Q3, a blue shift of the absorption of Q4 was found ($\lambda_{\text{max}}(\text{QA}) = 413 \text{ nm}$, $\lambda_{\text{max}}(\text{Q3}) = 487 \text{ nm}$), evidencing the crucial importance of unsubstituted phenol groups to get an absorption centered in the visible range (See Figure 30). Photolysis experiments done in acetonitrile and under air revealed the photolysis process to be very fast at 365 nm but slow at 405 nm (See Figure 31), indicating the low photochemical activity of this dye at 405 nm. A different situation was found for the two-component Q4/Iod combination for which an efficient photobleaching of the solutions could be demonstrated both at 365 and 405 nm.

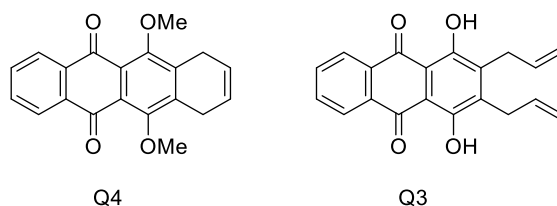


Figure 29. Chemical structure of Q4.

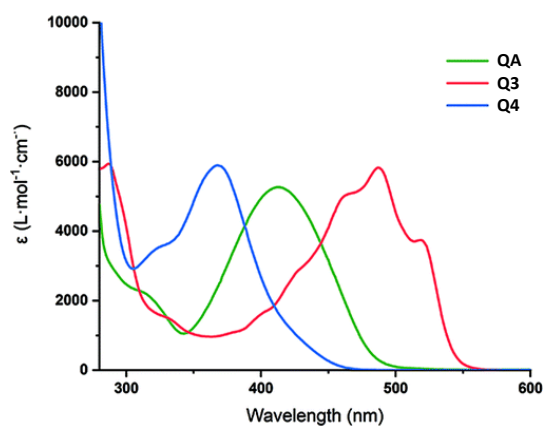


Figure 30. UV-visible absorption spectra of QA, Q3 and Q4 in acetonitrile. Reproduced with permission of Ref. [359]

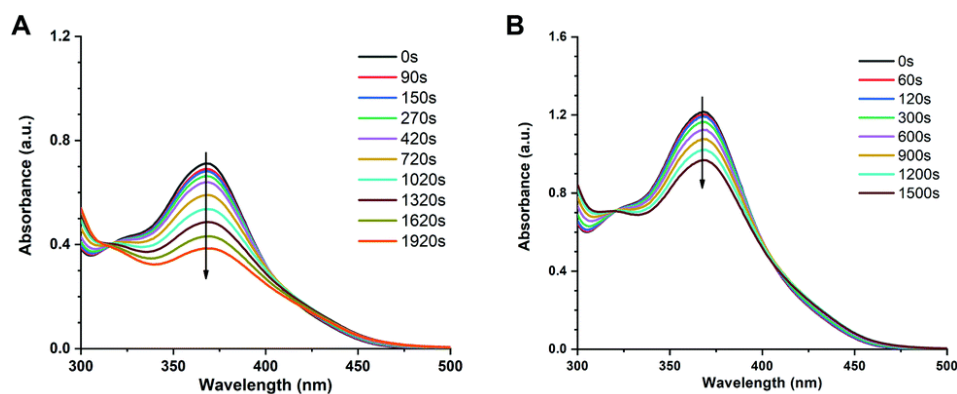
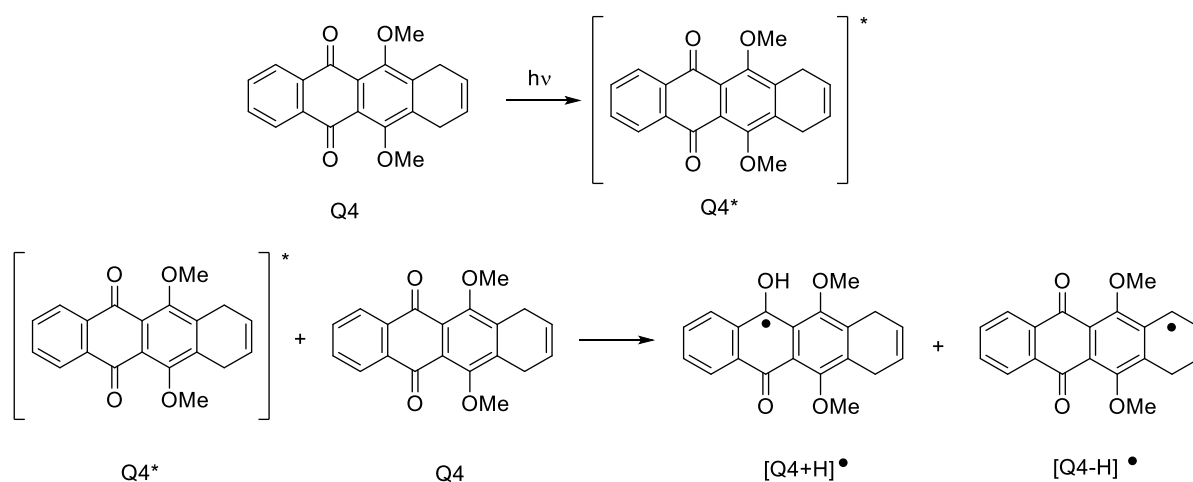


Figure 31. Steady state photolysis experiments done at 365 nm (A) and 405 nm (B) for Q4 in acetonitrile under air. Reproduced with permission of Ref. [359]

To support the efficient photobleaching detected in solution but also its ability to act as monocomponent system, the following mechanism was proposed, based on theoretical calculations (See Scheme 7).



Scheme 7. Mechanism of photoinitiation proposed with Q4.

Notably, upon photoexcitation of Q4, an intermolecular hydrogen abstraction process in the excited state can occur, producing two initiating radicals [Q4+H]• and [Q4-H]•. Theoretical calculations also revealed [Q4-H]• radicals to be less reactive than [Q4+H]• radicals due to a more localized single electron and a higher steric hindrance around the odd electron. Comparison of the photoinitiating abilities of QA, Q3 and Q4 during the FRP of TPGDA and HDDA used as monocomponent systems revealed QA and Q4 to exhibit similar reactivities in TPGDA and HDDA both at 365 and 405 nm. A lower reactivity of QA compared to Q4 could however be evidenced at 405 nm in HDDA, even if a similar monomer conversion could be obtained after 800 s of irradiation. Due to a low absorption of Q3, a lower monomer conversion was obtained in both monomers irrespective of the irradiation wavelength (See Figure 32).

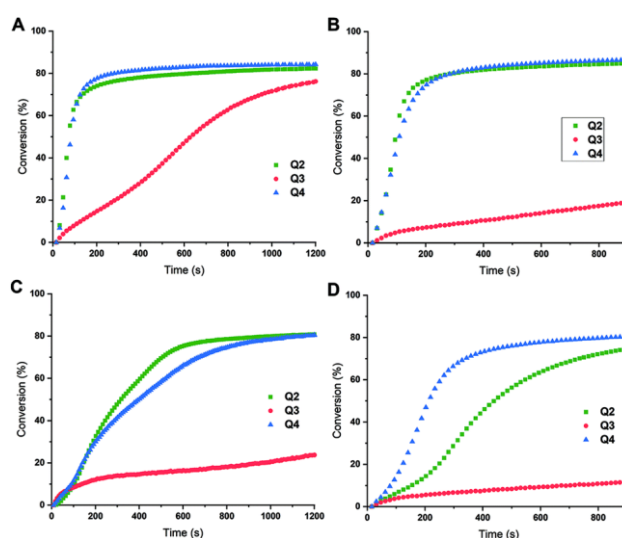


Figure 32. TPGDA (A, B) and HDDA (C, D) conversions determined upon excitation at 365 nm (A, C) and 405 nm (B, D) and by using the different dyes as monocomponent systems (1 wt%). Reproduced with permission of Ref. [359]

Interestingly, during the FRP of TMPTA, similar monomer conversions could be obtained for the different dyes used alone (1 wt%) or in combination with Iod (3 wt%), evidencing the dominant role of hydrogen abstraction mechanism in the polymerization process. Considering that the thiol-ene reaction is also promoted by free radical species, the polymerization of a trithiol/TMPTA (50%/50% w/w) blend was also examined, enabling to get TMPTA conversions higher than 84% and trithiol conversions higher than 44% (See Table 8).

Table 8. Monomer conversions obtained during the thiol-ene polymerization of a TMPTA/trithiol (50%/50% v/v) blend) upon irradiation at 365 and 405 nm using 1 wt% of dyes.

| | LED at 365 nm | | | LED at 405 nm | | |
|----------|---------------|----|----|---------------|----|----|
| | QA | Q3 | Q4 | QA | Q3 | Q4 |
| TMPTA | 93 | 90 | 86 | 86 | 84 | 92 |
| Trithiol | 59 | 54 | 46 | 44 | 47 | 51 |

Finally, the possibility to initiate the cationic polymerization of EPOX with the two-component dye/Iod (1%/3% w/w) system was also examined as well as the concomitant polymerization of a TMPTA/EPOX blend with these systems at 365 and 405 nm. In these different experiments, the lowest monomer conversions were obtained with Q3, in accordance with the lower molar extinction coefficients of Q3 at these two irradiation wavelengths.

2.6. Iodonium salt based on anthraquinone

Still with aim at developing mono-component systems, in 2021, Xiao and coworkers prepared an iodonium salt bearing an anthraquinone as the chromophore (Ant-Iod) (See Figure 33). For comparison, another iodonium salt was also prepared with a natural dye, namely a flavone (Flav-Iod).[360]

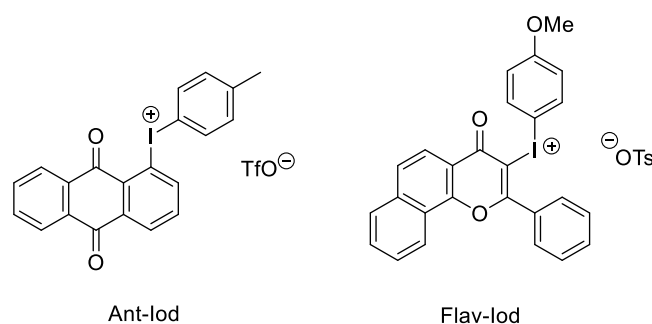


Figure 33. Chemical structure of Ant-Iod and Flav-Iod.

By introducing a flavone or an anthraquinone moiety as the chromophores, an absorption extending until 425 nm could be detected in acetonitrile whereas no absorption after 300 nm could be detected for the parent Iod1 (See Figure 34). Absorption maxima located at 336 nm for Ant-Iod and 344 nm for Flav-Iod were respectively determined. The red-shifted absorption of Flav-Iod compared to Ant-Iod is directly related to its more extended π -conjugation. Considering that Iod1 was used as a reference iodonium salt, polymerization

experiments were carried out by irradiating in the 250-650 nm range but also in the 320-480 nm range.

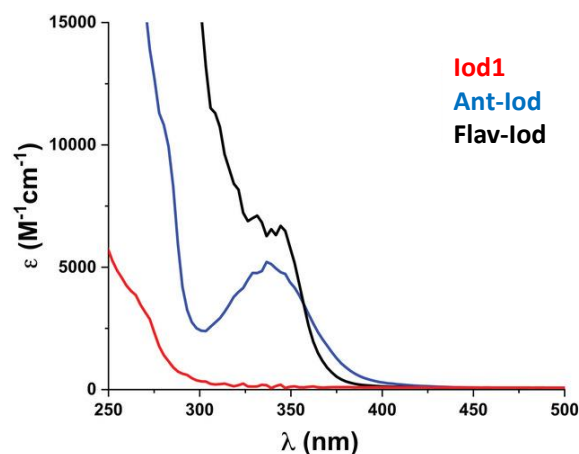


Figure 34. UV-visible absorption spectra of Iod1, Ant-Iod and Flav-Iod. Reproduced with permission of Ref. [360]

As shown in the Figure 35 during the FRP of TMPTA, Ant-Iod and Flav-Iod could act as mono-component systems and outperform Iod1 due to higher molar extinction coefficients in the visible range and thus a better adequation with the light source (250-650 nm range). This trend was confirmed by irradiating in the 320-480 nm range. In this spectral range, Flav-Iod clearly outperformed Ant-Iod and Iod1. TMPTA conversions of 46% (250-650 nm range) and 41% (320-480 nm range) were obtained with Flav-Iod.

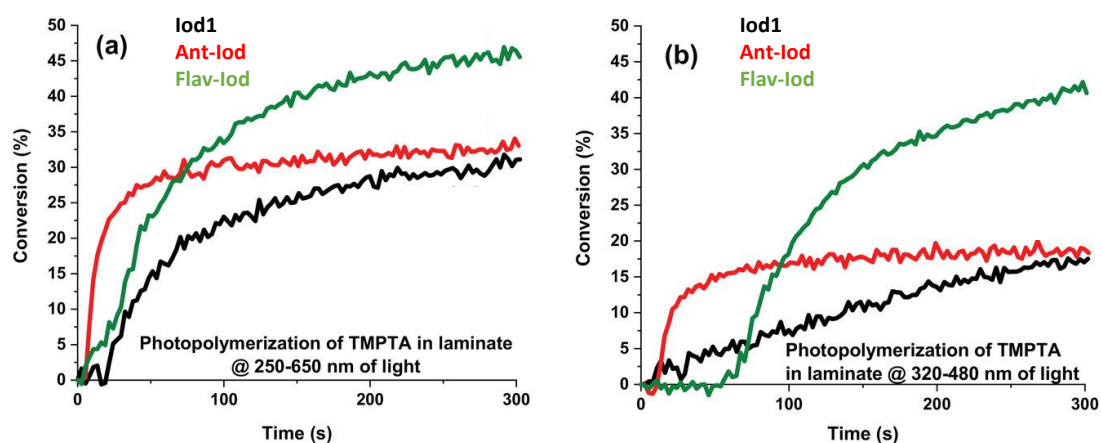


Figure 35. TMPTA conversions obtained with the different iodonium salts ($C = 29.6 \mu\text{mol/g}$) used as mono-component photoinitiating systems in different irradiation conditions.

Reproduced with permission of Ref. [360]

The monomer conversions could be improved upon addition of EDB, assigned to the formation of charge transfer complex (CTC) with EDB, improving the light absorption properties.[129,207,361–363] Using the two-component dye/EDB system, TMPTA conversions

of 25, 30 and 40 % could be obtained while reducing the iodonium concentration to only 8.4 $\mu\text{mol/g}$ (and $[\text{EDB}] = 103.5 \mu\text{mol/g}$) (See Figure 36). Considering the Iod1/EDB combination is considered as a reference system, the two newly developed iodonium salts therefore exhibited higher monomer conversions than Iod1 due to improved light absorption properties.

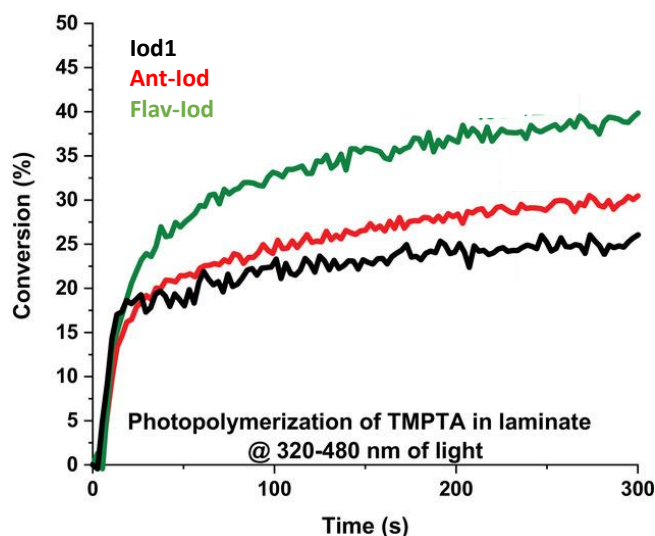


Figure 36. TMPTA conversions obtained with the iodonium salt/EDB combinations. Reproduced with permission of Ref. [360]

2.7. Anthraquinones of extended aromaticities

One of the key-element to get high molar extinction coefficients in the visible range consists in extending the aromaticity of the dyes. This point was examined by Sokołowska in 2012 and two benzo[2,3-*b*]phenazine derived anthraquinones were proposed, namely dyes IIIa and IIIc (See Figure 37). To investigate their photoinitiating abilities, different electron donors and acceptors were used, as shown in Figure 37. By extending the conjugation in IIIa and IIIc, absorption maxima located at 288 and 370 nm were respectively found in 1-methyl-2-pyrrolidinone. Noticeably, by introducing the electron-donating methoxy group, a red-shift of the absorption by ca 82 nm was detected for IIIc compared to IIIa, resulting from an intramolecular charge transfer. Among electron donors and acceptors tested during the FRP of TMPTA, the best monomer conversions were obtained with A2 and D2. Concerning the polymerization rates, this is with A1 and D1 that the polymerizations were the fastest at the beginning of the polymerization. Parallel to the FRP of TMPTA, the cationic polymerization of cyclohexane oxide was also examined with IIIa and IIIc. With the two dyes, high monomer conversions could be obtained using A3 and A4 as the additives i.e. the iodonium salts.

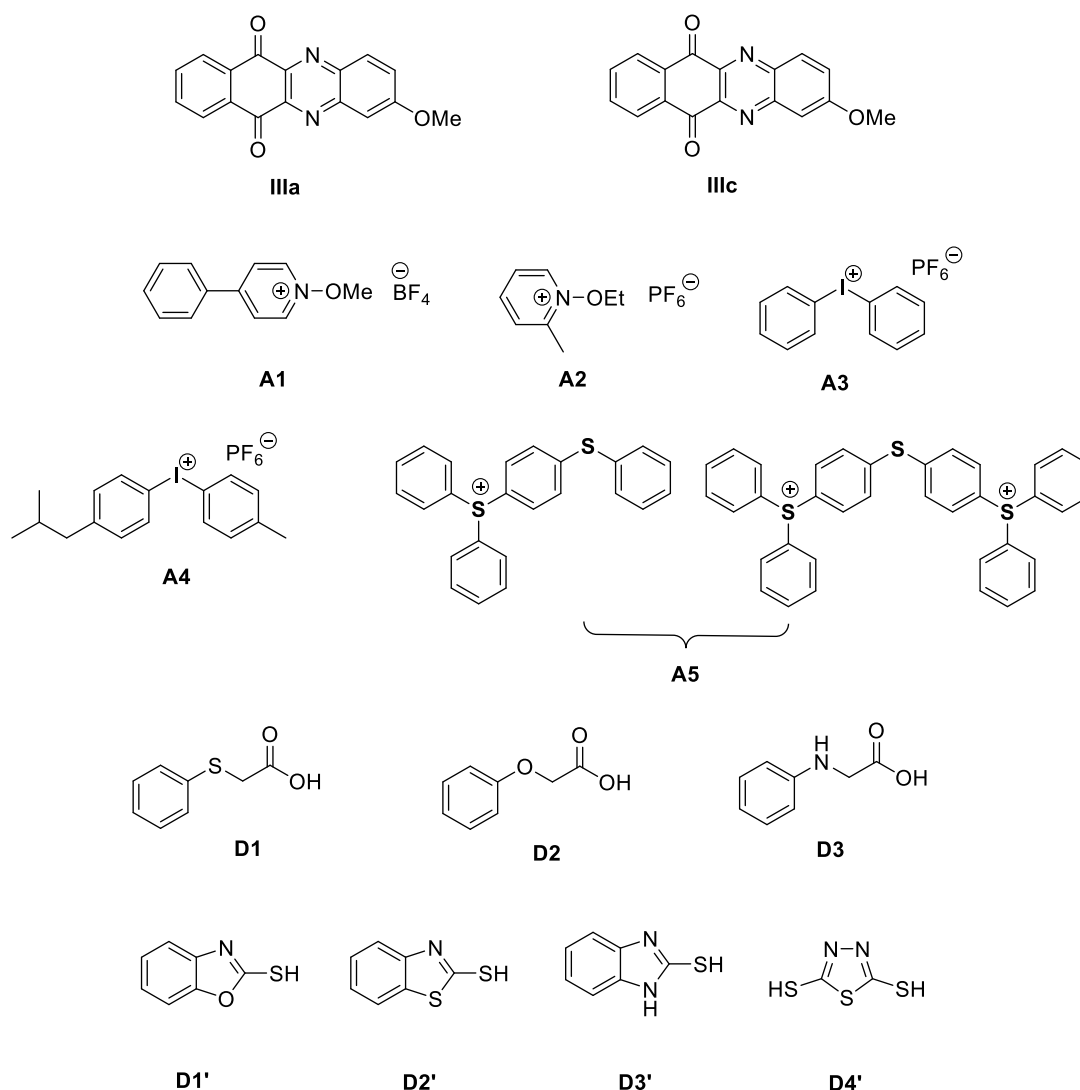


Figure 37. Chemical structures of IIIa and IIIc, different electron donors and acceptors.

Conclusion

To conclude, anthraquinones have been introduced as the chromophore in a wide range of photoinitiators so that polymerization experiments could be carried out from the UV range up to 700 nm. By connecting anthraquinones to phthalocyanine, panchromatic photoinitiators could even be obtained. At present, the design of water-soluble anthraquinones is still lacking and only one supramolecular architecture based on cyclodextrin has been reported to date. Besides, polymerization in water offers a unique opportunity to polymerize in conditions more respectful from the environment. To date, no Type I photoinitiators have been designed with anthraquinone. Besides, a significant simplification of the composition of the resin could be obtained with these structures. Indeed, only multicomponent systems have been reported at a few exceptions. Considering the remarkable light absorption properties of anthraquinones, and in light of the numerous structures that have been developed, the future challenge of photoinitiators (water-solubility, migratability, simplification of the photocurable resins with the design of monocomponent

systems) will be certainly addressed in the coming years. Another major focus of future works will also consist in designing photobleachable photoinitiators. Indeed, if the possibility of designing highly efficient photoinitiating systems with anthraquinone has been demonstrated, none of them have been reported to be capable to bleach at present. Future works will also consist in developing anthraquinones for photocontrolled/living radical polymerization. At present, this aspect of photopolymerization has not been investigated yet.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

References

- [1] J. Lalevée, H. Mokbel, J.-P. Fouassier, Recent Developments of Versatile Photoinitiating Systems for Cationic Ring Opening Polymerization Operating at Any Wavelengths and under Low Light Intensity Sources, *Molecules*. 20 (2015) 7201–7221. <https://doi.org/10.3390/molecules20047201>.
- [2] C. Chatgililoglu, J. Lalevée, Recent Applications of the (TMS)₃SiH Radical-Based Reagent, *Molecules*. 17 (2012) 527–555. <https://doi.org/10.3390/molecules17010527>.
- [3] J. Lalevée, S. Telitel, M.A. Tehfe, J.P. Fouassier, D.P. Curran, E. Lacôte, N-Heterocyclic Carbene Boranes Accelerate Type I Radical Photopolymerizations and Overcome Oxygen Inhibition, *Angew. Chem. Int. Ed.* 51 (2012) 5958–5961.
- [4] J. Lalevée, J.-P. Fouassier, *Dyes and Chromophores in Polymer Science*, ISTE Ltd and John Wiley & Sons Inc, Hoboken, NJ, USA, 2015. <https://www.wiley.com/en-us/Dyes+and+Chromophores+in+Polymer+Science-p-9781848217423> (accessed February 11, 2023).
- [5] Y. Zhang, Y. Xu, A. Simon-Masseron, J. Lalevée, Radical photoinitiation with LEDs and applications in the 3D printing of composites, *Chem. Soc. Rev.* 50 (2021) 3824–3841. <https://doi.org/10.1039/D0CS01411G>.
- [6] F. Jasinski, P.B. Zetterlund, A.M. Braun, A. Chemtob, Photopolymerization in dispersed systems, *Prog. Polym. Sci.* 84 (2018) 47–88. <https://doi.org/10.1016/j.progpolymsci.2018.06.006>.
- [7] C. Noè, M. Hakkarainen, M. Sangermano, Cationic UV-Curing of Epoxidized Biobased Resins, *Polymers*. 13 (2021) 89. <https://doi.org/10.3390/polym13010089>.
- [8] Y. Yuan, C. Li, R. Zhang, R. Liu, J. Liu, Low volume shrinkage photopolymerization system using hydrogen-bond-based monomers, *Prog. Org. Coat.* 137 (2019) 105308. <https://doi.org/10.1016/j.porgcoat.2019.105308>.
- [9] I.V. Khudyakov, J.C. Legg, M.B. Purvis, B.J. Overton, Kinetics of Photopolymerization of Acrylates with Functionality of 1–6, *Ind. Eng. Chem. Res.* 38 (1999) 3353–3359. <https://doi.org/10.1021/ie990306i>.

- [10] S.H. Dickens, J.W. Stansbury, K.M. Choi, C.J.E. Floyd, Photopolymerization Kinetics of Methacrylate Dental Resins, *Macromolecules*. 36 (2003) 6043–6053.
<https://doi.org/10.1021/ma021675k>.
- [11] A. Maffezzoli, A.D. Pietra, S. Rengo, L. Nicolais, G. Valletta, Photopolymerization of dental composite matrices, *Biomaterials*. 15 (1994) 1221–1228.
[https://doi.org/10.1016/0142-9612\(94\)90273-9](https://doi.org/10.1016/0142-9612(94)90273-9).
- [12] T. Dikova, J. Maximov, V. Todorov, G. Georgiev, V. Panov, Optimization of Photopolymerization Process of Dental Composites, *Processes*. 9 (2021) 779.
<https://doi.org/10.3390/pr9050779>.
- [13] A. Andreu, P.-C. Su, J.-H. Kim, C.S. Ng, S. Kim, I. Kim, J. Lee, J. Noh, A.S. Subramanian, Y.-J. Yoon, 4D printing materials for vat photopolymerization, *Addit. Manuf.* 44 (2021) 102024. <https://doi.org/10.1016/j.addma.2021.102024>.
- [14] H. Chen, G. Noirbent, Y. Zhang, K. Sun, S. Liu, D. Brunel, D. Gigmes, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Photopolymerization and 3D/4D applications using newly developed dyes: Search around the natural chalcone scaffold in photoinitiating systems, *Dyes Pigments*. 188 (2021) 109213.
<https://doi.org/10.1016/j.dyepig.2021.109213>.
- [15] A. Bagheri, J. Jin, Photopolymerization in 3D Printing, *ACS Appl. Polym. Mater.* 1 (2019) 593–611. <https://doi.org/10.1021/acsapm.8b00165>.
- [16] J.P. Fouassier, J. Lalevée, Three-component photoinitiating systems: towards innovative tailor made high performance combinations, *RSC Adv.* 2 (2012) 2621–2629.
<https://doi.org/10.1039/C2RA00892K>.
- [17] J. Lalevée, S. Telitel, P. Xiao, M. Lepeltier, F. Dumur, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, Metal and metal-free photocatalysts: mechanistic approach and application as photoinitiators of photopolymerization, *Beilstein J. Org. Chem.* 10 (2014) 863–876.
<https://doi.org/10.3762/bjoc.10.83>.
- [18] W. Tomal, H.C. Kiliclar, P. Fiedor, J. Ortyl, Y. Yagci, Visible Light Induced High Resolution and Swift 3D Printing System by Halogen Atom Transfer, *Macromol. Rapid Commun.* 44 (2023) 2200661. <https://doi.org/10.1002/marc.202200661>.
- [19] A.H. Bonardi, F. Dumur, T.M. Grant, G. Noirbent, D. Gigmes, B.H. Lessard, J.-P. Fouassier, J. Lalevée, High Performance Near-Infrared (NIR) Photoinitiating Systems Operating under Low Light Intensity and in the Presence of Oxygen, *Macromolecules*. 51 (2018) 1314–1324. <https://doi.org/10.1021/acs.macromol.8b00051>.
- [20] F. Dumur, Recent Advances on Photoinitiating Systems Designed for Solar Photocrosslinking Polymerization Reactions, *Eur. Polym. J.* (2023) 111988.
<https://doi.org/10.1016/j.eurpolymj.2023.111988>.
- [21] F. Dumur, Recent advances on photobleachable visible light photoinitiators of polymerization, *Eur. Polym. J.* 186 (2023) 111874.
<https://doi.org/10.1016/j.eurpolymj.2023.111874>.
- [22] J. Zhang, J. Lalevée, J. Zhao, B. Graff, M.H. Stenzel, P. Xiao, Dihydroxyanthraquinone derivatives: natural dyes as blue-light-sensitive versatile photoinitiators of photopolymerization, *Polym. Chem.* 7 (2016) 7316–7324.
<https://doi.org/10.1039/C6PY01550F>.
- [23] J. Zhao, J. Lalevée, H. Lu, R. MacQueen, S.H. Kable, T.W. Schmidt, M.H. Stenzel, P. Xiao, A new role of curcumin: as a multicolor photoinitiator for polymer fabrication under household UV to red LED bulbs, *Polym. Chem.* 6 (2015) 5053–5061.
<https://doi.org/10.1039/C5PY00661A>.

- [24] J.V. Crivello, U. Bulut, Curcumin: A naturally occurring long-wavelength photosensitizer for diaryliodonium salts, *J. Polym. Sci. Part Polym. Chem.* 43 (2005) 5217–5231. <https://doi.org/10.1002/pola.21017>.
- [25] W. Han, H. Fu, T. Xue, T. Liu, Y. Wang, T. Wang, Facilely prepared blue-green light sensitive curcuminoids with excellent bleaching properties as high performance photosensitizers in cationic and free radical photopolymerization, *Polym. Chem.* 9 (2018) 1787–1798. <https://doi.org/10.1039/C8PY00166A>.
- [26] A. Mishra, S. Daswal, Curcumin, A Novel Natural Photoinitiator for the Copolymerization of Styrene and Methylmethacrylate, *J. Macromol. Sci. Part A.* 42 (2005) 1667–1678. <https://doi.org/10.1080/10601320500246974>.
- [27] B. Bao, J. You, D. Li, H. Zhan, L. Zhang, M. Li, T. Wang, Double benzylidene ketones as photoinitiators for visible light photopolymerization, *J. Photochem. Photobiol. Chem.* 429 (2022) 113938. <https://doi.org/10.1016/j.jphotochem.2022.113938>.
- [28] H. Fu, Y. Qiu, J. You, T. Hao, B. Fan, J. Nie, T. Wang, Photopolymerization of acrylate resin and ceramic suspensions with benzylidene ketones under blue/green LED, *Polymer.* 184 (2019) 121841. <https://doi.org/10.1016/j.polymer.2019.121841>.
- [29] F. Dumur, Recent advances on benzylidene ketones as photoinitiators of polymerization, *Eur. Polym. J.* 178 (2022) 111500. <https://doi.org/10.1016/j.eurpolymj.2022.111500>.
- [30] Y. Zhao, W. Wang, F. Wu, Y. Zhou, N. Huang, Y. Gu, Q. Zou, W. Yang, Polyethylene glycol-functionalized benzylidene cyclopentanone dyes for two-photon excited photodynamic therapy, *Org. Biomol. Chem.* 9 (2011) 4168–4175. <https://doi.org/10.1039/C0OB01278E>.
- [31] Y. Fang, T. Liu, Q. Zou, Y. Zhao, F. Wu, Cationic benzylidene cyclopentanone photosensitizers for selective photodynamic inactivation of bacteria over mammalian cells, *RSC Adv.* 5 (2015) 56067–56074. <https://doi.org/10.1039/C5RA06143A>.
- [32] J. Xue, Y. Zhao, F. Wu, D.-C. Fang, Effect of Bridging Position on the Two-Photon Polymerization Initiating Efficiencies of Novel Coumarin/Benzylidene Cyclopentanone Dyes, *J. Phys. Chem. A.* 114 (2010) 5171–5179. <https://doi.org/10.1021/jp909745q>.
- [33] F. Dumur, Recent advances on benzylidene cyclopentanones as visible light photoinitiators of polymerization, *Eur. Polym. J.* 181 (2022) 111639. <https://doi.org/10.1016/j.eurpolymj.2022.111639>.
- [34] A.E. Egorov, A.A. Kostyukov, D.A. Shcherbakov, D.A. Kolymagin, D.A. Chubich, R.P. Matital, M.V. Arsenyev, I.D. Burtsev, M.G. Mestergazi, E.R. Zhiganshina, S.A. Chesnokov, A.G. Vitukhnovsky, V.A. Kuzmin, Benzylidene Cyclopentanone Derivative Photoinitiator for Two-Photon Photopolymerization-Photochemistry and 3D Structures Fabrication for X-ray Application, *Polymers.* 15 (2023). <https://doi.org/10.3390/polym15010071>.
- [35] J. Li, X. Zhang, S. Ali, M.Y. Akram, J. Nie, X. Zhu, The effect of polyethylene glycoldiacrylate complexation on type II photoinitiator and promotion for visible light initiation system, *J. Photochem. Photobiol. Chem.* 384 (2019) 112037. <https://doi.org/10.1016/j.jphotochem.2019.112037>.
- [36] J. Li, S. Li, Y. Li, R. Li, J. Nie, X. Zhu, In situ monitoring of photopolymerization by photoinitiator with luminescence characteristics, *J. Photochem. Photobiol. Chem.* 389 (2020) 112225. <https://doi.org/10.1016/j.jphotochem.2019.112225>.

- [37] J. Li, Y. Hao, M. Zhong, L. Tang, J. Nie, X. Zhu, Synthesis of furan derivative as LED light photoinitiator: One-pot, low usage, photobleaching for light color 3D printing, *Dyes Pigments*. 165 (2019) 467–473. <https://doi.org/10.1016/j.dyepig.2019.03.011>.
- [38] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gimes, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Novel ketone derivative-based photoinitiating systems for free radical polymerization under mild conditions and 3D printing, *Polym. Chem.* 11 (2020) 5767–5777. <https://doi.org/10.1039/D0PY00990C>.
- [39] C. Brahmi, M. Benlifa, C. Vaulot, L. Michelin, F. Dumur, A. Airoudj, F. Morlet-Savary, B. Raveau, L. Bousselmi, J. Lalevée, New hybrid perovskites/polymer composites for the photodegradation of organic dyes, *Eur. Polym. J.* 157 (2021) 110641. <https://doi.org/10.1016/j.eurpolymj.2021.110641>.
- [40] H. Mokbel, F. Dumur, B. Raveau, F. Morlet-Savary, C. Simonnet-Jégat, D. Gimes, J. Toufaily, T. Hamieh, J.P. Fouassier, J. Lalevée, Perovskites as new radical photoinitiators for radical and cationic polymerizations, *Org. Chem. More Radic. Ever Before*. 72 (2016) 7686–7690. <https://doi.org/10.1016/j.tet.2016.03.057>.
- [41] J. Zhang, F. Dumur, P. Horcajada, C. Livage, P. Xiao, J.P. Fouassier, D. Gimes, J. Lalevée, Iron-Based Metal-Organic Frameworks (MOF) as Photocatalysts for Radical and Cationic Polymerizations under Near UV and Visible LEDs (385–405 nm), *Macromol. Chem. Phys.* 217 (2016) 2534–2540. <https://doi.org/10.1002/macp.201600352>.
- [42] P. Garra, D. Brunel, G. Noirbent, B. Graff, F. Morlet-Savary, C. Dietlin, V.F. Sidorkin, F. Dumur, D. Duché, D. Gimes, J.-P. Fouassier, J. Lalevée, Ferrocene-based (photo)redox polymerization under long wavelengths, *Polym. Chem.* 10 (2019) 1431–1441. <https://doi.org/10.1039/C9PY00059C>.
- [43] S. Telitel, F. Dumur, D. Campolo, J. Poly, D. Gimes, J.P. Fouassier, J. Lalevée, Iron complexes as potential photocatalysts for controlled radical photopolymerizations: A tool for modifications and patterning of surfaces, *J. Polym. Sci. Part Polym. Chem.* 54 (2016) 702–713. <https://doi.org/10.1002/pola.27896>.
- [44] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gimes, J. Lalevée, Iron complexes as photoinitiators for radical and cationic polymerization through photoredox catalysis processes, *J. Polym. Sci. Part Polym. Chem.* 53 (2015) 42–49. <https://doi.org/10.1002/pola.27435>.
- [45] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gimes, J. Lalevée, Visible-light-sensitive photoredox catalysis by iron complexes: Applications in cationic and radical polymerization reactions, *J. Polym. Sci. Part Polym. Chem.* 54 (2016) 2247–2253. <https://doi.org/10.1002/pola.28098>.
- [46] J. Zhang, D. Campolo, F. Dumur, P. Xiao, J.P. Fouassier, D. Gimes, J. Lalevée, Iron Complexes in Visible-Light-Sensitive Photoredox Catalysis: Effect of Ligands on Their Photoinitiation Efficiencies, *ChemCatChem*. 8 (2016) 2227–2233. <https://doi.org/10.1002/cctc.201600320>.
- [47] F. Dumur, Recent advances on ferrocene-based photoinitiating systems, *Eur. Polym. J.* 147 (2021) 110328. <https://doi.org/10.1016/j.eurpolymj.2021.110328>.
- [48] F. Dumur, Recent advances on iron-based photoinitiators of polymerization, *Eur. Polym. J.* 139 (2020) 110026. <https://doi.org/10.1016/j.eurpolymj.2020.110026>.
- [49] J. Zhang, N. Zivic, F. Dumur, C. Guo, Y. Li, P. Xiao, B. Graff, D. Gimes, J.P. Fouassier, J. Lalevée, Panchromatic photoinitiators for radical, cationic and thiol-ene polymerization reactions: A search in the diketopyrrolopyrrole or indigo dye series, *Mater. Today Commun.* 4 (2015) 101–108. <https://doi.org/10.1016/j.mtcomm.2015.06.007>.

- [50] P. Xiao, W. Hong, Y. Li, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmès, J. Lalevée, Diketopyrrolopyrrole dyes: Structure/reactivity/efficiency relationship in photoinitiating systems upon visible lights, *Polymer*. 55 (2014) 746–751. <https://doi.org/10.1016/j.polymer.2014.01.003>.
- [51] P. Xiao, W. Hong, Y. Li, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmès, J. Lalevée, Green light sensitive diketopyrrolopyrrole derivatives used in versatile photoinitiating systems for photopolymerizations, *Polym. Chem.* 5 (2014) 2293–2300. <https://doi.org/10.1039/C3PY01599H>.
- [52] F. Dumur, C.R. Mayer, E. Dumas, F. Miomandre, M. Frigoli, F. Sécheresse, New Chelating Stilbazonium-Like Dyes from Michler's Ketone, *Org. Lett.* 10 (2008) 321–324. <https://doi.org/10.1021/ol702793j>.
- [53] L. Cao, Y. Wang, Photocatalysis of viologens for photoinitiated polymerization using carboxylic acid as electron donors, *J. Photochem. Photobiol. Chem.* 333 (2017) 63–69. <https://doi.org/10.1016/j.jphotochem.2016.10.019>.
- [54] W. Schnabel, Cationic photopolymerization with the aid of pyridinium-type salts, *Macromol. Rapid Commun.* 21 (2000) 628–642. [https://doi.org/10.1002/1521-3927\(20000601\)21:10<628::AID-MARC628>3.0.CO;2-Q](https://doi.org/10.1002/1521-3927(20000601)21:10<628::AID-MARC628>3.0.CO;2-Q).
- [55] F. Hammoud, A. Pavlou, A. Petropoulos, B. Graff, M.G. Siskos, A. Hijazi, F. Morlet-Savary, F. Dumur, J. Lalevée, Naphthoquinone-based imidazolyl esters as blue-light-sensitive Type I photoinitiators, *Polym. Chem.* 13 (2022) 4817–4831. <https://doi.org/10.1039/D2PY00753C>.
- [56] A. Al Mousawi, C. Poriel, F. Dumur, J. Toufaily, T. Hamieh, J.P. Fouassier, J. Lalevée, Zinc Tetraphenylporphyrin as High Performance Visible Light Photoinitiator of Cationic Photosensitive Resins for LED Projector 3D Printing Applications, *Macromolecules*. 50 (2017) 746–753. <https://doi.org/10.1021/acs.macromol.6b02596>.
- [57] G. Noirbent, Y. Xu, A.-H. Bonardi, D. Gigmès, J. Lalevée, F. Dumur, Metalated porphyrins as versatile visible light and NIR photoinitiators of polymerization, *Eur. Polym. J.* 139 (2020) 110019. <https://doi.org/10.1016/j.eurpolymj.2020.110019>.
- [58] L. Breloy, V. Brezová, S. Richeter, S. Clément, J.-P. Malval, S. Abbad Andaloussi, D.-L. Versace, Bio-based porphyrins pyropheophorbide a and its Zn-complex as visible-light photosensitizers for free-radical photopolymerization, *Polym. Chem.* 13 (2022) 1658–1671. <https://doi.org/10.1039/D1PY01714D>.
- [59] A. Al Mousawi, P. Garra, X. Sallenave, F. Dumur, J. Toufaily, T. Hamieh, B. Graff, D. Gigmès, J.P. Fouassier, J. Lalevée, π -Conjugated Dithienophosphole Derivatives as High Performance Photoinitiators for 3D Printing Resins, *Macromolecules*. 51 (2018) 1811–1821. <https://doi.org/10.1021/acs.macromol.8b00044>.
- [60] F. Dumur, D. Gigmès, J.-P. Fouassier, J. Lalevée, Organic Electronics: An El Dorado in the Quest of New Photocatalysts for Polymerization Reactions, *Acc. Chem. Res.* 49 (2016) 1980–1989. <https://doi.org/10.1021/acs.accounts.6b00227>.
- [61] F. Dumur, Recent Advances on Visible Light Thiophene-based Photoinitiators of Polymerization, *Eur. Polym. J.* (2022) 111120. <https://doi.org/10.1016/j.eurpolymj.2022.111120>.
- [62] B. Corakci, S.O. Hacıoglu, L. Toppare, U. Bulut, Long wavelength photosensitizers in photoinitiated cationic polymerization: The effect of quinoxaline derivatives on photopolymerization, *Polymer*. 54 (2013) 3182–3187. <https://doi.org/10.1016/j.polymer.2013.04.008>.

- [63] P. Xiao, F. Dumur, D. Thirion, S. Fagour, A. Vacher, X. Sallenave, F. Morlet-Savary, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Multicolor Photoinitiators for Radical and Cationic Polymerization: Monofunctional vs Polyfunctional Thiophene Derivatives, *Macromolecules*. 46 (2013) 6786–6793. <https://doi.org/10.1021/ma401389t>.
- [64] S. Liu, H. Chen, Y. Zhang, K. Sun, Y. Xu, F. Morlet-Savary, B. Graff, G. Noirbent, C. Pigot, D. Brunel, M. Nechab, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, Monocomponent Photoinitiators based on Benzophenone-Carbazole Structure for LED Photoinitiating Systems and Application on 3D Printing, *Polymers*. 12 (2020) 1394. <https://doi.org/10.3390/polym12061394>.
- [65] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Variations on the Benzophenone Skeleton: Novel High Performance Blue Light Sensitive Photoinitiating Systems, *Macromolecules*. 46 (2013) 7661–7667. <https://doi.org/10.1021/ma401766v>.
- [66] J. Zhang, M. Frigoli, F. Dumur, P. Xiao, L. Ronchi, B. Graff, F. Morlet-Savary, J.P. Fouassier, D. Gigmes, J. Lalevée, Design of Novel Photoinitiators for Radical and Cationic Photopolymerizations under Near UV and Visible LEDs (385, 395, and 405 nm)., *Macromolecules*. 47 (2014) 2811–2819. <https://doi.org/10.1021/ma500612x>.
- [67] S. Liu, D. Brunel, G. Noirbent, A. Mau, H. Chen, F. Morlet-Savary, B. Graff, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, New multifunctional benzophenone-based photoinitiators with high migration stability and their applications in 3D printing, *Mater. Chem. Front.* 5 (2021) 1982–1994. <https://doi.org/10.1039/D0QM00885K>.
- [68] S. Liu, D. Brunel, K. Sun, Y. Zhang, H. Chen, P. Xiao, F. Dumur, J. Lalevée, Novel Photoinitiators Based on Benzophenone-Triphenylamine Hybrid Structure for LED Photopolymerization, *Macromol. Rapid Commun.* 41 (2020) 2000460. <https://doi.org/10.1002/marc.202000460>.
- [69] S. Liu, D. Brunel, K. Sun, Y. Xu, F. Morlet-Savary, B. Graff, P. Xiao, F. Dumur, J. Lalevée, A monocomponent bifunctional benzophenone–carbazole type II photoinitiator for LED photoinitiating systems, *Polym. Chem.* 11 (2020) 3551–3556. <https://doi.org/10.1039/D0PY00644K>.
- [70] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, Trifunctional Photoinitiators Based on a Triazine Skeleton for Visible Light Source and UV LED Induced Polymerizations, *Macromolecules*. 45 (2012) 8639–8647. <https://doi.org/10.1021/ma301931p>.
- [71] J.-T. Lin, J. Lalevee, Efficacy Modeling of New Multi-Functional Benzophenone-Based System for Free-Radical/Cationic Hybrid Photopolymerization Using 405 nm LED, (2021). <https://doi.org/10.20944/preprints202106.0502.v1>.
- [72] J. Zhang, D. Campolo, F. Dumur, P. Xiao, D. Gigmes, J.P. Fouassier, J. Lalevée, The carbazole-bound ferrocenium salt as a specific cationic photoinitiator upon near-UV and visible LEDs (365–405 nm), *Polym. Bull.* 73 (2016) 493–507. <https://doi.org/10.1007/s00289-015-1506-1>.
- [73] A. Al Mousawi, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Carbazole Scaffold Based Photoinitiator/Photoredox Catalysts: Toward New High Performance Photoinitiating Systems and Application in LED Projector 3D Printing Resins, *Macromolecules*. 50 (2017) 2747–2758. <https://doi.org/10.1021/acs.macromol.7b00210>.
- [74] A. Al Mousawi, D.M. Lara, G. Noirbent, F. Dumur, J. Toufaily, T. Hamieh, T.-T. Bui, F. Goubard, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Carbazole Derivatives with Thermally Activated Delayed Fluorescence Property as Photoinitiators/Photoredox

- Catalysts for LED 3D Printing Technology, *Macromolecules*. 50 (2017) 4913–4926.
<https://doi.org/10.1021/acs.macromol.7b01114>.
- [75] A. Al Mousawi, P. Garra, F. Dumur, T.-T. Bui, F. Goubard, J. Toufaily, T. Hamieh, B. Graff, D. Gignes, J.P. Fouassier, J. Lalevée, Novel Carbazole Skeleton-Based Photoinitiators for LED Polymerization and LED Projector 3D Printing, *Molecules*. 22 (2017) 2143. <https://doi.org/10.3390/molecules22122143>.
- [76] A.A. Mousawi, A. Arar, M. Ibrahim-Ouali, S. Duval, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, B. Graff, D. Gignes, J.-P. Fouassier, J. Lalevée, Carbazole-based compounds as photoinitiators for free radical and cationic polymerization upon near visible light illumination, *Photochem. Photobiol. Sci.* 17 (2018) 578–585.
<https://doi.org/10.1039/C7PP00400A>.
- [77] M. Abdallah, D. Magaldi, A. Hijazi, B. Graff, F. Dumur, J.-P. Fouassier, T.-T. Bui, F. Goubard, J. Lalevée, Development of new high-performance visible light photoinitiators based on carbazole scaffold and their applications in 3d printing and photocomposite synthesis, *J. Polym. Sci. Part Polym. Chem.* 57 (2019) 2081–2092.
<https://doi.org/10.1002/pola.29471>.
- [78] F. Dumur, Recent advances on carbazole-based photoinitiators of polymerization, *Eur. Polym. J.* 125 (2020) 109503. <https://doi.org/10.1016/j.eurpolymj.2020.109503>.
- [79] S. Liu, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Nitro-Carbazole Based Oxime Esters as Dual Photo/Thermal Initiators for 3D Printing and Composite Preparation, *Macromol. Rapid Commun.* 42 (2021) 2100207. <https://doi.org/10.1002/marc.202100207>.
- [80] F. Hammoud, A. Hijazi, S. Duval, J. Lalevée, F. Dumur, 5,12-Dihydroindolo[3,2-a]carbazole: A promising scaffold for the design of visible light photoinitiators of polymerization, *Eur. Polym. J.* 162 (2022) 110880.
<https://doi.org/10.1016/j.eurpolymj.2021.110880>.
- [81] S. Liu, N. Giacoletto, M. Schmitt, M. Nechab, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Effect of Decarboxylation on the Photoinitiation Behavior of Nitrocarbazole-Based Oxime Esters, *Macromolecules*. 55 (2022) 2475–2485.
<https://doi.org/10.1021/acs.macromol.2c00294>.
- [82] F. Hammoud, A. Hijazi, M. Ibrahim-Ouali, J. Lalevée, F. Dumur, Chemical engineering around the 5,12-dihydroindolo[3,2-a]carbazole scaffold : Fine tuning of the optical properties of visible light photoinitiators of polymerization, *Eur. Polym. J.* (2022) 111218. <https://doi.org/10.1016/j.eurpolymj.2022.111218>.
- [83] C. Xu, S. Gong, X. Wu, Y. Wu, Q. Liao, Y. Xiong, Z. Li, H. Tang, High-efficient carbazole-based photo-bleachable dyes as free radical initiators for visible light polymerization, *Dyes Pigments*. 198 (2022) 110039.
<https://doi.org/10.1016/j.dyepig.2021.110039>.
- [84] F. Dumur, Recent advances on carbazole-based oxime esters as photoinitiators of polymerization, *Eur. Polym. J.* 175 (2022) 111330.
<https://doi.org/10.1016/j.eurpolymj.2022.111330>.
- [85] F. Hammoud, N. Giacoletto, M. Nechab, B. Graff, A. Hijazi, F. Dumur, J. Lalevée, 5,12-Dialkyl-5,12-dihydroindolo[3,2-a]carbazole-Based Oxime-Esters for LED Photoinitiating Systems and Application on 3D Printing, *Macromol. Mater. Eng.* n/a (2022) 2200082.
<https://doi.org/10.1002/mame.202200082>.
- [86] W. Liao, Q. Liao, Y. Xiong, Z. Li, H. Tang, Design, synthesis and properties of carbazole-indenedione based photobleachable photoinitiators for photopolymerization,

- J. Photochem. Photobiol. Chem. 435 (2023) 114297.
<https://doi.org/10.1016/j.jphotochem.2022.114297>.
- [87] F.-C. Bin, M. Guo, T. Li, Y.-C. Zheng, X.-Z. Dong, J. Liu, F. Jin, M.-L. Zheng, Carbazole-based Anion Ionic Water-Soluble Two-Photon Initiator for Achieving 3D Hydrogel Structures, *Adv. Funct. Mater.* n/a (2023) 2300293.
<https://doi.org/10.1002/adfm.202300293>.
- [88] J. Kirschner, A. Baralle, J. Paillard, B. Graff, J.-M. Becht, J.E. Klee, J. Lalevée, Silyl Glyoximides: Toward a New Class of Visible Light Photoinitiators, *Macromol. Chem. Phys.* 223 (2022) 2100500. <https://doi.org/10.1002/macp.202100500>.
- [89] M. Topa-Skwarczyńska, M. Galek, M. Jankowska, F. Morlet-Savary, B. Graff, J. Lalevée, R. Popielarz, J. Ortyl, Development of the first panchromatic BODIPY-based one-component iodonium salts for initiating the photopolymerization processes, *Polym. Chem.* 12 (2021) 6873–6893. <https://doi.org/10.1039/D1PY01263K>.
- [90] Y. Xu, T. Feng, T. Yang, H. Wei, H. Yang, G. Li, M. Zhao, S. Liu, W. Huang, Q. Zhao, Utilizing Intramolecular Photoinduced Electron Transfer to Enhance Photothermal Tumor Treatment of Aza-BODIPY-Based Near-Infrared Nanoparticles, *ACS Appl. Mater. Interfaces.* 10 (2018) 16299–16307. <https://doi.org/10.1021/acsami.8b03568>.
- [91] A. Skotnicka, J. Kabatc, New BODIPY Dyes Based on Benzoxazole as Photosensitizers in Radical Polymerization of Acrylate Monomers, *Materials.* 15 (2022).
<https://doi.org/10.3390/ma15020662>.
- [92] P. Lu, K.-Y. Chung, A. Stafford, M. Kiker, K. Kafle, Z.A. Page, Boron dipyrromethene (BODIPY) in polymer chemistry, *Polym. Chem.* 12 (2021) 327–348.
<https://doi.org/10.1039/D0PY01513J>.
- [93] S. Telitel, N. Blanchard, S. Schweizer, F. Morlet-Savary, B. Graff, J.-P. Fouassier, J. Lalevée, BODIPY derivatives and boranil as new photoinitiating systems of cationic polymerization exhibiting a tunable absorption in the 400–600 nm spectral range, *Polymer.* 54 (2013) 2071–2076. <https://doi.org/10.1016/j.polymer.2013.02.013>.
- [94] S. Telitel, J. Lalevée, N. Blanchard, T. Kavalli, M.-A. Tehfe, S. Schweizer, F. Morlet-Savary, B. Graff, J.-P. Fouassier, Photopolymerization of Cationic Monomers and Acrylate/Divinylether Blends under Visible Light Using Pyrromethene Dyes, *Macromolecules.* 45 (2012) 6864–6868. <https://doi.org/10.1021/ma301293m>.
- [95] Q. Ma, S. Liu, M. Le Dot, H. Mokbel, Y. Zhang, B. Graff, J. Lalevée, Imidazole based dual photo/thermal initiators for highly efficient radical polymerization under air with a metal-free approach, *Polym. Chem.* 12 (2021) 6386–6391.
<https://doi.org/10.1039/D1PY01079D>.
- [96] M.-A. Tehfe, F. Dumur, B. Graff, J.-L. Clément, D. Gimes, F. Morlet-Savary, J.-P. Fouassier, J. Lalevée, New Cleavable Photoinitiator Architecture with Huge Molar Extinction Coefficients for Polymerization in the 340–450 nm Range., *Macromolecules.* 46 (2013) 736–746. <https://doi.org/10.1021/ma3024359>.
- [97] H. Mokbel, F. Dumur, J. Lalevée, On demand NIR activated photopolyaddition reactions, *Polym. Chem.* 11 (2020) 4250–4259. <https://doi.org/10.1039/D0PY00639D>.
- [98] H. Mokbel, B. Graff, F. Dumur, J. Lalevée, NIR Sensitizer Operating under Long Wavelength (1064 nm) for Free Radical Photopolymerization Processes, *Macromol. Rapid Commun.* 41 (2020) 2000289. <https://doi.org/10.1002/marc.202000289>.
- [99] V. Launay, F. Dumur, D. Gimes, J. Lalevée, Near-infrared light for polymer re-shaping and re-processing applications, *J. Polym. Sci.* 59 (2021) 2193–2200.
<https://doi.org/10.1002/pol.20210450>.

- [100] A. Caron, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, Near-Infrared PhotoInitiating Systems: Photothermal versus Triplet–Triplet Annihilation-Based Upconversion Polymerization, *Macromol. Rapid Commun.* 42 (2021) 2100047. <https://doi.org/10.1002/marc.202100047>.
- [101] A.-H. Bonardi, F. Bonardi, F. Morlet-Savary, C. Dietlin, G. Noirbent, T.M. Grant, J.-P. Fouassier, F. Dumur, B.H. Lessard, D. Gigmes, J. Lalevée, Photoinduced Thermal Polymerization Reactions, *Macromolecules.* 51 (2018) 8808–8820. <https://doi.org/10.1021/acs.macromol.8b01741>.
- [102] V. Launay, F. Dumur, L. Pieuchot, J. Lalevée, Safe near infrared light for fast polymers surface sterilization using organic heaters, *Mater. Chem. Front.* 6 (2022) 1172–1179. <https://doi.org/10.1039/D1QM01609A>.
- [103] V. Launay, R. Wolf, F. Dumur, J. Lalevée, Photothermal activation in the near infrared range for 4-dimensional printing using relevant organic dyes, *Addit. Manuf.* 58 (2022) 103031. <https://doi.org/10.1016/j.addma.2022.103031>.
- [104] N. Zivic, M. Bouzrati-Zerrelli, S. Villotte, F. Morlet-Savary, C. Dietlin, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, A novel naphthalimide scaffold based iodonium salt as a one-component photoacid/photoinitiator for cationic and radical polymerization under LED exposure, *Polym. Chem.* 7 (2016) 5873–5879. <https://doi.org/10.1039/C6PY01306F>.
- [105] A.-H. Bonardi, S. Zahouily, C. Dietlin, B. Graff, F. Morlet-Savary, M. Ibrahim-Ouali, D. Gigmes, N. Hoffmann, F. Dumur, J. Lalevée, New 1,8-Naphthalimide Derivatives as Photoinitiators for Free-Radical Polymerization Upon Visible Light, *Catalysts.* 9 (2019) 637. <https://doi.org/10.3390/catal9080637>.
- [106] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Naphthalimide-Tertiary Amine Derivatives as Blue-Light-Sensitive Photoinitiators, *ChemPhotoChem.* 2 (2018) 481–489. <https://doi.org/10.1002/cptc.201800006>.
- [107] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Naphthalimide Derivatives: Substituent Effects on the Photoinitiating Ability in Polymerizations under Near UV, Purple, White and Blue LEDs (385, 395, 405, 455, or 470 nm), *Macromol. Chem. Phys.* 216 (2015) 1782–1790. <https://doi.org/10.1002/macp.201500150>.
- [108] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Naphthalimide-phthalimide derivative based photoinitiating systems for polymerization reactions under blue lights, *J. Polym. Sci. Part Polym. Chem.* 53 (2015) 665–674. <https://doi.org/10.1002/pola.27490>.
- [109] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, A benzophenone-naphthalimide derivative as versatile photoinitiator of polymerization under near UV and visible lights, *J. Polym. Sci. Part Polym. Chem.* 53 (2015) 445–451. <https://doi.org/10.1002/pola.27451>.
- [110] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, N-[2-(Dimethylamino)ethyl]-1,8-naphthalimide derivatives as photoinitiators under LEDs, *Polym. Chem.* 9 (2018) 994–1003. <https://doi.org/10.1039/C8PY00055G>.
- [111] J. Zhang, F. Dumur, P. Xiao, B. Graff, D. Bardelang, D. Gigmes, J.P. Fouassier, J. Lalevée, Structure Design of Naphthalimide Derivatives: Toward Versatile Photoinitiators for Near-UV/Visible LEDs, 3D Printing, and Water-Soluble Photoinitiating Systems, *Macromolecules.* 48 (2015) 2054–2063. <https://doi.org/10.1021/acs.macromol.5b00201>.

- [112] J. Zhang, N. Zivic, F. Dumur, P. Xiao, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, UV-violet-blue LED induced polymerizations: Specific photoinitiating systems at 365, 385, 395 and 405 nm, *Polymer*. 55 (2014) 6641–6648.
<https://doi.org/10.1016/j.polymer.2014.11.002>.
- [113] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Blue Light Sensitive Dyes for Various Photopolymerization Reactions: Naphthalimide and Naphthalic Anhydride Derivatives., *Macromolecules*. 47 (2014) 601–608.
<https://doi.org/10.1021/ma402376x>.
- [114] P. Xiao, F. Dumur, M. Frigoli, M.-A. Tehfe, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Naphthalimide based methacrylated photoinitiators in radical and cationic photopolymerization under visible light, *Polym. Chem.* 4 (2013) 5440–5448.
<https://doi.org/10.1039/C3PY00766A>.
- [115] G. Noirbent, F. Dumur, Recent advances on naphthalic anhydrides and 1,8-naphthalimide-based photoinitiators of polymerization, *Eur. Polym. J.* 132 (2020) 109702. <https://doi.org/10.1016/j.eurpolymj.2020.109702>.
- [116] M. Rahal, H. Mokbel, B. Graff, V. Pertici, D. Gigmes, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Naphthalimide-Based Dyes as Photoinitiators under Visible Light Irradiation and their Applications: Photocomposite Synthesis, 3D printing and Polymerization in Water, *ChemPhotoChem*. 5 (2021) 476–490. <https://doi.org/10.1002/cptc.202000306>.
- [117] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, M. Ibrahim-Ouali, F. Dumur, J. Lalevée, Naphthyl-Naphthalimides as High-Performance Visible Light Photoinitiators for 3D Printing and Photocomposites Synthesis, *Catalysts*. 11 (2021).
<https://doi.org/10.3390/catal11111269>.
- [118] N. Zivic, J. Zhang, D. Bardelang, F. Dumur, P. Xiao, T. Jet, D.-L. Versace, C. Dietlin, F. Morlet-Savary, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Novel naphthalimide-amine based photoinitiators operating under violet and blue LEDs and usable for various polymerization reactions and synthesis of hydrogels, *Polym. Chem.* 7 (2015) 418–429. <https://doi.org/10.1039/C5PY01617G>.
- [119] P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.P. Fouassier, J. Lalevée, Design of High Performance Photoinitiators at 385–405 nm: Search around the Naphthalene Scaffold, *Macromolecules*. 47 (2014) 973–978.
<https://doi.org/10.1021/ma402622v>.
- [120] P. Xiao, F. Dumur, J. Zhang, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Amino and nitro substituted 2-amino-1H-benzo[de]isoquinoline-1,3(2H)-diones: as versatile photoinitiators of polymerization from violet-blue LED absorption to a panchromatic behavior, *Polym. Chem.* 6 (2015) 1171–1179. <https://doi.org/10.1039/C4PY01409J>.
- [121] H. Chen, L. Pieuchot, P. Xiao, F. Dumur, J. Lalevée, Water-soluble/visible-light-sensitive naphthalimide derivative-based photoinitiating systems: 3D printing of antibacterial hydrogels, *Polym. Chem.* 13 (2022) 2918–2932. <https://doi.org/10.1039/D2PY00417H>.
- [122] S. Liu, N. Giacoletto, B. Graff, F. Morlet-Savary, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, N-naphthalimide ester derivatives as Type I photoinitiators for LED photopolymerization, *Mater. Today Chem.* 26 (2022) 101137.
<https://doi.org/10.1016/j.mtchem.2022.101137>.
- [123] J. Lalevée, F. Dumur, M.-A. Tehfe, A. Zein-Fakih, D. Gigmes, F. Morlet-Savary, B. Graff, J.-P. Fouassier, Dye photosensitized cationic ring-opening polymerization: Search for new dye skeletons, *Polymer*. 53 (2012) 4947–4954.
<https://doi.org/10.1016/j.polymer.2012.08.067>.

- [124] F. Dumur, Recent advances on visible light Triphenylamine-based photoinitiators of polymerization, *Eur. Polym. J.* 166 (2022) 111036. <https://doi.org/10.1016/j.eurpolymj.2022.111036>.
- [125] D. Ladika, G. Noirbent, F. Dumur, D. Gigmes, A. Mourka, G.D. Barmparis, M. Farsari, D. Gray, Synthesis and application of triphenylamine-based aldehydes as photoinitiators for multi-photon lithography, *Appl. Phys. A.* 128 (2022) 745. <https://doi.org/10.1007/s00339-022-05887-1>.
- [126] F. Dumur, Recent Advances on Anthracene-based Photoinitiators of Polymerization, *Eur. Polym. J.* (2022) 111139. <https://doi.org/10.1016/j.eurpolymj.2022.111139>.
- [127] C. Brahmi, M. Benlifa, C. Vulot, L. Michelin, F. Dumur, F. Millange, M. Frigoli, A. Airoudj, F. Morlet-Savary, L. Bouselmi, J. Lalevée, New hybrid MOF/polymer composites for the photodegradation of organic dyes, *Eur. Polym. J.* 154 (2021) 110560. <https://doi.org/10.1016/j.eurpolymj.2021.110560>.
- [128] C. Brahmi, M. Benlifa, C. Vulot, L. Michelin, F. Dumur, E. Gkaniatsou, C. Sicard, A. Airoudj, F. Morlet-Savary, L. Bouselmi, J. Lalevée, New Hybrid Fe-based MOFs/Polymer Composites for the Photodegradation of Organic Dyes, *ChemistrySelect.* 6 (2021) 8120–8132. <https://doi.org/10.1002/slct.202102194>.
- [129] F. Dumur, Recent Advances on Furan-Based Visible Light Photoinitiators of Polymerization, *Catalysts.* 13 (2023). <https://doi.org/10.3390/catal13030493>.
- [130] M.-A. Tehfe, A. Zein-Fakih, J. Lalevée, F. Dumur, D. Gigmes, B. Graff, F. Morlet-Savary, T. Hamieh, J.-P. Fouassier, New pyridinium salts as versatile compounds for dye sensitized photopolymerization, *Eur. Polym. J.* 49 (2013) 567–574. <https://doi.org/10.1016/j.eurpolymj.2012.10.010>.
- [131] P. Xiao, M. Frigoli, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Julolidine or Fluorenone Based Push–Pull Dyes for Polymerization upon Soft Polychromatic Visible Light or Green Light., *Macromolecules.* 47 (2014) 106–112. <https://doi.org/10.1021/ma402196p>.
- [132] H. Mokbel, F. Dumur, B. Graff, C.R. Mayer, D. Gigmes, J. Toufaily, T. Hamieh, J.-P. Fouassier, J. Lalevée, Michler's Ketone as an Interesting Scaffold for the Design of High-Performance Dyes in Photoinitiating Systems Upon Visible Light, *Macromol. Chem. Phys.* 215 (2014) 783–790. <https://doi.org/10.1002/macp.201300779>.
- [133] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, New Push–Pull Dyes Derived from Michler's Ketone For Polymerization Reactions Upon Visible Lights., *Macromolecules.* 46 (2013) 3761–3770. <https://doi.org/10.1021/ma400766z>.
- [134] H. Mokbel, F. Dumur, C.R. Mayer, F. Morlet-Savary, B. Graff, D. Gigmes, J. Toufaily, T. Hamieh, J.-P. Fouassier, J. Lalevée, End capped polyenic structures as visible light sensitive photoinitiators for polymerization of vinyl ethers, *Dyes Pigments.* 105 (2014) 121–129. <https://doi.org/10.1016/j.dyepig.2014.02.002>.
- [135] S. Telitel, F. Dumur, T. Kavalli, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, The 1,3-bis(dicyanomethylidene)indane skeleton as a (photo) initiator in thermal ring opening polymerization at RT and radical or cationic photopolymerization, *RSC Adv.* 4 (2014) 15930–15936. <https://doi.org/10.1039/C3RA42819B>.
- [136] P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, L. Vidal, D. Gigmes, J.P. Fouassier, J. Lalevée, Structural Effects in the Indanedione Skeleton for the Design of Low Intensity

- 300–500 nm Light Sensitive Initiators., *Macromolecules*. 47 (2014) 26–34.
<https://doi.org/10.1021/ma402149g>.
- [137] K. Sun, S. Liu, C. Pigot, D. Brunel, B. Graff, M. Nechab, D. Gigmes, F. Morlet-Savary, Y. Zhang, P. Xiao, F. Dumur, J. Lalevée, Novel Push–Pull Dyes Derived from 1H-cyclopenta[b]naphthalene-1,3(2H)-dione as Versatile Photoinitiators for Photopolymerization and Their Related Applications: 3D Printing and Fabrication of Photocomposites, *Catalysts*. 10 (2020) 1196. <https://doi.org/10.3390/catal10101196>.
- [138] K. Sun, S. Liu, H. Chen, F. Morlet-Savary, B. Graff, C. Pigot, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, N-ethyl carbazole-1-allylidene-based push-pull dyes as efficient light harvesting photoinitiators for sunlight induced polymerization, *Eur. Polym. J.* 147 (2021) 110331. <https://doi.org/10.1016/j.eurpolymj.2021.110331>.
- [139] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Push–pull (thio)barbituric acid derivatives in dye photosensitized radical and cationic polymerization reactions under 457/473 nm laser beams or blue LEDs, *Polym. Chem.* 4 (2013) 3866–3875. <https://doi.org/10.1039/C3PY00372H>.
- [140] K. Sun, H. Chen, Y. Zhang, F. Morlet-Savary, B. Graff, P. Xiao, F. Dumur, J. Lalevée, High-performance sunlight induced polymerization using novel push-pull dyes with high light absorption properties, *Eur. Polym. J.* 151 (2021) 110410. <https://doi.org/10.1016/j.eurpolymj.2021.110410>.
- [141] H. Mokbel, F. Dumur, S. Telitel, L. Vidal, P. Xiao, D.-L. Versace, M.-A. Tehfe, F. Morlet-Savary, B. Graff, J.-P. Fouassier, D. Gigmes, J. Toufaily, T. Hamieh, J. Lalevée, Photoinitiating systems of polymerization and in situ incorporation of metal nanoparticles into polymer matrices upon exposure to visible light: push–pull malonate and malononitrile based dyes, *Polym. Chem.* 4 (2013) 5679–5687. <https://doi.org/10.1039/C3PY00846K>.
- [142] S. Helmy, S. Oh, F.A. Leibfarth, C.J. Hawker, J. Read de Alaniz, Design and Synthesis of Donor–Acceptor Stenhouse Adducts: A Visible Light Photoswitch Derived from Furfural, *J. Org. Chem.* 79 (2014) 11316–11329. <https://doi.org/10.1021/jo502206g>.
- [143] K. Sun, C. Pigot, Y. Zhang, T. Borjigin, F. Morlet-Savary, B. Graff, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, Sunlight Induced Polymerization Photoinitiated by Novel Push–Pull Dyes: Indane-1,3-Dione, 1H-Cyclopenta[b]Naphthalene-1,3(2H)-Dione and 4-Dimethoxyphenyl-1-Allylidene Derivatives, *Macromol. Chem. Phys.* 223 (2022) 2100439. <https://doi.org/10.1002/macp.202100439>.
- [144] C. Pigot, G. Noirbent, D. Brunel, F. Dumur, Recent advances on push–pull organic dyes as visible light photoinitiators of polymerization, *Eur. Polym. J.* 133 (2020) 109797. <https://doi.org/10.1016/j.eurpolymj.2020.109797>.
- [145] P. Xiao, F. Dumur, M. Frigoli, B. Graff, F. Morlet-Savary, G. Wantz, H. Bock, J.P. Fouassier, D. Gigmes, J. Lalevée, Perylene derivatives as photoinitiators in blue light sensitive cationic or radical curable films and panchromatic thiol-ene polymerizable films, *Eur. Polym. J.* 53 (2014) 215–222. <https://doi.org/10.1016/j.eurpolymj.2014.01.024>.
- [146] P. Xiao, F. Dumur, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Red-Light-Induced Cationic Photopolymerization: Perylene Derivatives as Efficient Photoinitiators, *Macromol. Rapid Commun.* 34 (2013) 1452–1458. <https://doi.org/10.1002/marc.201300383>.
- [147] F. Dumur, Recent advances on perylene-based photoinitiators of polymerization, *Eur. Polym. J.* 159 (2021) 110734. <https://doi.org/10.1016/j.eurpolymj.2021.110734>.

- [148] M.-A. Tehfe, F. Dumur, B. Graff, D. Gignes, J.-P. Fouassier, J. Lalevée, Green-Light-Induced Cationic Ring Opening Polymerization Reactions: Perylene-3,4:9,10-bis(Dicarboximide) as Efficient Photosensitizers, *Macromol. Chem. Phys.* 214 (2013) 1052–1060. <https://doi.org/10.1002/macp.201200728>.
- [149] I. Pyszka, Ł. Skowroński, B. Jędrzejewska, Study on New Dental Materials Containing Quinoxaline-Based Photoinitiators in Terms of Exothermicity of the Photopolymerization Process, *Int. J. Mol. Sci.* 24 (2023). <https://doi.org/10.3390/ijms24032752>.
- [150] I. Pyszka, B. Jędrzejewska, Photoinitiation abilities of indeno- and indoloquinoxaline derivatives and mechanical properties of dental fillings based on multifunctional acrylic monomers and glass ionomer, *Polymer*. 266 (2023) 125625. <https://doi.org/10.1016/j.polymer.2022.125625>.
- [151] N. Arsu, M. Aydın, Photoinduced free radical polymerization initiated with quinoxalines, *Angew. Makromol. Chem.* 270 (1999) 1–4. [https://doi.org/10.1002/\(SICI\)1522-9505\(19990901\)270:1<1::AID-APMC1>3.0.CO;2-2](https://doi.org/10.1002/(SICI)1522-9505(19990901)270:1<1::AID-APMC1>3.0.CO;2-2).
- [152] M. Aydın, N. Arsu, Photoinitiated free radical polymerization of methylmethacrylate by using of quinoxalines in the presence of aldehydes, *Prog. Org. Coat.* 56 (2006) 338–342. <https://doi.org/10.1016/j.porgcoat.2006.06.006>.
- [153] U. Bulut, G.E. Gunbas, L. Toppare, A quinoxaline derivative as a long wavelength photosensitizer for diaryliodonium salts, *J. Polym. Sci. Part Polym. Chem.* 48 (2010) 209–213. <https://doi.org/10.1002/pola.23779>.
- [154] U. Bulut, M. Kolay, S. Tarkuc, Y.A. Udum, L. Toppare, Quinoxaline derivatives as long wavelength photosensitizers in photoinitiated cationic polymerization of diaryliodonium salts, *Prog. Org. Coat.* 73 (2012) 215–218. <https://doi.org/10.1016/j.porgcoat.2011.11.004>.
- [155] X. Cao, F. Jin, Y.-F. Li, W.-Q. Chen, X.-M. Duan, L.-M. Yang, Triphenylamine-modified quinoxaline derivatives as two-photon photoinitiators, *New J. Chem.* 33 (2009) 1578–1582. <https://doi.org/10.1039/B900464E>.
- [156] D. Karaca Balta, S. Keskin, F. Karasu, N. Arsu, Quinoxaline derivatives as photoinitiators in UV-cured coatings, *Prog. Org. Coat.* 60 (2007) 207–210. <https://doi.org/10.1016/j.porgcoat.2007.07.024>.
- [157] Z. Kucybała, I. Pyszka, J. Pačzkowski, Development of new dyeing photoinitiators for free radical polymerization based on the 1H-pyrazolo[3,4-b]quinoxaline skeleton. Part 2, *J. Chem. Soc. Perkin Trans. 2.* (2000) 1559–1567. <https://doi.org/10.1039/B000583P>.
- [158] R. Podsiadły, A.M. Szymczak, K. Podemska, The synthesis of novel, visible-wavelength, oxidizable polymerization sensitizers based on the 8-halogeno-5,12-dihydroquinoxalino[2,3-b]quinoxaline skeleton, *Dyes Pigments.* 82 (2009) 365–371. <https://doi.org/10.1016/j.dyepig.2009.02.008>.
- [159] J.-Y. Yao, H.-H. Hou, X.-D. Ma, H.-J. Xu, Z.-X. Shi, J. Yin, X.-S. Jiang, Combining photo-cleavable and hydrogen-abstracting groups in quinoxaline with thioether bond as hybrid photoinitiator, *Chin. Chem. Lett.* 28 (2017) 6–12. <https://doi.org/10.1016/j.ccllet.2016.06.008>.
- [160] L. Sun, X. Jiang, J. Yin, Study of methoxyphenylquinoxalines (MOPQs) as photoinitiators in the negative photo-resist, *Prog. Org. Coat.* 67 (2010) 225–232. <https://doi.org/10.1016/j.porgcoat.2009.12.005>.
- [161] B.T. Ercan, S.S. Gultekin, T. Yesil, H. Dincalp, S. Koyuncu, Y. Yagci, C. Zafer, Highly conjugated isoindigo and quinoxaline dyes as sunlight photosensitizers for onium salt-

- photoinitiated cationic polymerization of epoxy resins, *Polym. Int.* 71 (2022) 867–873. <https://doi.org/10.1002/pi.6357>.
- [162] M.-A. Tehfe, F. Dumur, E. Contal, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, New insights into radical and cationic polymerizations upon visible light exposure: role of novel photoinitiator systems based on the pyrene chromophore, *Polym. Chem.* 4 (2013) 1625–1634. <https://doi.org/10.1039/C2PY20950K>.
- [163] S. Telitel, F. Dumur, T. Faury, B. Graff, M.-A. Tehfe, D. Gigmes, J.-P. Fouassier, J. Lalevée, New core-pyrene π structure organophotocatalysts usable as highly efficient photoinitiators, *Beilstein J. Org. Chem.* 9 (2013) 877–890. <https://doi.org/10.3762/bjoc.9.101>.
- [164] N. Uchida, H. Nakano, T. Igarashi, T. Sakurai, Nonsalt 1-(arylmethoxy)pyrene photoinitiators capable of initiating cationic polymerization, *J. Appl. Polym. Sci.* 131 (2014). <https://doi.org/10.1002/app.40510>.
- [165] A. Mishra, S. Daswal, 1-(Bromoacetyl)pyrene, a novel photoinitiator for the copolymerization of styrene and methylmethacrylate, *Radiat. Phys. Chem.* 75 (2006) 1093–1100. <https://doi.org/10.1016/j.radphyschem.2006.01.013>.
- [166] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Design of new Type I and Type II photoinitiators possessing highly coupled pyrene–ketone moieties, *Polym. Chem.* 4 (2013) 2313–2324. <https://doi.org/10.1039/C3PY21079K>.
- [167] F. Dumur, Recent advances on pyrene-based photoinitiators of polymerization, *Eur. Polym. J.* 126 (2020) 109564. <https://doi.org/10.1016/j.eurpolymj.2020.109564>.
- [168] M.-A. Tehfe, F. Dumur, N. Vilà, B. Graff, C.R. Mayer, J.P. Fouassier, D. Gigmes, J. Lalevée, A Multicolor Photoinitiator for Cationic Polymerization and Interpenetrated Polymer Network Synthesis: 2,7-Di-tert-butylidimethyldihydropyrene, *Macromol. Rapid Commun.* 34 (2013) 1104–1109. <https://doi.org/10.1002/marc.201300302>.
- [169] S. Telitel, F. Dumur, D. Gigmes, B. Graff, J.P. Fouassier, J. Lalevée, New functionalized aromatic ketones as photoinitiating systems for near visible and visible light induced polymerizations, *Polymer.* 54 (2013) 2857–2864. <https://doi.org/10.1016/j.polymer.2013.03.062>.
- [170] M.-A. Tehfe, J. Lalevée, S. Telitel, E. Contal, F. Dumur, D. Gigmes, D. Bertin, M. Nechab, B. Graff, F. Morlet-Savary, J.-P. Fouassier, Polyaromatic Structures as Organo-Photoinitiator Catalysts for Efficient Visible Light Induced Dual Radical/Cationic Photopolymerization and Interpenetrated Polymer Networks Synthesis, *Macromolecules.* 45 (2012) 4454–4460. <https://doi.org/10.1021/ma300760c>.
- [171] M. Ghali, M. Benltifa, C. Brahmi, L. Elbassi, F. Dumur, C. Simonnet-Jégat, L. Bousselmi, J. Lalevée, LED and solar photodecomposition of erythrosine B and rose Bengal using H₃PMo₁₂O₄₀/polymer photocatalyst, *Eur. Polym. J.* 159 (2021) 110743. <https://doi.org/10.1016/j.eurpolymj.2021.110743>.
- [172] C. Brahmi, M. Benltifa, M. Ghali, F. Dumur, C. Simonnet-Jégat, M. Valérie, F. Morlet-Savary, L. Bousselmi, J. Lalevée, Performance improvement of the photocatalytic process for the degradation of pharmaceutical compounds using new POM/polymer photocatalysts, *J. Environ. Chem. Eng.* 9 (2021) 106015. <https://doi.org/10.1016/j.jece.2021.106015>.
- [173] C. Brahmi, M. Benltifa, M. Ghali, F. Dumur, C. Simonnet-Jégat, V. Monnier, F. Morlet-Savary, L. Bousselmi, J. Lalevée, Polyoxometalates/polymer composites for the photodegradation of bisphenol-A, *J. Appl. Polym. Sci.* 138 (2021) 50864. <https://doi.org/10.1002/app.50864>.

- [174] M.-A. Tehfe, F. Dumur, P. Xiao, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, New chromone based photoinitiators for polymerization reactions under visible light, *Polym. Chem.* 4 (2013) 4234–4244. <https://doi.org/10.1039/C3PY00536D>.
- [175] J. You, H. Fu, D. Zhao, T. Hu, J. Nie, T. Wang, Flavonol dyes with different substituents in photopolymerization, *J. Photochem. Photobiol. Chem.* 386 (2020) 112097. <https://doi.org/10.1016/j.jphotochem.2019.112097>.
- [176] A. Al Mousawi, P. Garra, M. Schmitt, J. Toufaily, T. Hamieh, B. Graff, J.P. Fouassier, F. Dumur, J. Lalevée, 3-Hydroxyflavone and N-Phenylglycine in High Performance Photoinitiating Systems for 3D Printing and Photocomposites Synthesis, *Macromolecules.* 51 (2018) 4633–4641. <https://doi.org/10.1021/acs.macromol.8b00979>.
- [177] Q. Ma, L. Buchon, V. Magné, B. Graff, F. Morlet-Savary, Y. Xu, M. Benlifa, S. Lakhdar, J. Lalevée, Charge Transfer Complexes (CTCs) with Pyridinium Salts: Toward Efficient Dual Photochemical/Thermal Initiators and 3D Printing Applications, *Macromol. Rapid Commun.* n/a (2022) 2200314. <https://doi.org/10.1002/marc.202200314>.
- [178] I. Kminek, Y. Yagci, W. Schnabel, A water-soluble poly(methylphenylsilylene) derivative as a photoinitiator of radical polymerization of hydrophilic vinyl monomers, *Polym. Bull.* 29 (1992) 277–282. <https://doi.org/10.1007/BF00944819>.
- [179] F. Dumur, Recent advances on visible light Phenothiazine-based photoinitiators of polymerization, *Eur. Polym. J.* 165 (2022) 110999. <https://doi.org/10.1016/j.eurpolymj.2022.110999>.
- [180] L. Deng, L. Tang, J. Qu, Novel chalcone-based phenothiazine derivative photoinitiators for visible light induced photopolymerization with photobleaching and good biocompatibility, *Prog. Org. Coat.* 167 (2022) 106859. <https://doi.org/10.1016/j.porgcoat.2022.106859>.
- [181] M. Rahal, M. Abdallah, T.-T. Bui, F. Goubard, B. Graff, F. Dumur, J. Toufaily, T. Hamieh, J. Lalevée, Design of new phenothiazine derivatives as visible light photoinitiators, *Polym. Chem.* 11 (2020) 3349–3359. <https://doi.org/10.1039/D0PY00497A>.
- [182] S. Li, J. Hu, S. Zhang, C. Feng, L. Zhang, C. Wang, Z. He, L. Zhang, Novel A- π -D- π -A structure two-photon polymerization initiators based on phenothiazine and carbazole derivatives, *Chem. Pap.* 75 (2021) 5249–5256. <https://doi.org/10.1007/s11696-021-01713-9>.
- [183] D.F. Grishin, O.S. Lizyakina, L.B. Vaganova, A.A. Kaltenberg, I.D. Grishin, Radical polymerization of methyl methacrylate in the presence of methylene blue and organobromides under visible light irradiation, *Iran. Polym. J.* 30 (2021) 1117–1126. <https://doi.org/10.1007/s13726-021-00951-8>.
- [184] D. Xu, X. Zou, Y. Zhu, Z. Yu, M. Jin, R. Liu, Phenothiazine-based charge-transfer complexes as visible-light photoinitiating systems for acrylate and thiol-ene photopolymerization, *Prog. Org. Coat.* 166 (2022) 106772. <https://doi.org/10.1016/j.porgcoat.2022.106772>.
- [185] Y. Zhu, D. Xu, Y. Zhang, Y. Zhou, Y. Yagci, R. Liu, Phenacyl Phenothiazinium Salt as a New Broad-Wavelength-Absorbing Photoinitiator for Cationic and Free Radical Polymerizations, *Angew. Chem. Int. Ed.* 60 (2021) 16917–16921. <https://doi.org/10.1002/anie.202104531>.
- [186] P. Chao, R. Gu, X. Ma, T. Wang, Y. Zhao, Thiophene-substituted phenothiazine-based photosensitisers for radical and cationic photopolymerization reactions under visible laser beams (405 and 455 nm), *Polym. Chem.* 7 (2016) 5147–5156. <https://doi.org/10.1039/C6PY01095D>.

- [187] T.F. Zhou, X.Y. Ma, W.X. Han, X.P. Guo, R.Q. Gu, L.J. Yu, J. Li, Y.M. Zhao, T. Wang, D–A dyes with phenothiazine–carbazole/triphenylamine as double donors in photopolymerization under 455 nm and 532 nm laser beams, *Polym. Chem.* 7 (2016) 5039–5049. <https://doi.org/10.1039/C6PY00918B>.
- [188] M. Wang, X. Ma, J. Yu, X. Jia, D. Han, T. Zhou, J. Yang, J. Nie, T. Wang, Aromatic amine–sulfone/sulfoxide conjugated D– π -A– π -D-type dyes in photopolymerization under 405 nm and 455 nm laser beams, *Polym. Chem.* 6 (2015) 4424–4435. <https://doi.org/10.1039/C5PY00502G>.
- [189] F. Hao, Z. Liu, M. Zhang, J. Liu, S. Zhang, J. Wu, H. Zhou, Y. Tian, Four new two-photon polymerization initiators with varying donor and conjugated bridge: Synthesis and two-photon activity, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* 118 (2014) 538–542. <https://doi.org/10.1016/j.saa.2013.09.051>.
- [190] M. Abdallah, A. Hijazi, B. Graff, J.-P. Fouassier, G. Rodeghiero, A. Gualandi, F. Dumur, P.G. Cozzi, J. Lalevée, Coumarin derivatives as versatile photoinitiators for 3D printing, polymerization in water and photocomposite synthesis, *Polym. Chem.* 10 (2019) 872–884. <https://doi.org/10.1039/C8PY01708E>.
- [191] M. Abdallah, F. Dumur, A. Hijazi, G. Rodeghiero, A. Gualandi, P.G. Cozzi, J. Lalevée, Keto-coumarin scaffold for photoinitiators for 3D printing and photocomposites, *J. Polym. Sci.* 58 (2020) 1115–1129. <https://doi.org/10.1002/pol.20190290>.
- [192] M. Abdallah, A. Hijazi, F. Dumur, J. Lalevée, Coumarins as Powerful Photosensitizers for the Cationic Polymerization of Epoxy-Silicones under Near-UV and Visible Light and Applications for 3D Printing Technology, *Molecules.* 25 (2020) 2063. <https://doi.org/10.3390/molecules25092063>.
- [193] M. Abdallah, A. Hijazi, P.G. Cozzi, A. Gualandi, F. Dumur, J. Lalevée, Boron Compounds as Additives for the Cationic Polymerization Using Coumarin Derivatives in Epoxy Silicones, *Macromol. Chem. Phys.* 222 (2021) 2000404. <https://doi.org/10.1002/macp.202000404>.
- [194] Q. Chen, Q. Yang, P. Gao, B. Chi, J. Nie, Y. He, Photopolymerization of Coumarin-Containing Reversible Photoresponsive Materials Based on Wavelength Selectivity, *Ind. Eng. Chem. Res.* 58 (2019) 2970–2975. <https://doi.org/10.1021/acs.iecr.8b05164>.
- [195] Z. Li, X. Zou, G. Zhu, X. Liu, R. Liu, Coumarin-Based Oxime Esters: Photobleachable and Versatile Unimolecular Initiators for Acrylate and Thiol-Based Click Photopolymerization under Visible Light-Emitting Diode Light Irradiation, *ACS Appl. Mater. Interfaces.* 10 (2018) 16113–16123. <https://doi.org/10.1021/acsami.8b01767>.
- [196] M. Rahal, H. Mokbel, B. Graff, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Mono vs. Difunctional Coumarin as Photoinitiators in Photocomposite Synthesis and 3D Printing, *Catalysts.* 10 (2020) 1202. <https://doi.org/10.3390/catal10101202>.
- [197] M. Rajeshirke, M.C. Sreenath, S. Chitrambalam, I.H. Joe, N. Sekar, Enhancement of NLO Properties in OBO Fluorophores Derived from Carbazole–Coumarin Chalcones Containing Carboxylic Acid at the N-Alkyl Terminal End, *J. Phys. Chem. C.* 122 (2018) 14313–14325. <https://doi.org/10.1021/acs.jpcc.8b02937>.
- [198] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, Design of keto-coumarin based photoinitiator for Free Radical Photopolymerization: Towards 3D printing and photocomposites applications, *Eur. Polym. J.* 154 (2021) 110559. <https://doi.org/10.1016/j.eurpolymj.2021.110559>.
- [199] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, G. Noirbent, D. Gimes, F. Dumur, J. Lalevée, 3-Carboxylic Acid and Formyl-Derived Coumarins as Photoinitiators in Photo-

Oxidation or Photo-Reduction Processes for Photopolymerization upon Visible Light: Photocomposite Synthesis and 3D Printing Applications, *Molecules*. 26 (2021).
<https://doi.org/10.3390/molecules26061753>.

- [200] F. Hammoud, N. Giacoletto, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gignes, F. Dumur, J. Lalevée, Substituent effects on the photoinitiation ability of coumarin-based oxime-ester photoinitiators for free radical photopolymerization, *Mater. Chem. Front.* 5 (2021) 8361–8370. <https://doi.org/10.1039/D1QM01310F>.
- [201] F. Dumur, Recent advances on coumarin-based photoinitiators of polymerization, *Eur. Polym. J.* 163 (2022) 110962. <https://doi.org/10.1016/j.eurpolymj.2021.110962>.
- [202] Z. Liu, F. Dumur, Recent advances on visible light Coumarin-based oxime esters as initiators of polymerization, *Eur. Polym. J.* 177 (2022) 111449. <https://doi.org/10.1016/j.eurpolymj.2022.111449>.
- [203] Y. Zhu, L. Li, Y. Zhang, Y. Ou, J. Zhang, Y. Yagci, R. Liu, Broad wavelength sensitive coumarin sulfonium salts as photoinitiators for cationic, free radical and hybrid photopolymerizations, *Prog. Org. Coat.* 174 (2023) 107272. <https://doi.org/10.1016/j.porgcoat.2022.107272>.
- [204] E.A. Kamoun, A. Winkel, M. Eisenburger, H. Menzel, Carboxylated camphorquinone as visible-light photoinitiator for biomedical application: Synthesis, characterization, and application, *Arab. J. Chem.* 9 (2016) 745–754. <https://doi.org/10.1016/j.arabjc.2014.03.008>.
- [205] A. Santini, I.T. Gallegos, C.M. Felix, Photoinitiators in Dentistry: A Review, *Prim. Dent. J.* 2 (2013) 30–33. <https://doi.org/10.1308/205016814809859563>.
- [206] H. Mokbel, J. Toufaily, T. Hamieh, F. Dumur, D. Campolo, D. Gignes, J.P. Fouassier, J. Ortyl, J. Lalevée, Specific cationic photoinitiators for near UV and visible LEDs: Iodonium versus ferrocenium structures, *J. Appl. Polym. Sci.* 132 (2015) 42759. <https://doi.org/10.1002/app.42759>.
- [207] S. Villotte, D. Gignes, F. Dumur, J. Lalevée, Design of Iodonium Salts for UV or Near-UV LEDs for Photoacid Generator and Polymerization Purposes, *Molecules*. 25 (2020) 149. <https://doi.org/10.3390/molecules25010149>.
- [208] M.A. Tasdelen, V. Kumbaraci, S. Jockusch, N.J. Turro, N. Talinli, Y. Yagci, Photoacid Generation by Stepwise Two-Photon Absorption: Photoinitiated Cationic Polymerization of Cyclohexene Oxide by Using Benzodioxinone in the Presence of Iodonium Salt, *Macromolecules*. 41 (2008) 295–297. <https://doi.org/10.1021/ma7023649>.
- [209] J.V. Crivello, J.H.W. Lam, Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization, *Macromolecules*. 10 (1977) 1307–1315. <https://doi.org/10.1021/ma60060a028>.
- [210] Y. He, W. Zhou, F. Wu, M. Li, E. Wang, Photoreaction and photopolymerization studies on squaraine dyes/iodonium salts combination, *J. Photochem. Photobiol. Chem.* 162 (2004) 463–471. [https://doi.org/10.1016/S1010-6030\(03\)00390-3](https://doi.org/10.1016/S1010-6030(03)00390-3).
- [211] L.I. Jun, L.I. Miaozen, S. Huaihai, Y. Yongyuan, W. Erjian, Photopolymerization Initiated by Dimethylaminochalcone/Diphenyliodonium Salt Combination System Sensitive to Visible Light, *Chin. J Polym Sci.* 11 (1993) 163–170.
- [212] N. Zivic, P.K. Kuroishi, F. Dumur, D. Gignes, A.P. Dove, H. Sardon, Recent Advances and Challenges in the Design of Organic Photoacid and Photobase Generators for Polymerizations, *Angew. Chem. Int. Ed.* 58 (2019) 10410–10422. <https://doi.org/10.1002/anie.201810118>.
- [213] F. Petko, M. Galek, E. Hola, M. Topa-Skwarczyńska, W. Tomal, M. Jankowska, M. Pilch, R. Popielarz, B. Graff, F. Morlet-Savary, J. Lalevee, J. Ortyl, Symmetric Iodonium Salts

Based on Benzylidene as One-Component Photoinitiators for Applications in 3D Printing, *Chem. Mater.* 34 (2022) 10077–10092.
<https://doi.org/10.1021/acs.chemmater.2c02796>.

- [214] F. Petko, M. Galek, E. Hola, R. Popielarz, J. Ortyl, One-Component Cationic Photoinitiators from Tunable Benzylidene Scaffolds for 3D Printing Applications, *Macromolecules*. 54 (2021) 7070–7087. <https://doi.org/10.1021/acs.macromol.1c01048>.
- [215] J. Lalevée, M. Peter, F. Dumur, D. Gigmes, N. Blanchard, M.-A. Tehfe, F. Morlet-Savary, J.P. Fouassier, Subtle Ligand Effects in Oxidative Photocatalysis with Iridium Complexes: Application to Photopolymerization, *Chem. – Eur. J.* 17 (2011) 15027–15031. <https://doi.org/10.1002/chem.201101445>.
- [216] J. Lalevée, M.-A. Tehfe, F. Dumur, D. Gigmes, N. Blanchard, F. Morlet-Savary, J.P. Fouassier, Iridium Photocatalysts in Free Radical Photopolymerization under Visible Lights, *ACS Macro Lett.* 1 (2012) 286–290. <https://doi.org/10.1021/mz2001753>.
- [217] J. Lalevée, F. Dumur, C.R. Mayer, D. Gigmes, G. Nasr, M.-A. Tehfe, S. Telitel, F. Morlet-Savary, B. Graff, J.P. Fouassier, Photopolymerization of N-Vinylcarbazole Using Visible-Light Harvesting Iridium Complexes as Photoinitiators, *Macromolecules*. 45 (2012) 4134–4141. <https://doi.org/10.1021/ma3005229>.
- [218] M.-A. Tehfe, M. Lepeltier, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Structural Effects in the Iridium Complex Series: Photoredox Catalysis and Photoinitiation of Polymerization Reactions under Visible Lights, *Macromol. Chem. Phys.* 218 (2017) 1700192. <https://doi.org/10.1002/macp.201700192>.
- [219] S. Telitel, F. Dumur, S. Telitel, O. Soppera, M. Lepeltier, Y. Guillaneuf, J. Poly, F. Morlet-Savary, P. Fioux, J.-P. Fouassier, D. Gigmes, J. Lalevée, Photoredox catalysis using a new iridium complex as an efficient toolbox for radical, cationic and controlled polymerizations under soft blue to green lights, *Polym. Chem.* 6 (2014) 613–624. <https://doi.org/10.1039/C4PY01358A>.
- [220] S. Telitel, F. Dumur, M. Lepeltier, D. Gigmes, J.-P. Fouassier, J. Lalevée, Photoredox process induced polymerization reactions: Iridium complexes for panchromatic photoinitiating systems, *Comptes Rendus Chim.* 19 (2016) 71–78. <https://doi.org/10.1016/j.crci.2015.06.016>.
- [221] F. Dumur, D. Bertin, D. Gigmes, Iridium (III) complexes as promising emitters for solid-state Light-Emitting Electrochemical Cells (LECs), *Int. J. Nanotechnol.* 9 (2012) 377–395. <https://doi.org/10.1504/IJNT.2012.045343>.
- [222] F. Dumur, G. Nasr, G. Wantz, C.R. Mayer, E. Dumas, A. Guerlin, F. Miomandre, G. Clavier, D. Bertin, D. Gigmes, Cationic iridium complex for the design of soft salt-based phosphorescent OLEDs and color-tunable light-emitting electrochemical cells, *Org. Electron.* 12 (2011) 1683–1694. <https://doi.org/10.1016/j.orgel.2011.06.014>.
- [223] N. Karaca, N. Ocal, N. Arsu, S. Jockusch, Thioxanthone-benzothiophenes as photoinitiator for free radical polymerization, *J. Photochem. Photobiol. Chem.* 331 (2016) 22–28. <https://doi.org/10.1016/j.jphotochem.2016.01.017>.
- [224] D.K. Balta, N. Cetiner, G. Temel, Z. Turgut, N. Arsu, An annelated thioxanthone as a new Type II initiator, *J. Photochem. Photobiol. Chem.* 199 (2008) 316–321. <https://doi.org/10.1016/j.jphotochem.2008.06.008>.
- [225] D.K. Balta, G. Temel, G. Goksu, N. Ocal, N. Arsu, Thioxanthone–Diphenyl Anthracene: Visible Light Photoinitiator, *Macromolecules*. 45 (2012) 119–125. <https://doi.org/10.1021/ma202168m>.

- [226] S. Dadashi-Silab, C. Aydogan, Y. Yagci, Shining a light on an adaptable photoinitiator: advances in photopolymerizations initiated by thioxanthenes, *Polym. Chem.* 6 (2015) 6595–6615. <https://doi.org/10.1039/C5PY01004G>.
- [227] T.N. Eren, N. Yasar, V. Aviyente, F. Morlet-Savary, B. Graff, J.P. Fouassier, J. Lalevee, D. Avci, Photophysical and Photochemical Studies of Novel Thioxanthone-Functionalized Methacrylates through LED Excitation, *Macromol. Chem. Phys.* 217 (2016) 1501–1512. <https://doi.org/10.1002/macp.201600051>.
- [228] J. Qiu, J. Wei, Thioxanthone photoinitiator containing polymerizable N-aromatic maleimide for photopolymerization, *J. Polym. Res.* 21 (2014) 559. <https://doi.org/10.1007/s10965-014-0559-4>.
- [229] H. Tar, D. Sevinc Esen, M. Aydin, C. Ley, N. Arsu, X. Allonas, Panchromatic Type II Photoinitiator for Free Radical Polymerization Based on Thioxanthone Derivative, *Macromolecules.* 46 (2013) 3266–3272. <https://doi.org/10.1021/ma302641d>.
- [230] Q. Wu, X. Wang, Y. Xiong, J. Yang, H. Tang, Thioxanthone based one-component polymerizable visible light photoinitiator for free radical polymerization, *RSC Adv.* 6 (2016) 66098–66107. <https://doi.org/10.1039/C6RA15349F>.
- [231] Q. Wu, K. Tang, Y. Xiong, X. Wang, J. Yang, H. Tang, High-Performance and Low Migration One-Component Thioxanthone Visible Light Photoinitiators, *Macromol. Chem. Phys.* 218 (2017) 1600484. <https://doi.org/10.1002/macp.201600484>.
- [232] X. Wu, M. Jin, J.-P. Malval, D. Wan, H. Pu, Visible light-emitting diode-sensitive thioxanthone derivatives used in versatile photoinitiating systems for photopolymerizations, *J. Polym. Sci. Part Polym. Chem.* 55 (2017) 4037–4045. <https://doi.org/10.1002/pola.28871>.
- [233] J. Lalevée, M.-A. Tehfe, F. Dumur, D. Gigmes, B. Graff, F. Morlet-Savary, J.-P. Fouassier, Light-Harvesting Organic Photoinitiators of Polymerization, *Macromol. Rapid Commun.* 34 (2013) 239–245. <https://doi.org/10.1002/marc.201200578>.
- [234] D.S. Esen, F. Karasu, N. Arsu, The investigation of photoinitiated polymerization of multifunctional acrylates with TX-BT by Photo-DSC and RT-FTIR, *Prog. Org. Coat.* 70 (2011) 102–107. <https://doi.org/10.1016/j.porgcoat.2010.10.010>.
- [235] J. Lalevée, N. Blanchard, M.A. Tehfe, C. Fries, F. Morlet-Savary, D. Gigmes, J.P. Fouassier, New thioxanthone and xanthone photoinitiators based on silyl radical chemistry, *Polym. Chem.* 2 (2011) 1077–1084. <https://doi.org/10.1039/C0PY00392A>.
- [236] T. Gencoglu, T.N. Eren, J. Lalevée, D. Avci, A Water Soluble, Low Migration, and Visible Light Photoinitiator by Thioxanthone-Functionalization of Poly(ethylene glycol)-Containing Poly(β -amino ester), *Macromol. Chem. Phys.* n/a (2022) 2100450. <https://doi.org/10.1002/macp.202100450>.
- [237] Y. Wang, R. Chen, D. Liu, C. Peng, J. Wang, X. Dong, New functionalized thioxanthone derivatives as type I photoinitiators for polymerization under UV-Vis LEDs, *New J. Chem.* (2023). <https://doi.org/10.1039/D2NJ05996G>.
- [238] H. Chen, G. Noirbent, K. Sun, D. Brunel, D. Gigmes, F. Morlet-Savary, Y. Zhang, S. Liu, P. Xiao, F. Dumur, J. Lalevée, Photoinitiators derived from natural product scaffolds: monochalcones in three-component photoinitiating systems and their applications in 3D printing, *Polym. Chem.* 11 (2020) 4647–4659. <https://doi.org/10.1039/D0PY00568A>.
- [239] L. Tang, J. Nie, X. Zhu, A high performance phenyl-free LED photoinitiator for cationic or hybrid photopolymerization and its application in LED cationic 3D printing, *Polym. Chem.* 11 (2020) 2855–2863. <https://doi.org/10.1039/D0PY00142B>.

- [240] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gimes, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Allyloxy ketones as efficient photoinitiators with high migration stability in free radical polymerization and 3D printing, *Dyes Pigments*. 185 (2021) 108900. <https://doi.org/10.1016/j.dyepig.2020.108900>.
- [241] Y. Xu, Z. Ding, H. Zhu, B. Graff, S. Knopf, P. Xiao, F. Dumur, J. Lalevée, Design of ketone derivatives as highly efficient photoinitiators for free radical and cationic photopolymerizations and application in 3D printing of composites, *J. Polym. Sci.* 58 (2020) 3432–3445. <https://doi.org/10.1002/pol.20200658>.
- [242] H. Chen, G. Noirbent, S. Liu, D. Brunel, B. Graff, D. Gimes, Y. Zhang, K. Sun, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, Bis-chalcone derivatives derived from natural products as near-UV/visible light sensitive photoinitiators for 3D/4D printing, *Mater. Chem. Front.* 5 (2021) 901–916. <https://doi.org/10.1039/D0QM00755B>.
- [243] S. Liu, Y. Zhang, K. Sun, B. Graff, P. Xiao, F. Dumur, J. Lalevée, Design of photoinitiating systems based on the chalcone-anthracene scaffold for LED cationic photopolymerization and application in 3D printing, *Eur. Polym. J.* 147 (2021) 110300. <https://doi.org/10.1016/j.eurpolymj.2021.110300>.
- [244] N. Giacoletto, F. Dumur, Recent Advances in bis-Chalcone-Based Photoinitiators of Polymerization: From Mechanistic Investigations to Applications, *Molecules*. 26 (2021) 3192. <https://doi.org/10.3390/molecules26113192>.
- [245] M. Ibrahim-Ouali, F. Dumur, Recent Advances on Chalcone-based Photoinitiators of Polymerization, *Eur. Polym. J.* (2021) 110688. <https://doi.org/10.1016/j.eurpolymj.2021.110688>.
- [246] H. Chen, G. Noirbent, S. Liu, Y. Zhang, K. Sun, F. Morlet-Savary, D. Gimes, P. Xiao, F. Dumur, J. Lalevée, In situ generation of Ag nanoparticles during photopolymerization by using newly developed dyes-based three-component photoinitiating systems and the related 3D printing applications and their shape change behavior, *J. Polym. Sci.* 59 (2021) 843–859. <https://doi.org/10.1002/pol.20210154>.
- [247] H. Chen, M. Vahdati, P. Xiao, F. Dumur, J. Lalevée, Water-Soluble Visible Light Sensitive Photoinitiating System Based on Charge Transfer Complexes for the 3D Printing of Hydrogels, *Polymers*. 13 (2021). <https://doi.org/10.3390/polym13183195>.
- [248] M.-A. Tehfe, F. Dumur, P. Xiao, M. Delgove, B. Graff, J.-P. Fouassier, D. Gimes, J. Lalevée, Chalcone derivatives as highly versatile photoinitiators for radical, cationic, thiol–ene and IPN polymerization reactions upon exposure to visible light, *Polym. Chem.* 5 (2014) 382–390. <https://doi.org/10.1039/C3PY00922J>.
- [249] K. Sun, Y. Xu, F. Dumur, F. Morlet-Savary, H. Chen, C. Dietlin, B. Graff, J. Lalevée, P. Xiao, In silico rational design by molecular modeling of new ketones as photoinitiators in three-component photoinitiating systems: application in 3D printing, *Polym. Chem.* 11 (2020) 2230–2242. <https://doi.org/10.1039/C9PY01874C>.
- [250] H. Chen, C. Regeard, H. Salmi, F. Morlet-Savary, N. Giacoletto, M. Nechab, P. Xiao, F. Dumur, J. Lalevée, Interpenetrating polymer network hydrogels using natural based dyes initiating systems: antibacterial activity and 3D/4D performance, *Eur. Polym. J.* (2022) 111042. <https://doi.org/10.1016/j.eurpolymj.2022.111042>.
- [251] S.-C. Yen, J.-S. Ni, Y.-C. Chen, Triphenylamine-functionalized chalcones as one-component type II visible-light-absorbing photoinitiators for free radical photopolymerization, *Eur. Polym. J.* 187 (2023) 111885. <https://doi.org/10.1016/j.eurpolymj.2023.111885>.

- [252] Y. Gao, J. Qu, New long-wavelength D- π -A- π -D chalcone photoinitiator for visible light polymerization with photobleaching and biocompatibility properties, *Polym. Chem.* 14 (2023) 952–962. <https://doi.org/10.1039/D2PY01601J>.
- [253] L. Deng, J. Qu, Synthesis and properties of novel bis-chalcone-based photoinitiators for LED polymerization with photobleaching and low migration, *Prog. Org. Coat.* 174 (2023) 107240. <https://doi.org/10.1016/j.porgcoat.2022.107240>.
- [254] F. Nzulu, S. Telitel, F. Stoffelbach, B. Graff, F. Morlet-Savary, J. Lalevée, L. Fensterbank, J.-P. Goddard, C. Ollivier, A dinuclear gold(i) complex as a novel photoredox catalyst for light-induced atom transfer radical polymerization, *Polym. Chem.* 6 (2015) 4605–4611. <https://doi.org/10.1039/C5PY00435G>.
- [255] P. Xiao, F. Dumur, J. Zhang, J.P. Fouassier, D. Gigmes, J. Lalevée, Copper Complexes in Radical Photoinitiating Systems: Applications to Free Radical and Cationic Polymerization upon Visible LEDs, *Macromolecules.* 47 (2014) 3837–3844. <https://doi.org/10.1021/ma5006793>.
- [256] P. Xiao, F. Dumur, J. Zhang, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper complexes: the effect of ligands on their photoinitiation efficiencies in radical polymerization reactions under visible light, *Polym. Chem.* 5 (2014) 6350–6357. <https://doi.org/10.1039/C4PY00925H>.
- [257] P. Xiao, J. Zhang, D. Campolo, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper and iron complexes as visible-light-sensitive photoinitiators of polymerization, *J. Polym. Sci. Part Polym. Chem.* 53 (2015) 2673–2684. <https://doi.org/10.1002/pola.27762>.
- [258] P. Garra, M. Carré, F. Dumur, F. Morlet-Savary, C. Dietlin, D. Gigmes, J.-P. Fouassier, J. Lalevée, Copper-Based (Photo)redox Initiating Systems as Highly Efficient Systems for Interpenetrating Polymer Network Preparation, *Macromolecules.* 51 (2018) 679–688. <https://doi.org/10.1021/acs.macromol.7b02491>.
- [259] P. Garra, F. Dumur, F. Morlet-Savary, C. Dietlin, D. Gigmes, J.P. Fouassier, J. Lalevée, Mechanosynthesis of a Copper complex for redox initiating systems with a unique near infrared light activation, *J. Polym. Sci. Part Polym. Chem.* 55 (2017) 3646–3655. <https://doi.org/10.1002/pola.28750>.
- [260] P. Garra, F. Dumur, A.A. Mousawi, B. Graff, D. Gigmes, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, Mechanosynthesized copper(I) complex based initiating systems for redox polymerization: towards upgraded oxidizing and reducing agents, *Polym. Chem.* 8 (2017) 5884–5896. <https://doi.org/10.1039/C7PY01244F>.
- [261] H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Copper photoredox catalyst “G1”: a new high performance photoinitiator for near-UV and visible LEDs, *Polym. Chem.* 8 (2017) 5580–5592. <https://doi.org/10.1039/C7PY01016H>.
- [262] H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Simultaneous initiation of radical and cationic polymerization reactions using the “G1” copper complex as photoredox catalyst: Applications of free radical/cationic hybrid photopolymerization in the composites and 3D printing fields, *Prog. Org. Coat.* 132 (2019) 50–61. <https://doi.org/10.1016/j.porgcoat.2019.02.044>.
- [263] A.A. Mousawi, A. Kermagoret, D.-L. Versace, J. Toufaily, T. Hamieh, B. Graff, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Copper photoredox catalysts for polymerization upon near UV or visible light: structure/reactivity/efficiency

- relationships and use in LED projector 3D printing resins, *Polym. Chem.* 8 (2017) 568–580. <https://doi.org/10.1039/C6PY01958G>.
- [264] A. Mau, G. Noirbent, C. Dietlin, B. Graff, D. Gigmes, F. Dumur, J. Lalevée, Panchromatic Copper Complexes for Visible Light Photopolymerization, *Photochem.* 1 (2021). <https://doi.org/10.3390/photochem1020010>.
- [265] A. Mau, C. Dietlin, F. Dumur, J. Lalevée, Concomitant initiation of radical and cationic polymerisations using new copper complexes as photoinitiators: Synthesis and characterisation of acrylate/epoxy interpenetrated polymer networks, *Eur. Polym. J.* 152 (2021) 110457. <https://doi.org/10.1016/j.eurpolymj.2021.110457>.
- [266] P. Garra, F. Dumur, D. Gigmes, A. Al Mousawi, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, Copper (Photo)redox Catalyst for Radical Photopolymerization in Shadowed Areas and Access to Thick and Filled Samples, *Macromolecules.* 50 (2017) 3761–3771. <https://doi.org/10.1021/acs.macromol.7b00622>.
- [267] P. Garra, F. Dumur, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, A New Highly Efficient Amine-Free and Peroxide-Free Redox System for Free Radical Polymerization under Air with Possible Light Activation, *Macromolecules.* 49 (2016) 6296–6309. <https://doi.org/10.1021/acs.macromol.6b01615>.
- [268] P. Garra, A. Kermagoret, A.A. Mousawi, F. Dumur, D. Gigmes, F. Morlet-Savary, C. Dietlin, J.P. Fouassier, J. Lalevée, New copper(I) complex based initiating systems in redox polymerization and comparison with the amine/benzoyl peroxide reference, *Polym. Chem.* 8 (2017) 4088–4097. <https://doi.org/10.1039/C7PY00726D>.
- [269] G. Noirbent, F. Dumur, Recent Advances on Copper Complexes as Visible Light Photoinitiators and (Photo) Redox Initiators of Polymerization, *Catalysts.* 10 (2020). <https://doi.org/10.3390/catal10090953>.
- [270] T. Borjigin, G. Noirbent, D. Gigmes, P. Xiao, F. Dumur, J. Lalevée, The new LED-Sensitive photoinitiators of Polymerization: Copper complexes in free radical and cationic photoinitiating systems and application in 3D printing, *Eur. Polym. J.* 162 (2022) 110885. <https://doi.org/10.1016/j.eurpolymj.2021.110885>.
- [271] M. Rahal, G. Noirbent, B. Graff, J. Toufaily, T. Hamieh, D. Gigmes, F. Dumur, J. Lalevée, Novel Copper Complexes as Visible Light Photoinitiators for the Synthesis of Interpenetrating Polymer Networks (IPNs), *Polymers.* 14 (2022). <https://doi.org/10.3390/polym14101998>.
- [272] J.-T. Lin, J. Lalevee, D.-C. Cheng, Efficacy analysis of new copper complex for visible light (455, 530 nm) radical/cationic photopolymerization: The synergic effects and catalytic cycle, *PLOS ONE.* 17 (2022) e0270679. <https://doi.org/10.1371/journal.pone.0270679>.
- [273] A.A. Mousawi, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, F. Goubard, T.-T. Bui, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Azahelicenes as visible light photoinitiators for cationic and radical polymerization: Preparation of photoluminescent polymers and use in high performance LED projector 3D printing resins, *J. Polym. Sci. Part Polym. Chem.* 55 (2017) 1189–1199. <https://doi.org/10.1002/pola.28476>.
- [274] A. Al Mousawi, M. Schmitt, F. Dumur, J. Ouyang, L. Favereau, V. Dorcet, N. Vanthuyne, P. Garra, J. Toufaily, T. Hamieh, B. Graff, J.P. Fouassier, D. Gigmes, J. Crassous, J. Lalevée, Visible Light Chiral Photoinitiator for Radical Polymerization and Synthesis of Polymeric Films with Strong Chiroptical Activity, *Macromolecules.* 51 (2018) 5628–5637. <https://doi.org/10.1021/acs.macromol.8b01085>.

- [275] M.-A. Tehfe, F. Dumur, S. Telitel, D. Gigmes, E. Contal, D. Bertin, F. Morlet-Savary, B. Graff, J.-P. Fouassier, J. Lalevée, Zinc-based metal complexes as new photocatalysts in polymerization initiating systems, *Eur. Polym. J.* 49 (2013) 1040–1049. <https://doi.org/10.1016/j.eurpolymj.2013.01.023>.
- [276] N. Giacoletto, M. Ibrahim-Ouali, F. Dumur, Recent advances on squaraine-based photoinitiators of polymerization, *Eur. Polym. J.* 150 (2021) 110427. <https://doi.org/10.1016/j.eurpolymj.2021.110427>.
- [277] P. Xiao, F. Dumur, T.T. Bui, F. Goubard, B. Graff, F. Morlet-Savary, J.P. Fouassier, D. Gigmes, J. Lalevée, Panchromatic Photopolymerizable Cationic Films Using Indoline and Squaraine Dye Based Photoinitiating Systems, *ACS Macro Lett.* 2 (2013) 736–740. <https://doi.org/10.1021/mz400316y>.
- [278] V. Launay, A. Caron, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, NIR Organic Dyes as Innovative Tools for Reprocessing/Recycling of Plastics: Benefits of the Photothermal Activation in the Near-Infrared Range, *Adv. Funct. Mater.* 31 (2021) 2006324. <https://doi.org/10.1002/adfm.202006324>.
- [279] A. Bonardi, F. Bonardi, G. Noirbent, F. Dumur, C. Dietlin, D. Gigmes, J.-P. Fouassier, J. Lalevée, Different NIR dye scaffolds for polymerization reactions under NIR light, *Polym. Chem.* 10 (2019) 6505–6514. <https://doi.org/10.1039/C9PY01447K>.
- [280] A. Balcerak, D. Kwiatkowska, J. Kabatc, Novel photoinitiators based on difluoroborate complexes of squaraine dyes for radical polymerization of acrylates upon visible light, *Polym. Chem.* 13 (2022) 220–234. <https://doi.org/10.1039/D1PY01294K>.
- [281] F. Dumur, Recent advances on visible light pyrrole-derived photoinitiators of polymerization, *Eur. Polym. J.* 173 (2022) 111254. <https://doi.org/10.1016/j.eurpolymj.2022.111254>.
- [282] Y. Li, U. Shaukat, S. Schlögl, T. Xue, J. Li, J. Nie, X. Zhu, A pyrrole–carbazole photoinitiator for radical and cationic visible light LED photopolymerization, *Eur. Polym. J.* 182 (2023) 111700. <https://doi.org/10.1016/j.eurpolymj.2022.111700>.
- [283] J. Zhang, P. Xiao, F. Dumur, C. Guo, W. Hong, Y. Li, D. Gigmes, B. Graff, J.-P. Fouassier, J. Lalevée, Polymeric Photoinitiators: A New Search toward High Performance Visible Light Photoinitiating Systems, *Macromol. Chem. Phys.* 217 (2016) 2145–2153. <https://doi.org/10.1002/macp.201600260>.
- [284] M. Abdallah, H. Le, A. Hijazi, M. Schmitt, B. Graff, F. Dumur, T.-T. Bui, F. Goubard, J.-P. Fouassier, J. Lalevée, Acridone derivatives as high performance visible light photoinitiators for cationic and radical photosensitive resins for 3D printing technology and for low migration photopolymer property, *Polymer.* 159 (2018) 47–58. <https://doi.org/10.1016/j.polymer.2018.11.021>.
- [285] J. Zhang, F. Dumur, M. Bouzrati, P. Xiao, C. Dietlin, F. Morlet-Savary, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Novel panchromatic photopolymerizable matrices: N,N'-dibutylquinacridone as an efficient and versatile photoinitiator, *J. Polym. Sci. Part Polym. Chem.* 53 (2015) 1719–1727. <https://doi.org/10.1002/pola.27615>.
- [286] M.-A. Tehfe, F. Dumur, E. Contal, B. Graff, D. Gigmes, J.-P. Fouassier, J. Lalevée, Novel Highly Efficient Organophotocatalysts: Truxene–Acridine-1,8-diones as Photoinitiators of Polymerization, *Macromol. Chem. Phys.* 214 (2013) 2189–2201. <https://doi.org/10.1002/macp.201300362>.
- [287] P. Xiao, F. Dumur, M.-A. Tehfe, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Difunctional acridinediones as photoinitiators of polymerization under UV and visible

- lights: Structural effects, *Polymer*. 54 (2013) 3458–3466.
<https://doi.org/10.1016/j.polymer.2013.04.055>.
- [288] P. Xiao, F. Dumur, M.-A. Tehfe, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Acridinediones: Effect of Substituents on Their Photoinitiating Abilities in Radical and Cationic Photopolymerization, *Macromol. Chem. Phys.* 214 (2013) 2276–2282.
<https://doi.org/10.1002/macp.201300363>.
- [289] Y. Wu, C. Dai, J. Ke, R. Tang, C. Huang, J. Wang, Y. Situ, H. Huang, Synthesis and characterization of low-migration bisacylphenylphosphine oxide photoinitiators, *Prog. Org. Coat.* 176 (2023) 107396. <https://doi.org/10.1016/j.porgcoat.2022.107396>.
- [290] M.-A. Tehfe, F. Dumur, P. Xiao, J. Zhang, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, J. Lalevée, Photoinitiators based on a phenazine scaffold: High performance systems upon near-UV or visible LED (385, 395 and 405 nm) irradiations, *Polymer*. 55 (2014) 2285–2293. <https://doi.org/10.1016/j.polymer.2014.04.005>.
- [291] J.M. Gallmetzer, S. Kröll, D. Werner, D. Wielend, M. Irimia-Vladu, E. Portenkirchner, N.S. Sariciftci, T.S. Hofer, Anthraquinone and its derivatives as sustainable materials for electrochemical applications – a joint experimental and theoretical investigation of the redox potential in solution, *Phys. Chem. Chem. Phys.* 24 (2022) 16207–16219.
<https://doi.org/10.1039/D2CP01717B>.
- [292] M. Zhao, X. Yang, G.C. Tsui, Q. Miao, Trifluoromethylation of Anthraquinones for n-Type Organic Semiconductors in Field Effect Transistors, *J. Org. Chem.* 85 (2020) 44–51.
<https://doi.org/10.1021/acs.joc.9b01263>.
- [293] L.-W. Luo, W. Ma, P. Dong, X. Huang, C. Yan, C. Han, P. Zheng, C. Zhang, J.-X. Jiang, Synthetic Control of Electronic Property and Porosity in Anthraquinone-Based Conjugated Polymer Cathodes for High-Rate and Long-Cycle-Life Na–Organic Batteries, *ACS Nano*. 16 (2022) 14590–14599. <https://doi.org/10.1021/acsnano.2c05090>.
- [294] S.S. Birajdar, M. Ourabi, B. Mirka, K.S. More, A.L. Puyad, B.H. Lessard, S.V. Bhosale, S.V. Bhosale, Direct Arylation: A Greener Synthesis of Anthraquinone–Naphthalene diimide-Based Small Chromophores for Applications in Organic Thin Film Transistors, *Chem. – Asian J.* 17 (2022) e202200887. <https://doi.org/10.1002/asia.202200887>.
- [295] E.M. Malik, C.E. Müller, Anthraquinones As Pharmacological Tools and Drugs, *Med. Res. Rev.* 36 (2016) 705–748. <https://doi.org/10.1002/med.21391>.
- [296] M. Sebak, F. Molham, C. Greco, M.A. Tammam, M. Sobeh, A. El-Demerdash, Chemical diversity, medicinal potentialities, biosynthesis, and pharmacokinetics of anthraquinones and their congeners derived from marine fungi: a comprehensive update, *RSC Adv.* 12 (2022) 24887–24921. <https://doi.org/10.1039/D2RA03610J>.
- [297] M.S. Malik, R.I. Alsantali, R.S. Jassas, A.A. Alsimaree, R. Syed, M.A. Alsharif, K. Kalpana, M. Morad, I.I. Althagafi, S.A. Ahmed, Journey of anthraquinones as anticancer agents – a systematic review of recent literature, *RSC Adv.* 11 (2021) 35806–35827.
<https://doi.org/10.1039/D1RA05686G>.
- [298] F.S. Dainton, M. Tordoff, The polymerization of acrylamide in aqueous solution. Part 3. – The hydrogen peroxide photosensitized reaction at 25° C, *Trans. Faraday Soc.* 53 (1957) 499–511. <https://doi.org/10.1039/TF9575300499>.
- [299] N. Geacintov, V. Stannett, E.W. Abrahamson, J.J. Hermans, Grafting onto cellulose and cellulose derivatives using ultraviolet irradiation, *J. Appl. Polym. Sci.* 3 (1960) 54–60.
<https://doi.org/10.1002/app.1960.070030707>.
- [300] M. Santappa, Q. Anwaruddin, Vinyl polymerisation, *Proc. Indian Acad. Sci. - Sect. A.* 68 (1968) 186–194. <https://doi.org/10.1007/BF03049419>.

- [301] Y. Ogiwara, H. Kubota, Photo-induced graft copolymerization of methyl methacrylate on cellulose, *J. Polym. Sci. [A1]*. 9 (1971) 2549–2559. <https://doi.org/10.1002/pol.1971.150090911>.
- [302] H. Kubota, A. Fukuda, Photopolymerization synthesis of poly(N-isopropylacrylamide) hydrogels, *J. Appl. Polym. Sci.* 65 (1997) 1313–1318. [https://doi.org/10.1002/\(SICI\)1097-4628\(19970815\)65:7<1313::AID-APP9>3.0.CO;2-L](https://doi.org/10.1002/(SICI)1097-4628(19970815)65:7<1313::AID-APP9>3.0.CO;2-L).
- [303] G. Geuskens, A. Etoc, P. Di Michele, Surface modification of polymers VII.: Photochemical grafting of acrylamide and N-isopropylacrylamide onto polyethylene initiated by anthraquinone-2-sulfonate adsorbed at the surface of the polymer, *Eur. Polym. J.* 36 (2000) 265–271. [https://doi.org/10.1016/S0014-3057\(99\)00192-5](https://doi.org/10.1016/S0014-3057(99)00192-5).
- [304] P.V. Zamotaev, N.J. Litsov, A.A. Kachan, Photochemical reactions of 9,10-anthraquinone and some of its derivatives in polyethylene, *Polym. Photochem.* 7 (1986) 139–152. [https://doi.org/10.1016/0144-2880\(86\)90050-3](https://doi.org/10.1016/0144-2880(86)90050-3).
- [305] A. Ledwith, G. Ndaalio, A.R. Taylor, Polymerization of Methyl Methacrylate Photoinitiated by Anthraquinone and 2-tert-Butylantraquinone, *Macromolecules*. 8 (1975) 1–7. <https://doi.org/10.1021/ma60043a001>.
- [306] Z.-T. Li, H. Kubota, Y. Ogiwara, Effect of solvent on anthraquinone-sensitized photopolymerization of methyl methacrylate, *J. Appl. Polym. Sci.* 27 (1982) 1465–1470. <https://doi.org/10.1002/app.1982.070270505>.
- [307] M.V. Encinas, C. Majmud, E.A. Lissi, Polymerization photoinitiated by carbonyl compounds. IX. Methyl methacrylate polymerization photoinitiated by anthraquinone in presence of triethylamine, *J. Polym. Sci. Part Polym. Chem.* 28 (1990) 2465–2474. <https://doi.org/10.1002/pola.1990.080280919>.
- [308] N.S. Allen, J.P. Hurley, A. Rahman, G.W. Follows, I. Weddell, Synthesis, properties and photocuring behaviour of poly(2-acrylamido-anthraquinone), *Eur. Polym. J.* 29 (1993) 1155–1160. [https://doi.org/10.1016/0014-3057\(93\)90143-4](https://doi.org/10.1016/0014-3057(93)90143-4).
- [309] T. Corrales, F. Catalina, C. Peinado, N.S. Allen, Free radical macrophotoinitiators: an overview on recent advances, *Photopolymerisation*. 159 (2003) 103–114. [https://doi.org/10.1016/S1010-6030\(03\)00175-8](https://doi.org/10.1016/S1010-6030(03)00175-8).
- [310] N.S. Allen, G. Pullen, M. Edge, I. Weddell, F. Catalina, Photoinitiator properties of 2-substituted amido and acryloxyanthraquinones, *Eur. Polym. J.* 31 (1995) 15–21. [https://doi.org/10.1016/0014-3057\(94\)00141-3](https://doi.org/10.1016/0014-3057(94)00141-3).
- [311] F. Catalina, C. Peinado, M. Blanco, T. Corrales, N.S. Allen, Synthesis, photochemical and photoinitiation activity of water-soluble copolymers with anthraquinone chromophores as side-chain groups, *Polymer*. 42 (2001) 1825–1832. [https://doi.org/10.1016/S0032-3861\(00\)00409-2](https://doi.org/10.1016/S0032-3861(00)00409-2).
- [312] N.S. Allen, J.P. Hurley, D. Bannister, G.W. Follows, S. Navaratnam, B.J. Parsons, Laser and microsecond flash photolysis of 2-substituted anthraquinones and photochemical cross-linking of nylon 6,6 polymer, *J. Photochem. Photobiol. Chem.* 68 (1992) 213–226. [https://doi.org/10.1016/1010-6030\(92\)85185-W](https://doi.org/10.1016/1010-6030(92)85185-W).
- [313] N.S. Allen, J.P. Hurley, D. Bannister, G.W. Follows, Photochemical crosslinking of nylon-6,6 induced by 2-substituted anthraquinones, *Eur. Polym. J.* 28 (1992) 1309–1314. [https://doi.org/10.1016/0014-3057\(92\)90224-P](https://doi.org/10.1016/0014-3057(92)90224-P).
- [314] N.S. Allen, G. Pullen, M. Shah, M. Edge, I. Weddell, R. Swart, F. Catalina, Photochemistry and photoinitiator properties of 2-substituted anthraquinones: 2. Photopolymerization and flash photolysis, *Polymer*. 36 (1995) 4665–4674. [https://doi.org/10.1016/0032-3861\(95\)96834-U](https://doi.org/10.1016/0032-3861(95)96834-U).

- [315] N.S. Allen, G. Pullen, M. Shah, M. Edge, D. Holdsworth, I. Weddell, R. Swart, F. Catalina, Photochemistry and photoinitiator properties of 2-substituted anthraquinones 1. Absorption and luminescence characteristics, *J. Photochem. Photobiol. Chem.* 91 (1995) 73–79. [https://doi.org/10.1016/1010-6030\(95\)04120-5](https://doi.org/10.1016/1010-6030(95)04120-5).
- [316] M. Tozuka, T. Igarashi, T. Sakurai, 1-(Arylmethoxy)-9,10-anthraquinones: Photoinitiators for Radical and Cationic Polymerizations, *Polym. J.* 41 (2009) 709–714. <https://doi.org/10.1295/polymj.PJ2009066>.
- [317] P. Hrdlovič, L. Taimr, J. Pospíšil, Derivatives of 9,10-anthraquinone; emission spectra in polymer matrices at 77K and efficiency as initiators of degradation, *Polym. Degrad. Stab.* 25 (1989) 73–88. [https://doi.org/10.1016/0141-3910\(89\)90125-0](https://doi.org/10.1016/0141-3910(89)90125-0).
- [318] H. Kaczmarek, A. Kamińska, M. Świątek, S. Sanyal, Photoinitiated degradation of polystyrene in the presence of low-molecular organic compounds, *Eur. Polym. J.* 36 (2000) 1167–1173. [https://doi.org/10.1016/S0014-3057\(99\)00175-5](https://doi.org/10.1016/S0014-3057(99)00175-5).
- [319] P. Zamotaev, O. Mityukhin, S. Luzgarev, 9,10-Anthraquinone derivatives as photoinitiators of crosslinking or degradation of polyethylene, *Polym. Degrad. Stab.* 35 (1992) 195–210. [https://doi.org/10.1016/0141-3910\(92\)90027-3](https://doi.org/10.1016/0141-3910(92)90027-3).
- [320] H.-Q. Xie, X.-G. Zhan, D. Xie, Study on esterification of acrylic phenolic resin by maleic anhydride and photocrosslinking properties of the alkali-soluble product, *J. Appl. Polym. Sci.* 98 (2005) 1607–1614. <https://doi.org/10.1002/app.21792>.
- [321] J.-F. Xing, W.-Q. Chen, X.-Z. Dong, T. Tanaka, X.-Y. Fang, X.-M. Duan, S. Kawata, Synthesis, optical and initiating properties of new two-photon polymerization initiators: 2,7-Bis(styryl)anthraquinone derivatives, *J. Photochem. Photobiol. Chem.* 189 (2007) 398–404. <https://doi.org/10.1016/j.jphotochem.2007.03.002>.
- [322] Z. Czech, J. Kabatc, M. Bartkowiak, A. Licbarski, K. Mozelewska, D. Kwiatkowska, Novel Photoreactive Pressure-Sensitive Adhesives (PSA) Based on Acrylics Containing Additionable Photoinitiators, *Materials.* 13 (2020). <https://doi.org/10.3390/ma13225151>.
- [323] G. Noirbent, F. Dumur, Photoinitiators of polymerization with reduced environmental impact: Nature as an unlimited and renewable source of dyes, *Eur. Polym. J.* 142 (2021) 110109. <https://doi.org/10.1016/j.eurpolymj.2020.110109>.
- [324] P. Bhattacharjee, S. Chatterjee, A. Achari, A. Saha, D. Nandi, C. Acharya, K. Chatterjee, S. Ghosh, S. Swarnakar, P. Jaisankar, A bis-indole/carbazole based C5-curcuminoid fluorescent probe with large Stokes shift for selective detection of biothiols and application to live cell imaging, *Analyst.* 145 (2020) 1184–1189. <https://doi.org/10.1039/C9AN02190F>.
- [325] A. Mishra, S. Daswal, Curcumin, a natural colorant as initiator for photopolymerization of styrene: kinetics and mechanism, *Colloid Polym. Sci.* 285 (2007) 1109–1117. <https://doi.org/10.1007/s00396-007-1662-4>.
- [326] M.M. Abdul-Monem, Naturally Derived Photoinitiators for Dental and Biomaterials Applications, *Eur. Dent. Res. Biomater. J.* 1 (2021) 72–78.
- [327] C. Müller, J. Schroeder, J. Troe, Intramolecular Hydrogen Bonding in 1,8-Dihydroxyanthraquinone, 1-Aminoanthraquinone, and 9-Hydroxyphenalenone Studied by Picosecond Time-Resolved Fluorescence Spectroscopy in a Supersonic Jet, *J. Phys. Chem. B.* 110 (2006) 19820–19832. <https://doi.org/10.1021/jp0614650>.
- [328] P.B. Poudel, D. Dhakal, R.T. Magar, J.K. Sohng, Microbial Biosynthesis of Chryszazin Derivatives in Recombinant *Escherichia coli* and Their Biological Activities, *Molecules.* 27 (2022). <https://doi.org/10.3390/molecules27175554>.

- [329] P. Ghosh, G.P. Devi, R. Priya, A. Amrita, A. Sivaramakrishna, S. Babu, R. Siva, Spectroscopic and In Silico Evaluation of Interaction of DNA with Six Anthraquinone Derivatives, *Appl. Biochem. Biotechnol.* 170 (2013) 1127–1137. <https://doi.org/10.1007/s12010-013-0259-2>.
- [330] A. Shockravi, Bruce J.M., Synthesis of 1,5-Dihydroxy-9,10-Anthraquinone, *Iran. J. Chem. Chem. Eng.* 14 (1995) 23–31. <https://doi.org/10.30492/ijcce.1995.10164>.
- [331] P. Sautrot-Ba, S. Jockusch, J.-P. Malval, V. Brezová, M. Rivard, S. Abbad-Andaloussi, A. Blacha-Grzechnik, D.-L. Versace, Quinizarin Derivatives as Photoinitiators for Free-Radical and Cationic Photopolymerizations in the Visible Spectral Range, *Macromolecules*. 53 (2020) 1129–1141. <https://doi.org/10.1021/acs.macromol.9b02448>.
- [332] L. Breloy, V. Brezová, Z. Barbieriková, Y. Ito, J. Akimoto, A. Chiappone, S. Abbad-Andaloussi, J.-P. Malval, D.-L. Versace, Methacrylated Quinizarin Derivatives for Visible-Light Mediated Photopolymerization: Promising Applications in 3D-Printing Biosourced Materials under LED@405 nm, *ACS Appl. Polym. Mater.* 4 (2022) 210–228. <https://doi.org/10.1021/acsapm.1c01210>.
- [333] P. Sautrot-Ba, V. Brezová, J.-P. Malval, A. Chiappone, L. Breloy, S. Abbad-Andaloussi, D.-L. Versace, Purpurin derivatives as visible-light photosensitizers for 3D printing and valuable biological applications, *Polym. Chem.* 12 (2021) 2627–2642. <https://doi.org/10.1039/D1PY00126D>.
- [334] C. Dollendorf, S.K. Kreth, S.W. Choi, H. Ritter, Polymerization of novel methacrylated anthraquinone dyes, *Beilstein J. Org. Chem.* 9 (2013) 453–459. <https://doi.org/10.3762/bjoc.9.48>.
- [335] F. Mauguière-Guyonnet, D. Burget, J.P. Fouassier, On the inhibiting effect of phenolic compounds in the photopolymerization of acrylates under high-intensity and polychromatic UV/visible lights, *J. Appl. Polym. Sci.* 103 (2007) 3285–3298. <https://doi.org/10.1002/app.25110>.
- [336] J.L. Kice, Inhibition of polymerization. II. Methyl acrylate, *J. Polym. Sci.* 19 (1956) 123–140. <https://doi.org/10.1002/pol.1956.120199113>.
- [337] C. Belon, X. Allonas, C. Croutxé-barghorn, J. Lalevée, Overcoming the oxygen inhibition in the photopolymerization of acrylates: A study of the beneficial effect of triphenylphosphine, *J. Polym. Sci. Part Polym. Chem.* 48 (2010) 2462–2469. <https://doi.org/10.1002/pola.24017>.
- [338] L. Pierau, D.-L. Versace, Light and Hydrogels: A New Generation of Antimicrobial Materials, *Materials*. 14 (2021). <https://doi.org/10.3390/ma14040787>.
- [339] M. Condat, P.-E. Mazeran, J.-P. Malval, J. Lalevée, F. Morlet-Savary, E. Renard, V. Langlois, S. Abbad Andaloussi, D.-L. Versace, Photoinduced curcumin derivative-coatings with antibacterial properties, *RSC Adv.* 5 (2015) 85214–85224. <https://doi.org/10.1039/C5RA19499G>.
- [340] P. Sautrot-Ba, J.-P. Malval, M. Weiss-Maurin, J. Paul, A. Blacha-Grzechnik, S. Tomane, P.-E. Mazeran, J. Lalevée, V. Langlois, D.-L. Versace, Paprika, Gallic Acid, and Visible Light: The Green Combination for the Synthesis of Biocide Coatings, *ACS Sustain. Chem. Eng.* 6 (2018) 104–109. <https://doi.org/10.1021/acssuschemeng.7b03723>.
- [341] J. Zhang, Nicholas S. Hill, J. Lalevée, J.-P. Fouassier, J. Zhao, B. Graff, T.W. Schmidt, S.H. Kable, M.H. Stenzel, M.L. Coote, P. Xiao, Multihydroxy-Anthraquinone Derivatives as Free Radical and Cationic Photoinitiators of Various Photopolymerizations under Green LED, *Macromol. Rapid Commun.* 39 (2018) 1800172. <https://doi.org/10.1002/marc.201800172>.

- [342] P. Xiao, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmes, J. Lalevée, Cationic and Thiol-Ene Photopolymerization upon Red Lights Using Anthraquinone Derivatives as Photoinitiators, *Macromolecules*. 46 (2013) 6744–6750. <https://doi.org/10.1021/ma401513b>.
- [343] S. Tomane, P. Sautrot-Ba, P.-E. Mazeran, J. Lalevée, B. Graff, F. Morlet-Savary, S. Abbad-Andaloussi, V. Langlois, D.-L. Versace, Photoinitiating Systems Based on Anthraquinone Derivatives: Synthesis of Antifouling and Biocide Coatings, *ChemPlusChem*. 82 (2017) 1298–1307. <https://doi.org/10.1002/cplu.201700365>.
- [344] J. Zhang, J. Lalevée, N.S. Hill, K. Launay, F. Morlet-Savary, B. Graff, M.H. Stenzel, M.L. Coote, P. Xiao, Disubstituted Aminoanthraquinone-Based Multicolor Photoinitiators: Photoinitiation Mechanism and Ability of Cationic Polymerization under Blue, Green, Yellow, and Red LEDs, *Macromolecules*. 51 (2018) 8165–8173. <https://doi.org/10.1021/acs.macromol.8b01763>.
- [345] J. Zhang, J. Lalevée, F. Morlet-Savary, B. Graff, P. Xiao, Photopolymerization under various monochromatic UV/visible LEDs and IR lamp: Diamino-anthraquinone derivatives as versatile multicolor photoinitiators, *Eur. Polym. J.* 112 (2019) 591–600. <https://doi.org/10.1016/j.eurpolymj.2018.10.021>.
- [346] X. Peng, J. Zhang, M.M. Banaszak Holl, P. Xiao, Thiol-Ene Photopolymerization under Blue, Green and Red LED Irradiation, *ChemPhotoChem*. 5 (2021) 571–581. <https://doi.org/10.1002/cptc.202100028>.
- [347] J. Zhang, J. Lalevée, N.S. Hill, X. Peng, D. Zhu, J. Kiehl, F. Morlet-Savary, M.H. Stenzel, M.L. Coote, P. Xiao, Photoinitiation Mechanism and Ability of Monoamino-Substituted Anthraquinone Derivatives as Cationic Photoinitiators of Polymerization under LEDs, *Macromol. Rapid Commun.* 40 (2019) 1900234. <https://doi.org/10.1002/marc.201900234>.
- [348] J. Zhang, J. Lalevée, N.S. Hill, J. Kiehl, D. Zhu, N. Cox, J. Langley, M.H. Stenzel, M.L. Coote, P. Xiao, Substituent Effects on Photoinitiation Ability of Monoaminoanthraquinone-Based Photoinitiating Systems for Free Radical Photopolymerization under LEDs, *Macromol. Rapid Commun.* 41 (2020) 2000166. <https://doi.org/10.1002/marc.202000166>.
- [349] F. Dumur, Recent advances on water-soluble photoinitiators of polymerization, *Eur. Polym. J.* 189 (2023) 111942. <https://doi.org/10.1016/j.eurpolymj.2023.111942>.
- [350] J. Xing, J. Liu, T. Zhang, L. Zhang, M. Zheng, X. Duan, A water soluble initiator prepared through host-guest chemical interaction for microfabrication of 3D hydrogels via two-photon polymerization, *J. Mater. Chem. B*. 2 (2014) 4318–4323. <https://doi.org/10.1039/C4TB00414K>.
- [351] Y. Tian, C.-Y. Chen, Y.-J. Cheng, A.C. Young, N.M. Tucker, A.K.-Y. Jen, Hydrophobic Chromophores in Aqueous Micellar Solution Showing Large Two-Photon Absorption Cross Sections, *Adv. Funct. Mater.* 17 (2007) 1691–1697. <https://doi.org/10.1002/adfm.200600916>.
- [352] L. Breloy, V. Brezová, A. Blacha-Grzechnik, M. Pisset, M.S. Yildirim, I. Yilmaz, Y. Yagci, D.-L. Versace, Visible Light Anthraquinone Functional Phthalocyanine Photoinitiator for Free-Radical and Cationic Polymerizations, *Macromolecules*. 53 (2020) 112–124. <https://doi.org/10.1021/acs.macromol.9b01630>.
- [353] K.K. Childress, K. Kim, D.J. Glugla, C.B. Musgrave, C.N. Bowman, J.W. Stansbury, Independent Control of Singlet Oxygen and Radical Generation via Irradiation of a Two-Color Photosensitive Molecule, *Macromolecules*. 52 (2019) 4968–4978. <https://doi.org/10.1021/acs.macromol.9b00424>.

- [354] N. Corrigan, J. Xu, C. Boyer, A Photoinitiation System for Conventional and Controlled Radical Polymerization at Visible and NIR Wavelengths, *Macromolecules*. 49 (2016) 3274–3285. <https://doi.org/10.1021/acs.macromol.6b00542>.
- [355] S.E. Korkut, G. Temel, D.K. Balta, N. Arsu, M.K. Şener, Type II photoinitiator substituted zinc phthalocyanine: Synthesis, photophysical and photopolymerization studies, *J. Lumin.* 136 (2013) 389–394. <https://doi.org/10.1016/j.jlumin.2012.12.025>.
- [356] K. Van Den Houwe, C. Evrard, J. Van Loco, F. Lynen, E. Van Hoeck, Migration of photoinitiators from cardboard into dry food: evaluation of Tenax® as a food simulant, *Food Addit. Contam. Part A*. 33 (2016) 913–920. <https://doi.org/10.1080/19440049.2016.1179562>.
- [357] J. Zhou, X. Allonas, X. Liu, Synthesis and characterization of organozirconiums with type-II photoinitiator ligands as multifunctional photoinitiators for free radical photopolymerization, *J. Photochem. Photobiol. Chem.* 356 (2018) 580–586. <https://doi.org/10.1016/j.jphotochem.2018.01.042>.
- [358] F. Courtecuisse, A. Belbakra, C. Croutxé-Barghorn, X. Allonas, C. Dietlin, Zirconium complexes to overcome oxygen inhibition in free-radical photopolymerization of acrylates: Kinetic, mechanism, and depth profiling, *J. Polym. Sci. Part Polym. Chem.* 49 (2011) 5169–5175. <https://doi.org/10.1002/pola.24984>.
- [359] Y. Zhu, J. Pi, Y. Zhang, D. Xu, Y. Yagci, R. Liu, A new anthraquinone derivative as a near UV and visible light photoinitiator for free-radical, thiol–ene and cationic polymerizations, *Polym. Chem.* 12 (2021) 3299–3306. <https://doi.org/10.1039/D1PY00347J>.
- [360] X. Peng, M. Yao, P. Xiao, Newly Synthesized Chromophore-linked Iodonium Salts as Photoinitiators of Free Radical Photopolymerization, *Macromol. Chem. Phys.* 222 (2021) 2100035. <https://doi.org/10.1002/macp.202100035>.
- [361] P. Garra, B. Graff, F. Morlet-Savary, C. Dietlin, J.-M. Becht, J.-P. Fouassier, J. Lalevée, Charge Transfer Complexes as Pan-Scaled Photoinitiating Systems: From 50 µm 3D Printed Polymers at 405 nm to Extremely Deep Photopolymerization (31 cm), *Macromolecules*. 51 (2018) 57–70. <https://doi.org/10.1021/acs.macromol.7b02185>.
- [362] J.-T. Lin, J. Lalevee, D.-C. Cheng, A Critical Review for Synergic Kinetics and Strategies for Enhanced Photopolymerizations for 3D-Printing and Additive Manufacturing, *Polymers*. 13 (2021). <https://doi.org/10.3390/polym13142325>.
- [363] K. Sun, P. Xiao, F. Dumur, J. Lalevée, Organic dye-based photoinitiating systems for visible-light-induced photopolymerization, *J. Polym. Sci.* 59 (2021) 1338–1389. <https://doi.org/10.1002/pol.20210225>.