



HAL
open science

Recent advances on visible light bodipys and related difluoroborane structures-based photoinitiating systems

Frédéric Dumur

► **To cite this version:**

Frédéric Dumur. Recent advances on visible light bodipys and related difluoroborane structures-based photoinitiating systems. *European Polymer Journal*, 2023, 196, pp.112241. 10.1016/j.eurpolymj.2023.112241 . hal-04148585

HAL Id: hal-04148585

<https://hal.science/hal-04148585v1>

Submitted on 3 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Recent advances on visible light bodipys and related difluoroborane structures-based photoinitiating systems

Frédéric Dumur^{a*}

^a Aix Marseille Univ, CNRS, ICR, UMR 7273, F-13397 Marseille, France

frederic.dumur@univ-amu.fr

Abstract

Photopolymerization is facing a revolution with the development of cheap and easily available LEDs that enable to polymerize in safe and energy-saving conditions. Bodipy constitutes a unique class of renowned dyes that are well-known for their high photoluminescence quantum yields, their exceptional molar extinction coefficients combined with a narrow absorption and emission band. In the constant search for new photoinitiating systems activable under low-light intensity and in the visible range, bodipys have been identified as a promising scaffold for the design of photoinitiators. Recently, several difluoroborane derivatives such as boranils, squaraine-derived structures or 2-phenacylbenzoxazole difluoroboranes have been proposed, expanding the scope of application of photopolymerization. In this review, the different bodipys, boranils, squaraine-based difluoroborate complexes and 2-phenacylbenzoxazole difluoroboranes used to elaborate photoinitiating systems and reported to date are presented. Efficiency of the newly developed photoinitiators will be compared to that of reference photoinitiating systems.

Keywords

Photoinitiator; visible light; photopolymerization; LED; bodipy; difluoroborane; boranil; squaraine

1. Introduction

During the past decades, visible light photopolymerization has been identified as a possible alternative with regards to the traditional UV photopolymerization.[1–18] At present, this historical approach is facing numerous criticisms, directly related to the range of wavelengths used to initiate the polymerization process. Indeed, UV light is known to cause skin cancers and eye damage. During polymerization, ozone is also produced, requiring specific safety conditions so that UV photopolymerization is now discarded in favor of visible light processes.[19,20] Intense research activity is supported by the numerous applications of photopolymerization, ranging from coatings and varnishes, solvent-free paints, dental restoration materials, adhesives, 3D and 4D printing or

microelectronics.[10,11,21–32] Interest for visible light photoinitiators is also supported by the higher light penetration that can be achieved in the visible range than in the UV range.[33] Notably, if the light penetration is limited to only a few hundreds of micrometres, this value can reach a few centimetres in the near-infrared range (See Figure 1), enabling to polymerize thick and filled samples.[34] If visible light photopolymerization constitutes an interesting approach, several drawbacks can be however mentioned. As the main drawback, visible light photoinitiators are strongly coloured compounds that often impose an undesired colour to the final polymers, what constitutes a severe limitation for industrial applications. Parallel to this, visible light photoinitiating systems are less reactive than the UV ones, and this lack of reactivity is directly related to the fact that visible light photons are less energetic than UV photons.

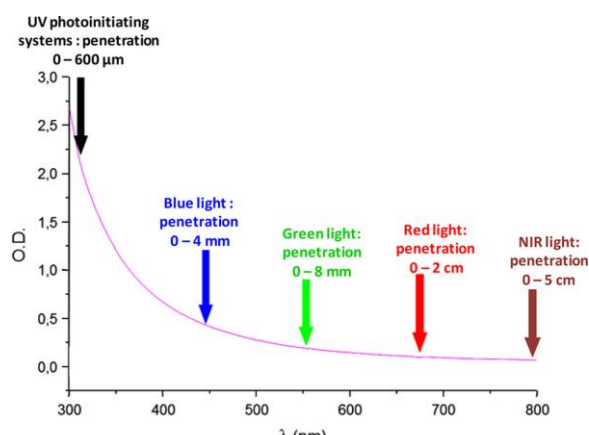
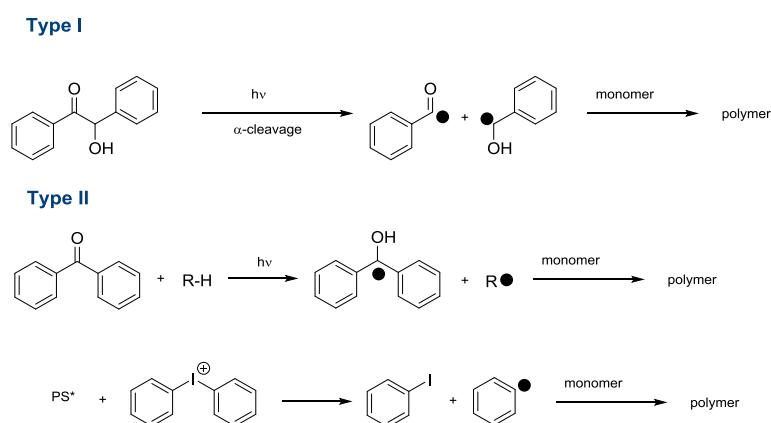


Figure 1. Light penetration in a polystyrene latex with an average diameter of 112 nm. Reprinted with permission from Ref.[33]

In this context of lack of reactivity of visible light photoinitiators, a significant effort has been done to investigate a maximum of structures and pyrenes,[35–43] cyanines,[44–52] anthracenes,[53] naphthalimides,[54–72] iodonium salts,[54,73–82] bodipy,[73,83–87] camphorquinones,[88,89] phenothiazines,[90–93] benzylidene ketones,[94–101] curcumin,[102–105] cyclohexanones,[106–109] carbazoles,[110–125] furan derivatives,[126] perylenes,[127–130] push-pull dyes,[2,3,131–145] benzophenones,[146–153] triphenylamines,[154,155] quinoxalines,[156–170] coumarins,[171–184] thiophenes,[185,186] thioxanthenes,[73,187–201] chalcones,[29,202–217] chromones and flavones,[218–220] glyoxylates,[221] photochroms,[222] diketopyrrolopyrroles[223,224] dithienophosphole derivatives,[225] acridine-1,8-diones,[226–228] NIR dyes,[45,229] naphthoquinones[230] and anthraquinones[231,232] have been examined to identify the most reactive structures. Search for efficient photoinitiating systems was not limited to purely organic compounds and metal complexes were also studied such as gold complexes[233] iridium complexes,[234–242] zinc complexes,[243] copper complexes,[244–262] gold complexes[233] or iron complexes.[246,263,264] Various structures have been examined as solar photoinitiators,[1,3–7,140,169,265–267] as water-soluble structures,[66,71,125,200,211,268–271] or as photobleachable photoinitiators.[124,176,216,272] With aim at generating initiating species, two main mechanisms of photoinitiation exists. The first one relies on dyes capable to

homolytically cleave upon photoexcitation. Such photoinitiators are named Type I photoinitiators. In this field, benzoin derivatives, acyloximino esters, trichloromethyl-S-triazine glyoxylates, oxime esters, benzylketals, hexaaryl biimidazoles (HABIs), phosphine oxides, α -haloacetophenones, α -aminoalkylacetophenones, hydroxyacetophenones, or *o*-acyl- α -oximino ketones were the most extensively studied.[273–275] Interest of this approach relies in the fact that Type I photoinitiators are monocomponent photoinitiating systems, greatly simplifying the elaboration of the photocurable resins. However, due to an irreversible cleavage upon irradiation and the consumption of photoinitiators during the polymerization process, a decrease of the photoinitiators concentration is detected over time, adversely affecting the efficiency of the polymerization process (See Scheme 1). This issue can be addressed with Type II photoinitiators as these photoinitiators can be used in catalytic amount. As drawback, Type II photoinitiators are not capable to initiate any polymerization alone so that the presence of additives is required to generate initiating species.[276] These molecules can produce radicals by hydrogen abstraction from aromatic ketones in the presence of hydrogen donors or by photoinduced electron transfer with onium salts.[106,188,193,277–281]



Scheme 1. Radical generation with Type I and Type II photoinitiators.

In the search for new structures, bodipy i.e. boron dipyrromethene or 4,4-difluoro-4-bora-3a,4a-diaza-s-indecene) have been identified as soon as 2000 as potential photoinitiators of polymerization.[282] These compounds are characterized by the presence of a BF_2 group connected to the dipyrromethene core. Bodipys are extensively used as fluorescent dyes for bioimaging, chemosensing and photodynamic therapy.[283,284] Bodipys are also used in organic electronics such as light-absorbing materials for dye-sensitized solar cells,[285–287] chromophores for nonlinear optical applications,[288,289] or as light-emitting materials for organic light-emitting diodes [290–293] so that chemistry of bodipys is well established, facilitating the development of bodipys devoted to photopolymerization. In this review, an overview of the different bodipys reported to date is provided. Considering that bodipys are investigated since 2000 as photoinitiators of polymerization, numerous comparisons have been established with reference compounds, enabling to estimate the real interest of these structures. It has to be noticed that a few examples of surface patterning were also reported

in the literature with bodipys conveniently modified for reacting via a click chemistry mechanism.[85,294,295] More recently, bodipys were also used as molecular rotors enabling to monitor two-photon polymerization using fluorescence lifetime measurements.[296] These points will not be discussed in this review. Parallel to bodipys which are the most recognized boron difluoride complexes, other difluoroborane derivatives were also examined as photoinitiators of polymerization such as 2-phenacylbenzoxazole difluoroboranes, boranils and squaraine-derived structures, evidencing the intense research activity existing around difluoroborane derivatives.

2. Bodipys as visible light photoinitiators of polymerization

2.1. Bodipys in multicomponent photoinitiating systems

The first reports mentioning the use of bodipys as photoinitiators of polymerization were concomitantly reported in 2000 by Yamaoka[282] and Kitamura.[297] Additional studies were subsequently carried out in 2003 by Sastre and coworkers on the same bodipys in order to get a deeper insight into the photophysical properties.[298] In combination with a radical generating reagent i.e. 3,3',4,4'-tetrakis(*tert*-butylperoxycarbonyl)benzophenone (BTTB), two bodipys were used as photosensitizers, namely 2,8-diethyl-1,3,5,7,9-pentamethylbipyrrromethene difluoroborate (EBP) and 1,3,5,7,9-pentamethylbipyrrromethene difluoroborate (HBP) for the free radical polymerization of acrylates (See Figure 2). Using a laser emitting at 532 nm, photoresists polymers could be prepared. Interestingly, by replacing the peripheral hydrogens of HBP by ethyl groups in EBP, photosensitivity of the resins could be greatly improved. Comparison with benchmark photoinitiators also revealed the sensitivity of the two bodipys to be higher than that of 3,3'-carbonylbis(7,7'-diethylaminocoumarin) (KCD) and 3-(2-benzimidazolyl)-7-(diethylamino)coumarin (C7) (See Figure 2), evidencing the interest to investigate such structures.[299]

In 2003, Fimia and coworkers developed an interesting approach for the photopolymerization of dry polymeric films using EBP as the radical initiator.[300] Holographic recording materials could be prepared in a simple way using a laser as the light source, poly(methyl methacrylate) (PMMA) as the binder, 2-hydroxyethylmethacrylate (HEMA) as the monomer and EBP as the photoinitiator. In 2006, EBP and HBP were revisited with a new bodipy i.e. EPP and used as photosensitizers for another photoacid generator namely *N*-hydroxynaphthalimide (NIOTf) (See Figure 2).[301] In this work, evidence of an electron transfer occurring from the singlet excited state of bodipys towards NIOTf was demonstrated. By electron spin resonance (ESR), formation of the radical cations of bodipys was also detected, providing an additional proof of a photoinduced electron transfer occurring from the photosensitizer to NIOTf. By using the appropriate binder polymer, the two-component EPP/NIOTf system proved to be efficient for printing technology using an argon ion laser as the light source.

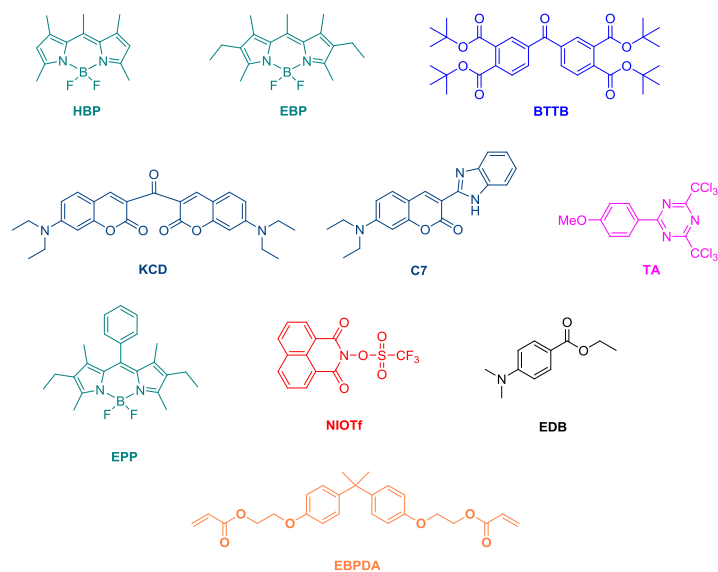


Figure 2. Chemical structures of different EPP, different benchmark photoinitiators used as reference compounds and different additives.

In 2022, a new bodipy ABA exhibiting a long-living triplet excited state by mean of a spin-orbit charge transfer intersystem crossing (SOCT-ISC) was proposed for the design of holographic recording materials (See Figure 3).[302]

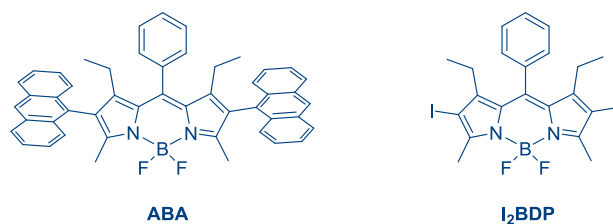


Figure 3. Chemical structures of ABA and I₂BDP.

From the photophysical mechanism viewpoint, a photoinduced electron transfer can be promoted between the peripheral electron-donating anthracenyl groups of ABA towards the central electron-deficient bodipy core, leading to the formation of a charge-transfer state (¹CT) which can be subsequently converted as a triplet excited state (T₁) by charge recombination.[303,304] Using this strategy, a triplet excited state as long as 3.65 ns could be determined in toluene. Noticeably, this molecule exhibited a strong solvatochromism both in absorption and emission. Thus, if a Stokes shift of only 46 nm was determined in toluene, this value increased up to 125 nm in acetonitrile. Similarly, an important variation of the triplet excited state lifetimes was demonstrated since this value decreased to only 1.13 ns in acetonitrile contrarily to 3.65 ns in toluene. Such variations are indicative of an intramolecular electron transfer existing between the peripheral anthracene moiety and the electrodeficient bodipy core.[305,306] Interestingly, ABA was proposed as the first heavy-atom-free SOCT-ISC photosensitizer that can efficiently operate in the solid state in combination with *N*-phenylglycine (NPG) for the free radical polymerization (FRP) of acrylates devoted to the holographic recording of diffractive structures. A high diffraction

efficiency up to 87% with a 220–260 mm thickness was determined using an energy exposure of 35 J/cm² and the two-component ABA/NPG system. These values are comparable to that obtained with the reference diiodo compound (I₂BDP).

In 2010, the first bodipy-based photoinitiating systems activable in less energetic conditions were proposed by Fouassier and coworkers.[307] In this work, a Xe lamp (I = 200 W) could be used to initiate the polymerization process. In order to reach a high monomer conversion, three-component systems based on HBP or EPP, ethyl 4-dimethylaminobenzoate (EDB) and triazine A (2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TA) as the co-initiators were designed and tested as photoinitiating systems for the free radical polymerization (FRP) of ethoxylated bisphenol A diacrylate (EBPDA) (See Figure 2). Surprisingly, the two-component dye/EDB systems could promote the FRP of EBPDA using EPP and HBP as the photosensitizers, but only slow polymerization processes and low monomer conversions could be determined, despite the formation of α -aminoalkyl radicals on EDB. Better monomer conversions and higher polymerization rates were obtained with the two-component dye/TA systems. Considering that EPP and HBP can both interact with the two additives to form initiating radicals, the design of three-component photoinitiating systems was thus investigated. After optimization of the conditions, a molar ratio of 1/5 for EDB/TA was identified as the best ratio for the two additives. Using these conditions, conversions of 74.1 and 76.5% were respectively determined with the three-component EPP/EDB/TA (0.1%/0.4%/5.5% w/w/w) and HBP/EDB/TA (0.1%/0.4%/5.5% w/w/w) systems after 15 min. of irradiation with a Xe lamp (See Table 1).

Table 1. Composition of the resins using different photoinitiators and two-component photoinitiating systems, final monomer conversions obtained after 15 min of irradiation and inhibition time during the polymerization experiments.

Run	Dye (%)	EDB (%)	TA (%)	Molar Ratio EDB/TA	Inhibition Time (s)	Final Conversion (%)
EPP 1	0.1	2.5	–	–	n.m. ^a	28.6
EPP 2	0.1	–	1	–	10.7	42.1
EPP 3	0.1	2.5	1	5/1	8.4	50.3
EPP 4	0.1	1.1	2.3	1/1	4.0	56.6
EPP 5	0.1	0.4	5.5	1/5	2.4	74.1
HBP 1	0.1	2.5	–	–	n.m. ^a	18.2
HBP 2	0.1	–	1	–	15.1	29.3
HBP 3	0.1	2.5	1	5/1	6.3	58.6

HBP 4	0.1	1.1	2.3	1/1	4.0	50.1
HBP 5	0.1	0.4	5.5	1/5	1.5	76.5

^a n.m.: not measurable.

Considering that bodipys interact both with TA and EDB, two possible mechanisms were proposed by the authors (See Figure 4). First, an oxidative pathway resulting after photoexcitation to the formation of the dye^{•+} radical cation and TA^{•-} radical anion (mechanism A). After cleavage of the TA^{•-} radical anion, TA_(-Cl)[•] radicals are formed, capable to initiate the FRP. In the presence of an amine (EDB), the dye^{•+} radical cation can be reduced to its initial redox state, regenerating the photosensitizer and enabling to introduce it in catalytic amount. Finally, EDB^{•+} can decompose, producing EDB_(-H)[•] radicals. Parallel to this first mechanism, a second one was also proposed, consisting in a reductive pathway (mechanism B). If the radical anion of the dye (dye^{•-}) is produced in first step, the same initiating radicals (EDB_(-H)[•] and TA_(-Cl)[•]) than that proposed in the mechanism A are in turn formed.

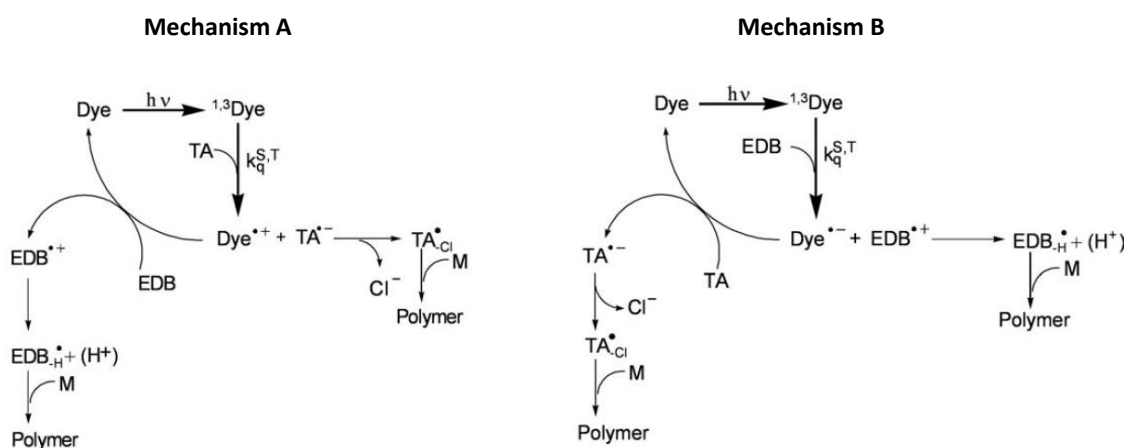


Figure 4. The two possible three-component photoinitiating systems occurring with the dye/EDB/TA systems. Reproduced with permission of Ref. [307]

This is only in 2012 that Fouassier and coworkers investigated the first bodipy-based photoinitiating system activated under low light intensity for the polymerization of cationic monomers and acrylate/divinyl ether blends (See Figure 5).[87] In that work, a laser diode emitting at 473 nm and displaying an intensity of 100 mW/cm² was used. The bodipy (PM) used in this study exhibited a broad absorption extending between 400 and 550 nm, with an absorption maximum peaking at 495 nm. When tested as a photosensitizer in combination with Iod1 and Iod2 for the cationic polymerization (CP) of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexyl-carboxylate (EPOX), excellent polymerization profiles could be obtained with the two-component systems whereas no polymerization could be obtained with PM, Iod1 or Iod2 alone, evidencing the crucial role of the photosensitizer in the mechanism of radical generation.

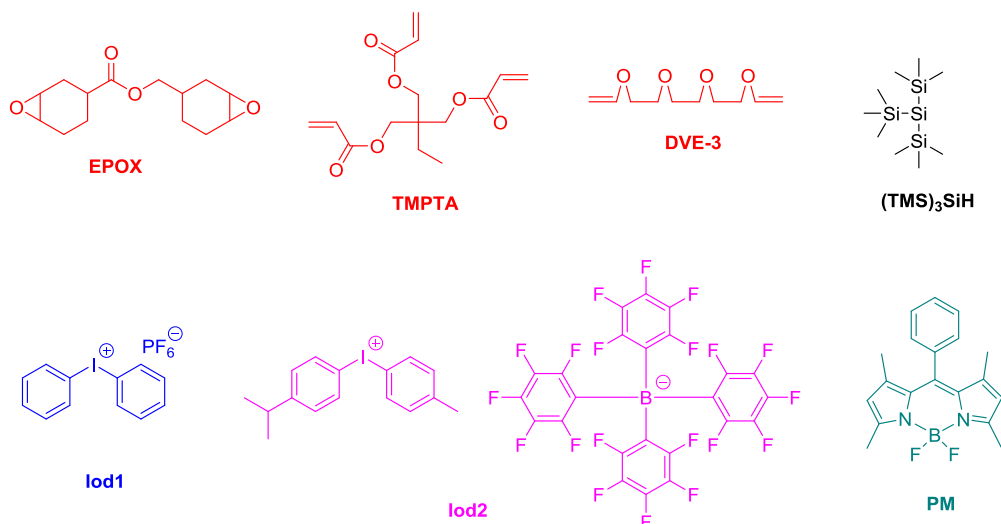
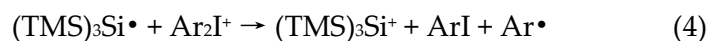
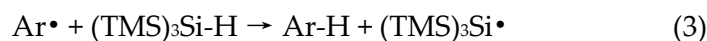
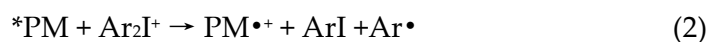


Figure 5. Chemical structures of PM, different monomers and additives.

Using the two-component PM/Iod1 (0.2%/3.5% w/w) system, a conversion of 40% could be obtained after 400 s of irradiation. By using the PM/Iod2 (0.2%/3% w/w) system, a conversion of 55% could be determined. Interestingly, higher EPOX conversions could be obtained with Iod2 compared to Iod1 and this improvement of monomer conversions was assigned to the lower nucleophilicity of tetrakis(pentafluorophenyl)borate ($(C_6F_5)_4B^-$) compared to hexafluorophosphate (PF_6^-), enabling a faster propagation of the polymerization reaction. This trend of reactivity was confirmed with another monomer, namely (epoxycyclohexylethyl)methylsiloxane-dimethylsiloxane copolymer (EPOX-Si). Finally, a breakthrough could be obtained in terms of monomer conversion by adding *tris*(trimethylsilyl)silane ($(TMS)_3SiH$) as a second additive. In the case of the PM/Iod2 (0.2%/3% w/w) system, addition of 3 wt% of $(TMS)_3SiH$ enabled to increase the EPOX conversion from 55% up to 90% (See Figure 6). This improvement of monomer conversion was assigned to the presence of an additional source of cationic species i.e. the silylium cations (in addition to the $PM^{\bullet+}$ radical cation formed by the two-component system) in the case of the three-component systems that can be produced according to the mechanism depicted below.



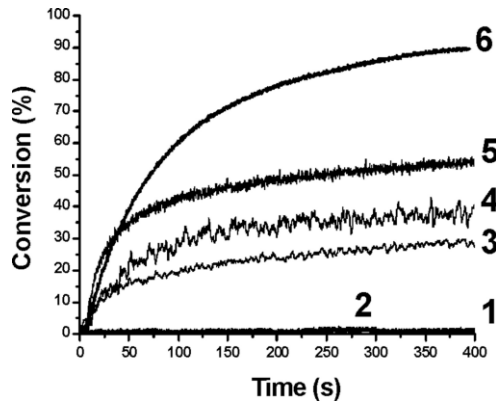


Figure 6. Photopolymerization profiles of EPOX using a laser diode emitting at 473 nm with different photoinitiating systems: (1) PM (0.2% w/w); (2) Iod1 (2% w/w); (3) PM/Iod1 (0.2%/2% w/w); (4) PM/Iod1 (0.2%/3.5% w/w); (5) PM/Iod2 (0.2%/3% w/w); and (6) PM/Iod2/(TMS)₃SiH (0.2%/3%/3% w/w). Reproduced with permission of Ref.[87]

By using triethyleneglycol divinyl ether (DVE-3) as the monomer, high monomer conversions could be obtained with the two-component PM/Iod1 (0.2%/2% w/w) system. In this case, a conversion as high as 95% could be determined within 25 s upon irradiation with a laser diode at 473 nm in laminate. Among the most interesting results and considering that radicals and cations are concomitantly produced by the photoinitiating system, the formation of interpenetrated polymer networks resulting from both the FRP of trimethylolpropane triacrylate (TMPTA) and the CP of DVE-3 was examined. Interestingly, crosslinked TMPTA/DVE-3 polymer networks could be produced while maintaining a remarkable DVE-3 conversion (around 85% vs. 100% when polymerized alone) (See Figure 7). In the case of TMPTA, an improvement of the monomer conversion was even detected (55% vs 30% alone) during the formation of interpenetrated polymer networks (IPNs). To support the enhancement of the TMPTA conversion during the formation of the TMPTA/DVE-3 polymer networks, formation of a vinyl ether/acrylate copolymer resulting from the electrophilic character of the acrylate radicals that can add on the electron rich vinyl ether was suggested. By this dual polymerization mode and this additional consumption of TMPTA by copolymerization with DVE-3, a higher TMPTA conversion could thus be observed.

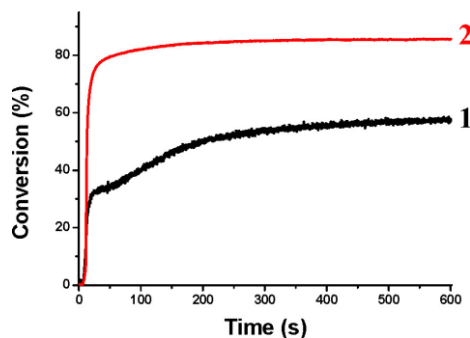
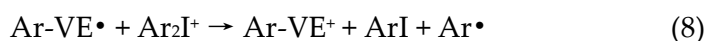
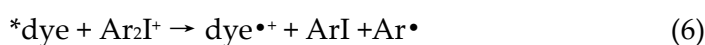


Figure 7. Photopolymerization profiles of a TMPTA/DVE-3 blend (50%/50%) using the PM/Iod1 initiating system (0.2%/3% w/w): (1) conversion of TMPTA and (2) conversion of DVE-3. Laser diode at 473 nm in laminate. Reproduced with permission of Ref.[87]

In 2013, an interesting structure/performance relationship was proposed for a series of seven bodipys (BDP-1-BDP-7) differing by the substitution pattern of the aromatic ring but also by the substituents introduced on the pyrromethene sides (See Figure 8).[86] By varying the substitution, dyes displaying absorption maxima located at 496 nm in acetonitrile for BDP-2 and BDP-4 up to 532 nm for BDP-6 could be determined (See Table 2). Considering that all dyes absorb in the 400-600 nm range, these bodipys were thus ideal candidates for the CP of epoxy, vinyl ether and epoxy-silicone monomers upon irradiation at 457, 473 and 532 nm. Influence of the substitution pattern was notably evidenced during the determination of the free energy changes ΔG . Indeed, if negative values of ΔG were determined for the dye/Iod2 systems, highly favorable electron transfers were determined for BDP-2 (-1.07 eV) whereas the ΔG values were reduced to only -0.5 eV for BDP-1 and BDP-6. By modifying the substitution pattern, structures of bodipys were determined as having a higher influence on the oxidation potentials than on the absorption properties. Using the dye/Iod2 systems at 473 nm, excellent DVE-3 conversions of 90, 80 and 65% were respectively obtained with BDP-2, BDP-1 and BDP-6. Conversely, low conversions were determined with BDP-3 and BDP-4, the conversions not exceeding 25% after 200 s of irradiation with the laser diode. These trends were confirmed during the photopolymerization experiments done at 457 and 532 nm. Here again, no polymerization processes could be initiated with the dyes alone or Iod2. Considering that no polymerization process could be initiated with the dyes alone, the formation of Ar-VE⁺ (with VE standing for vinyl ether group) as the initiating species with the two-component dye/Iod2 system was proposed and formed according to the mechanism depicted below (see equations 5-8, for clarity acronym of DVE-3 has been reduced to vinyl ether (VE) in the mechanism).



Especially, the participation of a radical pathway in equations 6-8 is in agreement with the higher monomer conversions obtained in laminate than under air. Indeed, oxygen can contribute to convert carbon-centered radicals as inactive peroxy radicals, adversely affecting the polymerization process.[308–311]

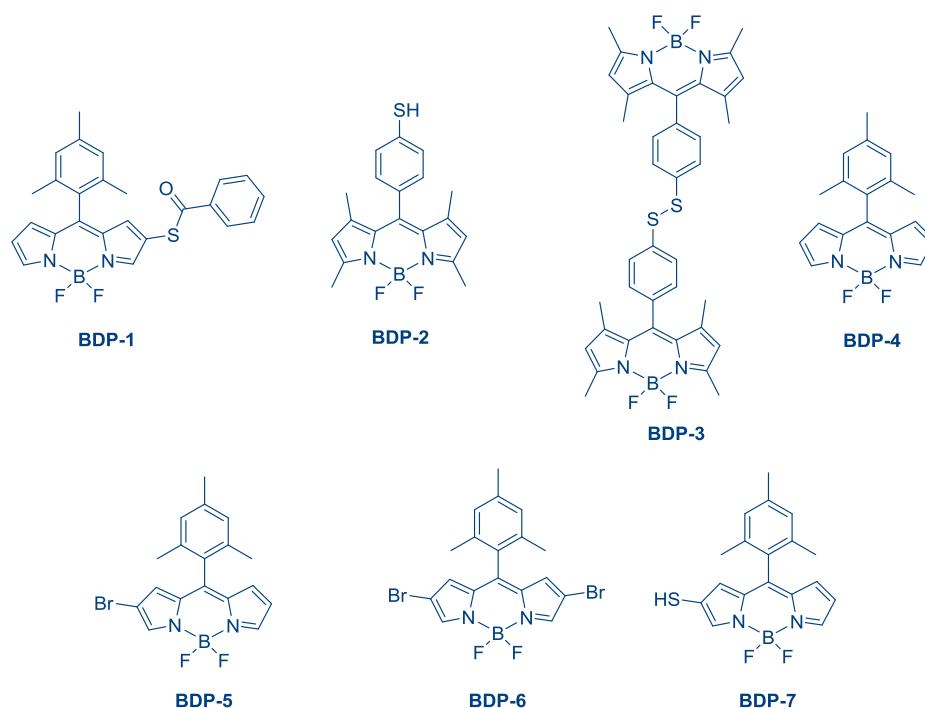
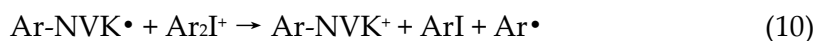


Figure 8. Chemical structures of dyes BDP-1- BDP-7.

Table 2. Absorption maxima of dyes 1-7 in acetonitrile.

Dye	BDP-1	BDP-2	BDP-3	BDP-4	BDP-5	BDP-6	BDP-7
λ_{\max} (nm)	504	496	498	496	512	532	508

Upon addition of *N*-vinylcarbazole (NVK), an improvement of the monomer conversion was detected for the different three-component dye/Iod2/NVK systems and assigned to the formation of an additional source of cations. As shown in equations 9 and 10, aryl radicals can react with NVK, producing Ar-NVK• radicals that can be subsequently oxidized by the iodonium salt, producing Ar-NVK⁺ cations. The concomitant presence of Ar-NVK⁺ and Ar-VE⁺ both contribute to improve the monomer conversion.



As interesting properties of these photoinitiating systems, a good photobleaching could be evidenced with these systems, demonstrating the interest of this family of bodipys to produce colorless coatings. Indeed, from the industrial viewpoint, the possibility to produce colorless coatings is determinant for numerous applications.[124,176,272] Finally, the cationic polymerization of EPOX was also examined under air, still upon irradiation at 473 nm with a laser diode. Using BDP-2 in the two-component BDP-2/Iod2 (0.2%/2% w/w) system, a conversion of 65% was determined after 200 s of irradiation.

The bodipy/iodonium salt combination was extensively studied in the literature and different monomers were used. For instance, by using BODIPY-1 and BODIPY-2, the cationic polymerization of bisphenol-A epoxy resin (diglycidyl ether of bisphenol A (DGEBA)) could be efficiently promoted upon irradiation with a halogen lamp (25 mW/cm²) but also upon irradiation at 460 and 540 nm using filters (See Figure 9).[312] Indeed, despite different substitutions, BODIPY-1 and BODIPY-2 showed similar absorption maxima located at 504 and 511 nm in dichloromethane respectively, with an absorption spectrum extending up to 550 nm.

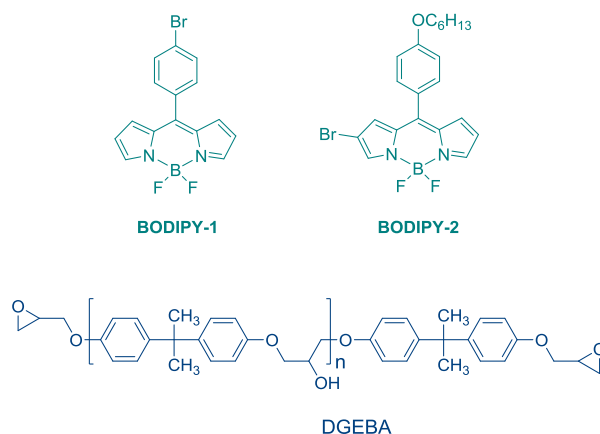


Figure 9. Chemical structures of BODIPY-1, BODIPY-2 and DGEBA.

Using the two-component dye/Iod1 (1%/2% w/w) systems for the CP of DGEBA, higher monomer conversions were obtained with BODIPY-1 than with BODIPY-2. Indeed, after 700 s of irradiation with a halogen lamp, a conversion of ca 65% could be obtained with BODIPY-1 whereas this value decreased to only 50% for BODIPY-2. Upon irradiation at 460 nm ($I = 17.5 \text{ mW/cm}^2$) and 540 nm ($I = 15 \text{ mW/cm}^2$), lower monomer conversions were obtained than with the halogen lamp and conversions around 20% were determined after 700 s of irradiation with the two-component BODIPY-1/Iod1 (1%/2% w/w) system.

In 2022, Ortyl and coworkers revisited HBP as an additive for a photocurable resin dedicated to 3D printing and already containing a photosensitizer i.e. diphenyl(2,4,6-trimethyl-benzoyl)phosphine oxide (TPO) (See Figure 10). Notably, the authors examined the influence of HBP on the polymerization rate, the polymerization shrinkage as well as the resolution of the final 3D-printed objects.[313] For the photopolymerization experiments done at 405 nm, a mixture of monomers was used, namely, trimethylolpropane triacrylate (TMPTA), ethoxylated bisphenol A diacrylate (EBPDA) and isobornyl acrylate (IBOA) in a weight ratio of 1:2:7 (See Figure 10). Interestingly, in thin films (25 μm), an increase of the acrylate conversions was obtained upon addition of HBP. The conversions increased from 55% for the reference photoinitiating system up to 61.5% upon addition of HBP (0.1 wt%). An opposite situation was found for thick films (0.5 mm), attributable to an inner filter effect adversely affecting the light penetration within the photocurable resin. In this case, a conversion of 74.5% was obtained for the resin containing HBP contrarily to 82% for the reference system. As a result of this slower polymerization rate combined with a lower

monomer conversion, a severe reduction of the polymerization shrinkage was also evidenced for the sample containing HBP (4.6% vs 5.4% shrinkage for the reference resin). Considering that the volumetric shrinkage is responsible of a decrease in the precision of the printed models, all 3D printed objects prepared with the resin containing HBP as an additive exhibited lower deformations than the objects prepared with the reference resin.

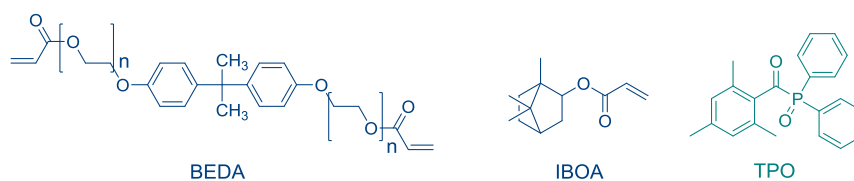


Figure 10. Chemical structures of different monomers and TPO.

Among the most interesting results of these last few years, the possibility to initiate a polymerization in the near infrared range with bodipys was examined. This point was notably examined in 2019 by Lalevée and coworkers with two different bodipys i.e. Bodipy_1 and Bodipy_2 (See Figure 11).[229] In order to reach a sufficient monomer conversion, a four-component photoinitiating system was used, namely dye/iodonium salt/phosphine/thermal initiator (0.1%/3%/2%/2% w/w/w/w). In that work, Blockbuilder® MA was selected as the thermal initiator, *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod3) as the iodonium salt and 4-(diphenylphosphino)benzoic acid (dppba) as the phosphine. Indeed, the FRP of acrylate being exothermic, addition of a thermal initiator in the resin enabled to take advantage of the exothermicity of the polymerization process, inducing the thermal decomposition of Blockbuilder® MA and introducing an additional source of initiating radicals within the resin. By the concomitant occurrence of the photochemical and the thermal modes, high monomer conversions could be achieved. From the absorption viewpoint, the two dyes exhibited similar absorption maxima, located at 500 and 492 nm respectively in acetonitrile (See Table 3 and Figure 12). Once again, it demonstrates that the group introduced at the bridgehead position of bodipys has only a slight influence on the position of the absorption maxima.

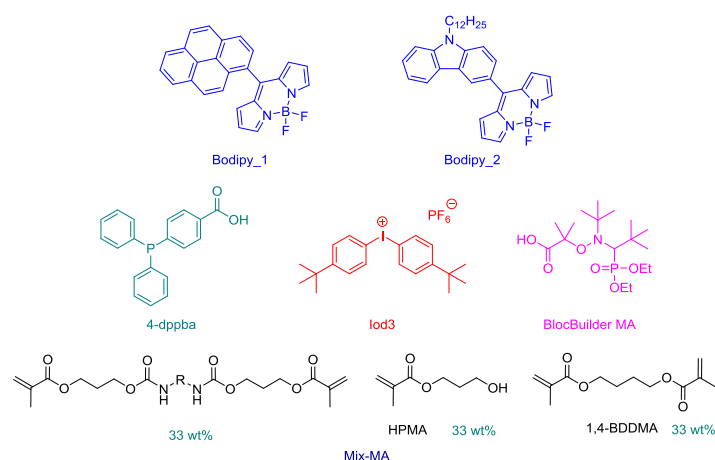


Figure 11. Chemical structures of Bodipy_1, Bodipy_2, 4-dppba, Iod3, Blocbuilder® MA and the mixture of monomers Mix-MA.

Noticeably, by replacing acetonitrile as the solvent by the mixture of monomers (Mix-MA) and additives used during the polymerization process, nearly a 3-fold enhancement of the molar extinction coefficients could be determined at 785 nm, whereas a twofold increase of the molar extinction coefficients was detected at 940 nm for Bodipy_1. It therefore demonstrates the crucial importance to determine the optical properties of the photoinitiating systems in conditions as close as those used during the polymerization process.

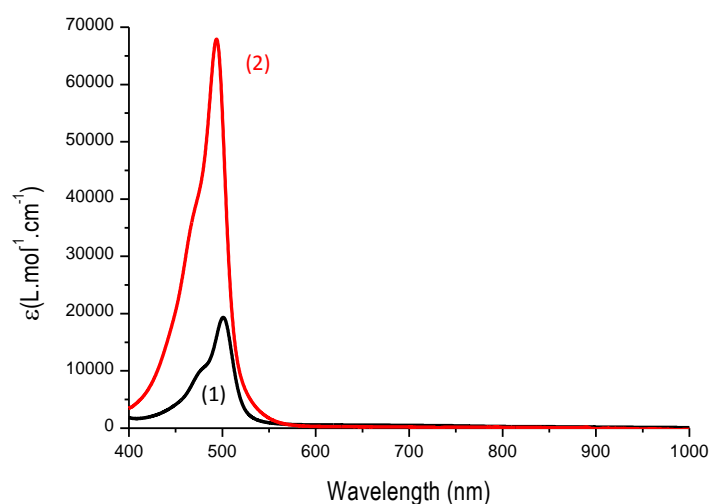


Figure 12. UV-visible absorption spectra of Bodipy_1 (1) and Bodipy_2 (2) in acetonitrile. Reproduced with permission of Ref. [229]

Table 3. Maximum absorption wavelengths in acetonitrile and molar extinction coefficients at different wavelengths in acetonitrile or in Mix-MA in the presence of the different additives.

	λ_{\max} (nm)	$\epsilon(\lambda_{\max})$ (L.mol ⁻¹ .cm ⁻¹)	$\epsilon(785\text{ nm})$ in ACN (L.mol ⁻¹ .cm ⁻¹)	$\epsilon(940\text{ nm})$ in ACN (L.mol ⁻¹ .cm ⁻¹)	$\epsilon(785\text{ nm})^a$ in Mix-MA (L.mol ⁻¹ .cm ⁻¹)	$\epsilon(940\text{ nm})^a$ in Mix-MA (L.mol ⁻¹ .cm ⁻¹)
Bodipy_1	500	18980	300	250	840	510
Bodipy_2	492	68080	170	100	n.d. ^b	n.d. ^b

^a: in presence of the polymerization additives: Iod3 (3 w%), 4-dppba (2 w%), BlocBuilder® MA (2w%). ^b n.d.: not determined.

Despite the low molar extinction coefficients both at 785 and 940 nm, this absorption was however sufficient to initiate a polymerization and the two dyes could promote the FRP of Mix-MA (a mixture composed of 33.3 wt% of (hydroxypropyl)methacrylate (HPMA), 33.3 wt% of 1,4-butanediol dimethacrylate (1,4-BDMA) and 33.3 wt% of a urethane dimethacrylate monomer (UDMA)). As shown in the Table 4, higher monomer conversions were determined at 785 nm than at 940 nm, consistent with a reduction of the molar extinction coefficients for the two dyes at longer wavelength. Interestingly, if the two bodipys could be used as photosensitizers for initiating the FRP of Mix-MA, the

photothermic effect that can produce NIR dyes was also beneficial for inducing the cleavage of a thermal initiator. Considering that the polymerization of acrylates is exothermic, the decomposition of Blocbuilder® MA could be induced. Parallel to this, phosphines are well-known to exhibit excellent properties to overcome oxygen inhibition.[308,309,314] In the present case, dppba can convert the unreactive peroxy radicals ROO• as alkoxy radicals RO•, enabling in turn to regenerate initiating species (See equations 11-16).

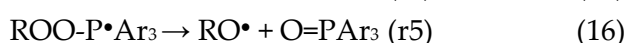
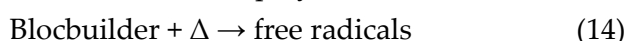


Table 4. Final monomer conversions obtained during the FRP of Mix-MA under air in the presence of dye/Iod3/4-dppba/BlocBuilder® MA (0.1%/3%/2%/2% w/w/w/w) upon irradiation with a Laser Diode at 785 nm or 940 nm; thickness = 1.4 mm.

	785 nm		940 nm	
	Final conversion	Time to reach the final conversion	Final conversion	Time to reach the final conversion
Bodipy_1	86%	196 s	84%	85 s
Bodipy_2	92%	356 s	60%	405 s

Recently, Page and coworkers examined different bodipys as photocatalysts of polymerization and this approach is relatively unusual for this family of compounds.[315] A structure/performance relationship could be established with a series of four bodipys bearing a mesitylene group at the bridgehead position and different halogens on the dipyrromethene sides (See Figure 13). It has to be noticed that BDP-4 and BDP-6 were previously examined in photopolymerization but not in the context of catalytic photoinitiating systems.

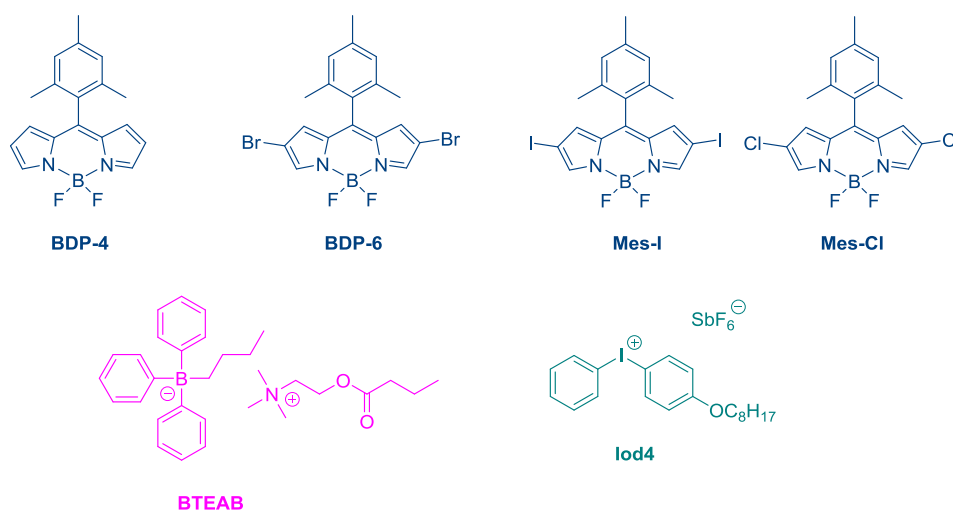


Figure 13. Chemical structures of different bodipys used as photocatalysts of polymerization.

Notably, the authors focused on halogens as the substituents for bodipys due to the well-known “heavy atom effect” attributed to halogen atoms that enables to enhance the spin-orbit coupling and thus favor the intersystem crossing (ISC) between the singlet and triplet excited state, resulting in long-lived triplet excited states.[316] In fact, triplet lifetimes of 370 ns could be determined for all halogenated bodipys. Parallel to this, halogens were also used as substituents enabling to efficiently tune the absorption properties of the dyes. Thus, a redshift of the absorption could be evidenced for all halogenated bodipys compared to the reference compound and absorption maxima located at 497, 523, 523 and 529 nm could be respectively determined for BDP-4, Mes-Cl, BDP-6 and Mes-I. To evidence the interest of these structures, isobornyl acrylate (IBOA), 2-hydroxyethyl acrylate and *N,N*-dimethylacrylamide were used as the monomers. The different dyes were mixed with 2-(butyryloxy)-*N,N,N*-trimethylethan-1-aminium butyltriphenylborate (BTEAB) as a donor initiator and [4-(octyloxy)phenyl](phenyl)iodonium hexafluoroantimonate (Iod4) as the acceptor initiator (See Figure 13). Noticeably, by using the three-component system for the FRP of IBOA upon irradiation at 530 nm with a LED ($I = 16 \text{ mW/cm}^2$), a two-fold enhancement of the polymerization rate was detected with the halogenated bodipys compared to the none-halogenated one. Additionally, a good correlation was established between the atomic number of the heavy atom and the polymerization rate. Thus, polymerization rates of 0.43, 0.91 and 0.95 M/s were determined for the three-component systems comprising Mes-Cl, BDP-6 and Mes-I. With the four tested photoinitiating systems, final monomer conversions of 80% were determined with IBOA, corresponding to the maximum conversion for this monomer. Fluorescence quenching experiments enabled to elucidate the mechanism and the different bodipys showed a higher ability to accept an electron from a donor than to donate an electron to an acceptor. It was thus concluded that the reductive pathway was the main mechanism producing initiating radicals, namely a radical anion of the bodipy and a butyl radical issued from the oxidization of the

triphenylalkylborate salt.[317] The mechanism depicted in the Figure 14 was proposed by the authors.

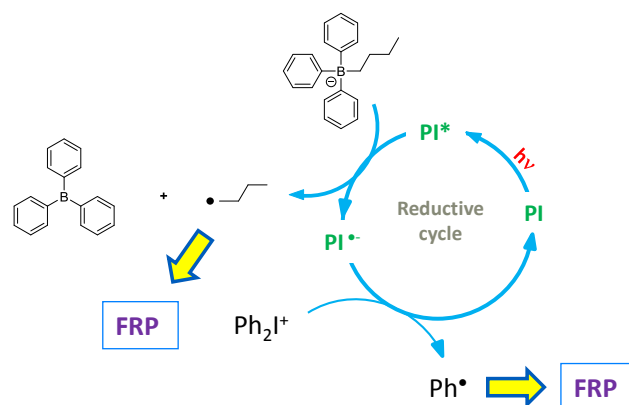


Figure 14. Photocatalytic system occurring with the three-component photoinitiating system.

Two aza-bodipys were also designed and synthesized, namely Aza-H and Aza-Br, in which the mesityl group at the meso bridgehead position of the Mes-X series was replaced by a nitrogen atom and electron donating groups were also introduced as peripheral groups (See Figure 15).[315] By applying this structural modification, a redshift of the absorption maxima by ca 135 nm could be achieved compared to the previous series. Thus, an absorption maximum at 660 nm was determined for Aza-Br, redshifted compared to that of the analogue BDP-6 (525 nm). Consequently, polymerization tests could be carried out at 656 and 740 nm. Here again, the benefits of the heavy atom effect in Aza-Br were confirmed. Impressively, the polymerization rate of IBOA was eight times faster at 740 nm compared to that obtained with Aza-H (0.66 ± 0.03 M/s with Aza-Br vs 0.08 ± 0.02 M/s for Aza-H), by using the three-component dye/BTEAB/Iod4 system at 740 nm. Halogenation thus constitutes a simple approach to increase the polymerization rate without requiring extensive synthetic work. Indeed, halogens can be introduced in good yields in a one-step synthesis starting from Aza-H.

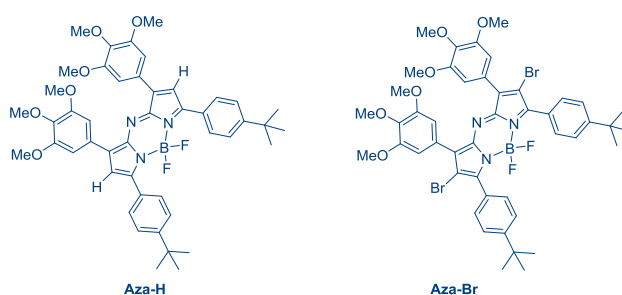


Figure 15. Chemical structures of Aza-H and Aza-Br.

The remarkable reactivity of Mes-I and Aza-Br in three-component systems were confirmed with the low light intensity that could be used to initiate the FRP of IBOA (0.01 mW/cm² and 1 mW/cm² respectively). Considering that the system is catalytic, low photosensitizer contents could also be used and efficient polymerization processes could be

maintained for catalyst loadings as low as 0.001 mol% and 0.004 mol% for Mes-I and Aza-Br respectively. Such low photocatalyst loadings are exceptional in photopolymerization. Finally, interest of these resins was demonstrated by mean of 3D printing experiments. As shown in the Figure 16, 3D objects displaying a remarkable spatial resolution could be prepared.

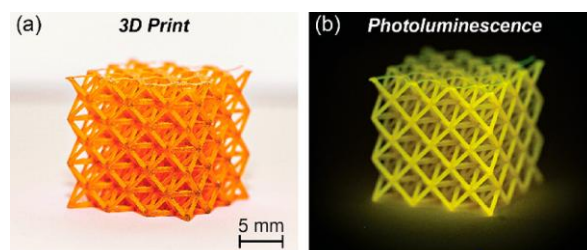


Figure 16. 3D objects prepared upon irradiation at 530 nm with a LED using BDP-6 as the photosensitizer for the three-component system BDP-6/BTEAB/Iod4 (0.1%/0.2%/2% w/w/w) and a mixture of *N,N*-dimethylacrylamide (DMA)/ trimethylolpropane triacrylate (TMPTA) (4/1 w/w) as the resin. (a) photo under room light (b) photo under UV light. Reproduced with permission of Ref.[315]

2.2. Bodipys in monocomponent systems.

In all the abovementioned examples, efficient photoinitiating systems could be prepared by using multicomponent systems. If the efficiency can't be denied, the use of three or even four-component systems can complexify the elaboration of the resin. Ideally, the use of monocomponent photoinitiators is preferred and this goal can be achieved with Type I photoinitiators.[117,122,183,221,274,318–328] Concerning Type II photoinitiators, this issue can be addressed by designing multifunctional compounds. This point was notably investigated by Ortyl and coworkers who developed a series of bodipy-substituted iodonium salts differing by the counteranions that could act as one-component systems and exhibited panchromatic properties (See Figure 17).[73]

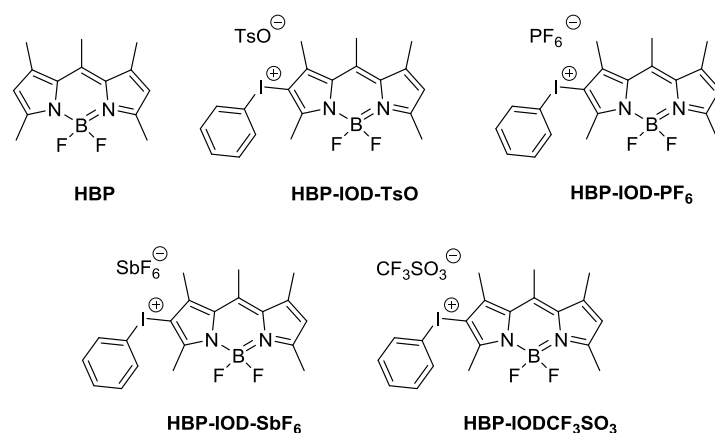


Figure 17. Chemical structures of BODIPY-based iodonium salts.

Absorption properties of these iodonium salts were remarkable by the broadness of the absorption spectra as well as the molar extinction coefficients at absorption maxima. Indeed, all BODIPYs exhibited an absorption extending between 250 and 600 nm so that photopolymerization experiments could be performed at 365, 405, 420, 450, 455, 470, 490, 505 and 530 nm (See Figure 18 and Table 5). Molar extinction coefficients as high as 28 076 M⁻¹.cm⁻¹ for HBP-IOD-TsO up to 31 620 M⁻¹.cm⁻¹ for HBP-IOD-PF₆ could be determined in acetonitrile.

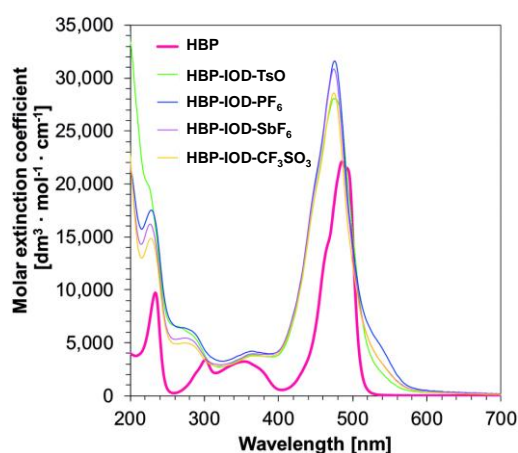


Figure 18. UV-visible absorption spectra of mono-component iodonium salts recorded in acetonitrile. Reproduced with permission of Ref. [73]

Table 5. Optical characteristics of a series of monocomponent iodonium salts at the absorption maximum and at different irradiation wavelengths.

	λ_{\max} (nm)	ϵ_{\max} (M ⁻¹ .cm ⁻¹)	ϵ_{365}	ϵ_{405}	ϵ_{420}	ϵ_{450}	ϵ_{455}	ϵ_{470}	ϵ_{490}	ϵ_{505}	ϵ_{530}
chromophore used to conjugate iodonium salts											
HBP	486	22115	2955	547	1070	6399	9025	15332	21585	7703	149
Cationic photoinitiators											
HBP -IOD-TSO	474	28076	3861	4257	7145	19209	21218	27227	22515	11979	2997
HBP -IOD-PF ₆	476	31620	4204	4657	7699	20412	22442	30047	21650	11454	5536
HBP -IOD-SbF ₆	475	30869	3950	4629	7570	20040	22122	29748	20393	10770	4057
HBP -IOD-CF ₃ SO ₃	474	28599	3757	4461	7308	19165	21012	27663	18677	10021	4089

Photolysis experiments revealed several important trends. First, the photolysis rates were determined as being directly related to the molar extinction coefficients of the salts at the irradiation wavelengths. Thus, at 530 nm, no photolysis could be detected at 530 nm for the different salts due to their low molar extinction coefficients at this wavelength (See Figure 19). Secondly, photolysis rates were strongly influenced by the counter-anions used to prepare the iodonium salts. Notably, by increasing the anion size, nucleophilicity of the

anion could be reduced, speeding up the photolysis. This trend evidenced during the photolysis experiments was confirmed during the polymerization experiments.

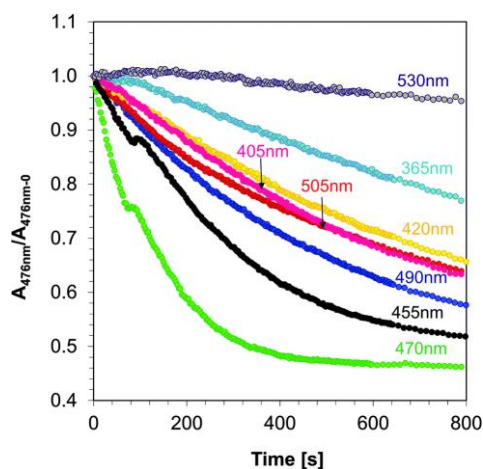


Figure 19. Dependence A/A_0 at 476 nm during the photolysis of HBP-IOD-PF6 upon irradiation with different diodes emitting at 365, 405, 420, 455, 470, 490, 505 and 530 nm. Reproduced with permission of Ref. [73]

Considering that the iodonium salts are asymmetrically substituted, the fragmentation mechanism was investigated by theoretical calculations. These calculations revealed the photodissociation of the different iodonium salts to occur on the phenyl side as a result of a lower bond dissociation energy (BDE) (32.44 kcal/mol on the phenyl side vs. 69.25 kcal/mol on the BODIPY side) (See Figure 20).

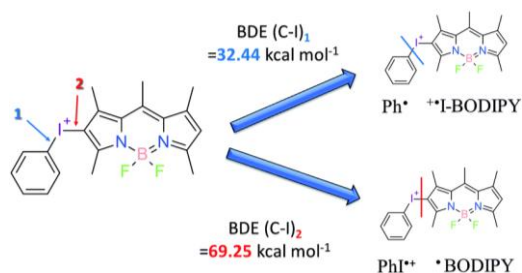


Figure 20. Dissociation mechanism of the BODIPY-based iodonium salts. Reproduced with permission of Ref. [73]

During the photopolymerization experiments, the cationic polymerization (CP) of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (EPOX) and triethylene glycol divinyl ether (TEGDVE) was examined. A good correlation between monomer conversions and molar extinction coefficients at the irradiation wavelengths was determined. In the case of EPOX, the highest conversions were obtained at 405 and 450 nm, with conversions of 79 and 70% respectively after 900 s of irradiation using HBP-Iod-PF6 (3 wt%) as the photoinitiator. As interesting feature, a dark polymerization process could be detected and 7.5% of additional conversion could be determined 700 s after the irradiation was interrupted using HBP-IOD-PF6 (3 wt%) and upon irradiation at 505 nm for only 200 s. While examining

the CP of TEGDVE, monomer conversions higher than 90% could be obtained at 365 and 455 nm (See Table 6).

Table 6. Monomer conversions obtained during the CP of EPOX and TEGDVE using HBP-Iod-PF6 (3 wt%) with different light sources.

monomer	ϵ ($M^{-1}.cm^{-1}$)	Light sources	Intensity of LEDs (mW/cm ²)	Conversion (%)
EPOX	4204	365 nm HP	22.8	64.6
EPOX	4657	405 nm HP	22.8	79.0
EPOX	20412	450 nm HP	22.8	70.0
EPOX	30047	470 nm	12.9	57.2
EPOX	11454	505 nm	7.9	63.0
TEGDVE	30047	470 nm	12.9	83.4
TEGDVE	22442	455 nm	12.9	90.8
TEGDVE	7699	420 nm	12.9	92.8
TEGDVE	4657	405 nm	12.9	88.7
TEGDVE	4204	365 nm HP	12.9	90.8
TEGDVE	21650	490 nm	5.1	90.5
TEGDVE	5536	530 nm	6.9	81.6
TEGDVE	22454	505 nm	7.9	69.3

Influence of the anions on the polymerization process and the final monomer conversions has been extensively reported in the literature. From these different works, a scale of reactivity has been proposed for the iodonium salts : $BF_4^- < PF_6^- < AsF_6^- < SbF_6^- < B(C_6F_5)_4^- < Ga(C_6F_5)_4^-$ [329], and the monomer conversions obtained with the bodipy-based iodonium salts were consistent with this scale. As shown in the Figure 21 during the CP of TEGDVE, the highest conversion was obtained with HBP-IOD-SbF6 whereas the lowest one was determined for HBP-IOD-TsO possessing the most nucleophilic anion of the series. Finally, the one-component bodipy-based iodonium salts have been obtained at the cost of extensive synthetic works. For this reason, a comparison of the photoinitiating abilities of the one-component iodonium salts with the reference two-component HBP/Iod1 system was carried out. Comparison of the monomer conversions obtained for HBP-IOD-PF6 at different wavelengths with that of the HBP/Iod1 system revealed the monomer conversion to be improved by ca 5% for the monocomponent system, therefore justifying the synthetic effort done in this work. By the concomitant presence of both the photosensitizer and the iodonium salt on a unique molecule, photoinduced electron transfer was facilitated by mean of intramolecular interactions.

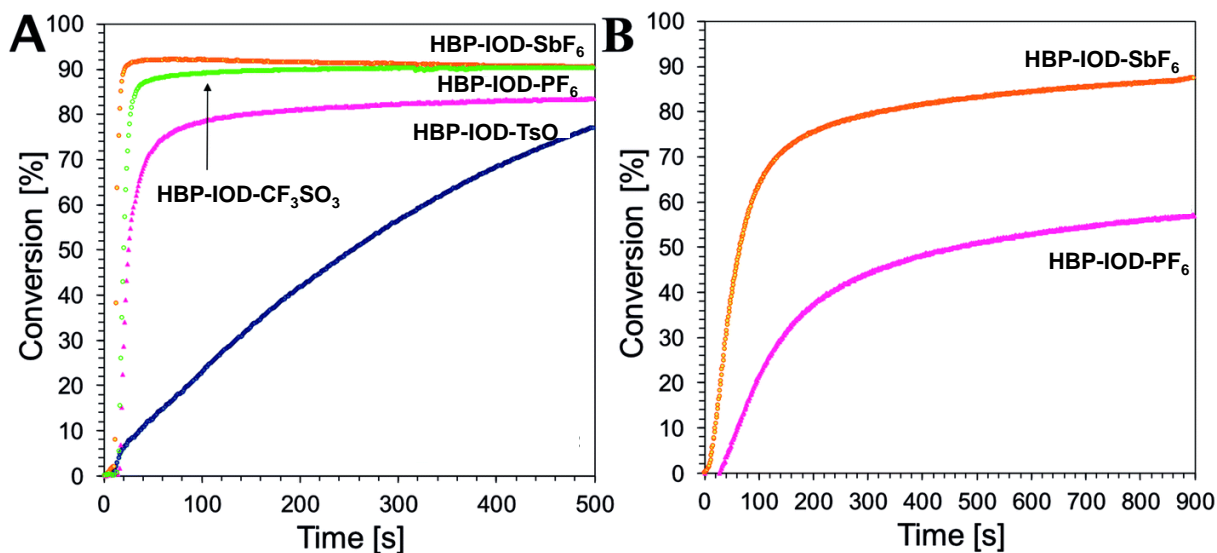


Figure 21. Polymerization profiles of: (A) TEGDVE and (B) EPOX upon irradiation at 470 nm using BODIPY-based iodonium salts differing by the counter-anions. Reproduced with permission of Ref. [73]

2.3. Bodipy-based photoacid generators

The cationic polymerization of epoxides can be promoted by the generation of cations or protons. Molecules that are capable to produce protons upon irradiation are named photoacid generators (PAGs) and this family of compounds has been extensively studied in the literature.[54,75,76,80,301,318,319,330–337] The first bodipy-based photoacid generators (PAG-1 and PAG-2) were proposed in 2020 by Zhang and coworkers (See Figure 22).[338] To achieve this goal, sulfonium salts were covalently linked to the bodipy scaffolds. The two PAGs showed absorption maxima at 509 and 566 nm in methanol. Due to the extended conjugation of PAG-2 compared to PAG-1, a redshift of the absorption maximum was logically detected. As drawback, a severe reduction of the photoluminescence quantum yields was determined for PAG-2 ($\varphi = 0.02$), far from that obtained for PAG-1 ($\varphi = 0.11$). Investigations of the photoacid generation quantum yield revealed PAG-1 to be a better candidate for photoinitiation since a yield of 7 and 4% were respectively determined.

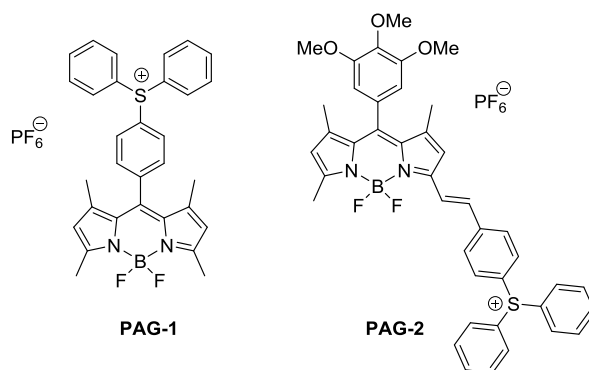


Figure 22. Chemical structures of bodipy-based photoacid generators.

Examination of the photoinitiating ability of PAG-2 during the CP of cyclohexene oxide revealed the polymerization process to be slow. Indeed, after 30 min. of irradiation at 595 nm ($I = 80 \text{ mW/cm}^2$), a conversion of only 21% was determined. However, PAG-1 and PAG-2 can be cited as the PAGs exhibiting the most redshifted absorption ever reported in the literature, what is remarkable. The proof of concept was done.

3. Difluoroborane structures other than bodipys

3.1. Boranils as visible light photoinitiators of polymerization

Boranils belongs to the family of borate complexes based on an aniline-imine or a salicylaldimine ligand and these compounds have been identified as a promising alternative to the traditional bodipys owing to their facile multi-gram scale syntheses and the facile tunability of their optical properties.[339,340] The first boranil derivative to be published as photoinitiator of polymerization was proposed by Lalevée and coworkers (See Figure 23).[86] A comparison of its photoinitiating ability with that of BDP-1-BDP-7 was established.

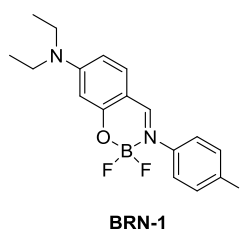


Figure 23. Chemical structure of BRN-1.

Compared to BDP-1-BDP-7 that exhibit absorption maxima between 496 and 532 nm, BRN-1 showed an absorption spectra blueshifted compared to the previous dyes and an absorption maximum located at 400 nm was determined. Polymerization tests revealed BRN-1 to be more reactive than BDP-1-BDP-7 during the photopolymerization of DVE-3. Indeed, if the best conversion was obtained with BDP-2 (90% conversion upon excitation at 473 nm for 200 s), a conversion of 100% could be obtained within 10 s at 405 nm with BRN-1 using the two-component dye/Iod2 system (See Figure 24). This remarkable photoinitiating ability can be put in parallel with the highly favorable free energy change determined for BRN-1 (-1.15 eV) compared to BDP-2 (-1.07 eV). As observed for BDP-1-BDP-7, a good photobleaching could be detected during the polymerization process. This trend was confirmed during the CP of EPOX and a conversion of 80% was obtained within the two-component BRN-1/Iod2 (0.2%/2% w/w) system at 405 nm, higher than that obtained with BDP-2 (65% after 200 s of irradiation at 473 nm under air).

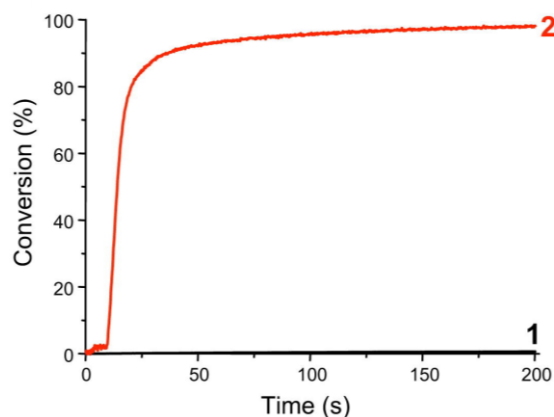


Figure 24. Polymerization profiles obtained with (1) Iod₂ (2 wt%) and (2) BRN-1/Iod₂ (0.2%/2% w/w) upon irradiation at 473 nm. Reproduced with permission of Ref.[86]

3.2 2-Phenacylbenzoxazole difluoroboranes

Boranils were not the only difluoroborane derivatives to be studied as photoinitiators. In 2022, a series of eight boron coordination compounds derived from benzoxazole bidentate ligands was proposed by Kabatc and coworkers for the free radical polymerization of acrylate monomers (See Figure 25).[84]

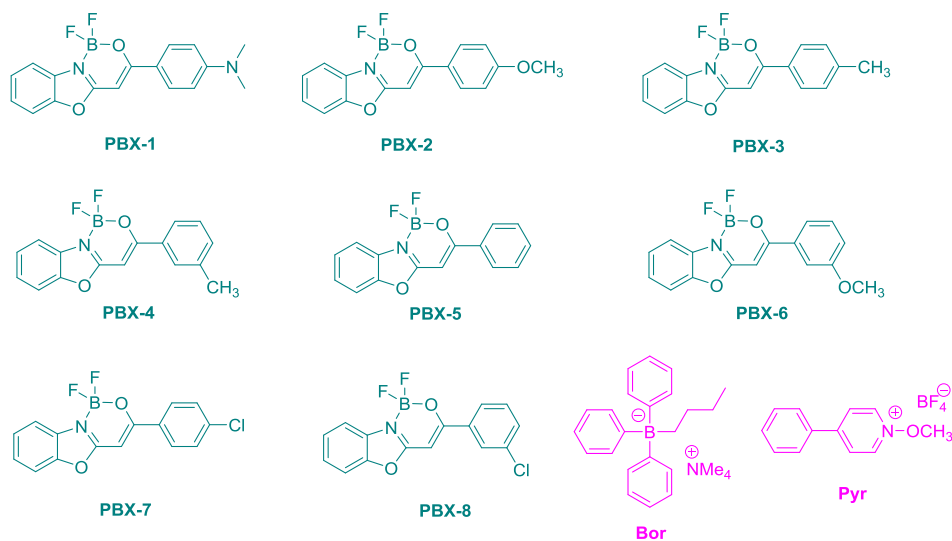


Figure 25. Chemical structures of PBX-1-PBX-8 and different additives.

2-Phenacylbenzoxazole difluoroboranes are a class of fluorescent dyes that are extensively used for biomedical applications such as biolabeling[341–343] and chemodosimetry.[344] From the absorption viewpoint, the absorption range of 2-phenacylbenzoxazole difluoroboranes is comparable to that of boranils, with absorption maxima ranging between 349 nm for PBX-5 up to 415 nm for PBX-1 comprising the most electron donating group of the series (See Table 7 and Figure 26).

Table 7. Absorption maxima of dyes PBX-1-PBX-8 in acetonitrile.

Dyes	PBX-1	PBX-2	PBX-3	PBX-4	PBX-5	PBX-6	PBX-7	PBX-8
Substituents	4-NMe ₂	4-OMe	4-Me	3-Me	H	3-OMe	4-Cl	3-Cl
λ_{\max} (nm)	415	359	351	350	349	351	352	350

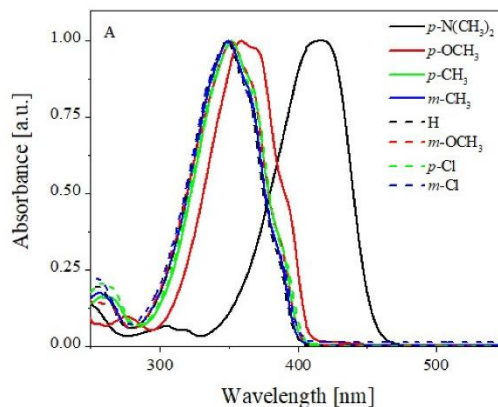


Figure 26. UV-visible absorption spectra of PBX-1-PBX-8 in acetonitrile. Reproduced with permission of Ref.[84]

Examination of the photoinitiating ability of PBX-1-PBX-8 with different co-initiators (tetramethylammonium *n*-butyltriphenylborate (Bor), Iod1 and *N*-methoxy-4-phenylpyridinium tetrafluoroborate (Pyr)) revealed the two-component dye/Pyr to furnish the highest monomer conversions, irrespective of the dyes during the FRP of TMPTA upon irradiation in the UV–visible range (300-500 nm). The highest monomer conversions (around 47%) were obtained with PBX-2, PBX-3 and PBX-4 as the photosensitizers.

Table 8. Monomer conversions determined with different two-component dye/co-initiator photoinitiating systems.

Dyes	Bor	Iod1	Pyr
PBX-1	28.2	35.6	39.2
PBX-2	34.4	25.9	47.7
PBX-3	38.2	23.3	47.1
PBX-4	38.3	24.5	47.4
PBX-5	27.8	25.5	41.4
PBX-6	35.2	22.6	45.1
PBX-7	32.3	22.5	36.7
PBX-8	37.1	21.3	39.2

Comparison with the reference camphorquinone/*N*-phenylglycine system[88,345–347] revealed the different PBX/Pyr systems to furnish slower polymerization rates. However, higher monomer conversions could be obtained with the PBX/Pyr systems. Thus, a

conversion of ca 20% could be obtained with the reference camphorquinone/*N*-phenylglycine system contrarily to 50% of the PBX-1/Pyr system.

3.3. Squaraine-based difluoroborate complexes as visible light photoinitiators of polymerization

Squaraines have been extensively studied by Kabatc and coworkers as visible light photoinitiators of polymerization.[145,348–350] In 2022, they proposed for the first time two squaraine-based difluoroborate complexes (BPSQ1 and BPSQ2) and compared their photoinitiating abilities to that of their corresponding squaraines (PSQ1 and PSQ2) (See Figure 27).[351] Three different co-initiators were used, namely Bor, Iod1 and Pyr. Upon formation of the difluoroborate complexes, no significant modification of the absorption properties was found since absorption maxima at 560, 569, 560 and 569 nm were respectively determined for PSQ1, PSQ2, BPSQ1 and BPSQ2 in THF. Noticeably, examination of their solvatochromic properties revealed all dyes to exhibit a negative solvatochromism meaning that the excited state is less polar than the ground state due to transfer of electron density from donor to acceptor after excitation. Due to this unusual behavior, it was concluded that more energy would be required for the excitation of the dyes.

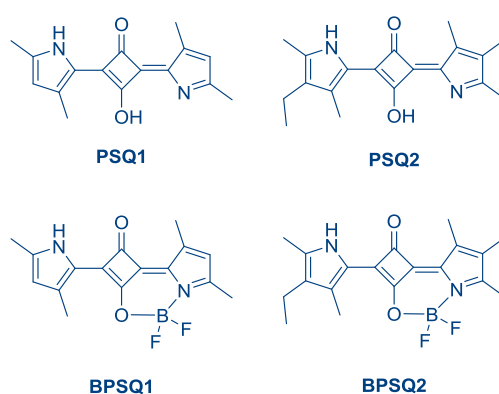


Figure 27. A series of squaraine derivatives used as visible light photoinitiators.

This unexpected behavior was confirmed during the FRP of TMPTA. Using PSQ1 and PSQ2 as the photosensitizers in combination with the different additives, the highest monomer conversions were obtained with the PSQ1/Iod1 and PSQ2/Iod1 combinations. However, the conversion was extremely low, around 12% after 20 min. of irradiation with a high-pressure mercury lamp. By using the difluoroborate complexes, worse results were obtained and the best monomer conversion of 10% was obtained with the BPSQ2/Iod1 system. Squaraine-based difluoroborate complexes were thus identified as poor candidates for photoinitiation, consistent with their unusual negative solvatochromism detected in solution.

3. Conclusion

To conclude, bodipys have been identified as candidates for photopolymerization processes done at long wavelengths. Over the years, several strategies have been established to design photoinitiating systems. Notably, mono-component systems have been prepared by combining within a unique molecule the chromophore and the iodonium moiety. By connecting sulfonium groups, photoacid generators could be prepared. The design of photobleachable photoinitiating systems could also be obtained, constituting a major achievement in the design of visible light photoinitiating systems. However, all difluoroborane derivatives are not excellent candidates for photoinitiation. Notably, squaraine derivatives and 2-phenacylbenzoxazole difluoroboranes only proved to be poor candidates for photoinitiation. Future works will consist in the simplification of the photocurable resins. Notably, no Type I photoinitiators have been reported to date with bodipys. However, several photocleavable groups can be easily introduced such as oxime esters that can be prepared in two steps after introduction of the aldehyde group. In the same spirit, glyoxylates can be introduced in one step by a Friedel-Craft reaction while offering a high photochemical reactivity. No water-soluble bodipys have been reported yet. In this field, several groups can be envisioned for providing water solubility such as sulfonates[171,182,269,352] or phosphonic acids.[270,271] Indeed, recent works have evidenced these two groups to be the best candidates for water-solubility and to outperform other groups such as carboxylates or ammonium groups. By rendering the photoinitiators water-soluble, it could pave the way towards greener polymerization conditions. Such structures will certainly be proposed in the coming years.

Acknowledgments

Aix Marseille University and the Centre National de la Recherche Scientifique (CNRS) are acknowledged for financial supports.

Conflicts of Interest

The authors declare no conflict of interest.

References

- [1] M.L. Allegranza, Z.M. DeMartini, A.J. Kloster, Z.A. Digby, D. Konkolewicz, Visible and sunlight driven RAFT photopolymerization accelerated by amines: kinetics and mechanism, *Polym. Chem.* 7 (2016) 6626–6636. <https://doi.org/10.1039/C6PY01433J>.
- [2] 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>.

- [3] 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>.
- [4] M. Ciftci, M.A. Tasdelen, Y. Yagci, Sunlight induced atom transfer radical polymerization by using dimanganese decacarbonyl, *Polym. Chem.* 5 (2014) 600–606. <https://doi.org/10.1039/C3PY01009K>.
- [5] C. Decker, T. Bendaikha, Interpenetrating polymer networks. II. Sunlight-induced polymerization of multifunctional acrylates, *J. Appl. Polym. Sci.* 70 (1998) 2269–2282. [https://doi.org/10.1002/\(SICI\)1097-4628\(19981212\)70:11<2269::AID-APP21>3.0.CO;2-D](https://doi.org/10.1002/(SICI)1097-4628(19981212)70:11<2269::AID-APP21>3.0.CO;2-D).
- [6] M.-A. Tehfe, J. Lalevée, D. Gigmes, J.P. Fouassier, Green Chemistry: Sunlight-Induced Cationic Polymerization of Renewable Epoxy Monomers Under Air, *Macromolecules.* 43 (2010) 1364–1370. <https://doi.org/10.1021/ma9025702>.
- [7] J. Wang, M. Rivero, A. Muñoz Bonilla, J. Sanchez-Marcos, W. Xue, G. Chen, W. Zhang, X. Zhu, Natural RAFT Polymerization: Recyclable-Catalyst-Aided, Opened-to-Air, and Sunlight-Photolyzed RAFT Polymerizations, *ACS Macro Lett.* 5 (2016) 1278–1282. <https://doi.org/10.1021/acsmacrolett.6b00818>.
- [8] J. Yu, Y. Gao, S. Jiang, F. Sun, Naphthalimide Aryl Sulfide Derivative Norrish Type I Photoinitiators with Excellent Stability to Sunlight under Near-UV LED, *Macromolecules.* 52 (2019) 1707–1717. <https://doi.org/10.1021/acs.macromol.8b02309>.
- [9] Y. Bao, Recent Trends in Advanced Photoinitiators for Vat Photopolymerization 3D Printing, *Macromol. Rapid Commun.* 43 (2022) 2200202. <https://doi.org/10.1002/marc.202200202>.
- [10] 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).
- [11] 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>.
- [12] 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>.
- [13] J. Lalevée, X. Allonas, J.P. Fouassier, Tris(trimethylsilyl)silane (TTMSS)-Derived Radical Reactivity toward Alkenes: A Combined Quantum Mechanical and Laser Flash Photolysis Study, *J. Org. Chem.* 72 (2007) 6434–6439. <https://doi.org/10.1021/jo0706473>.
- [14] C. Chatgililoglu, J. Lalevée, Recent Applications of the (TMS)₃SiH Radical-Based Reagent, *Molecules.* 17 (2012) 527–555. <https://doi.org/10.3390/molecules17010527>.
- [15] P. Garra, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, Redox two-component initiated free radical and cationic polymerizations: Concepts, reactions and applications, *Prog. Polym. Sci.* 94 (2019) 33–56. <https://doi.org/10.1016/j.progpolymsci.2019.04.003>.
- [16] F. Dumur, The future of visible light photoinitiators of polymerization for photocrosslinking applications, *Eur. Polym. J.* 187 (2023) 111883. <https://doi.org/10.1016/j.eurpolymj.2023.111883>.

- [17] 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>.
- [18] M. El-Roz, J. Lalevée, X. Allonas, J.P. Fouassier, Mechanistic Investigation of the Silane, Germane, and Stannane Behavior When Incorporated in Type I and Type II Photoinitiators of Polymerization in Aerated Media, *Macromolecules*. 42 (2009) 8725–8732. <https://doi.org/10.1021/ma9017313>.
- [19] B.K. Armstrong, A. Krickler, The epidemiology of UV induced skin cancer, *Consequences Expo. Sunlightelements Assess Prot.* 63 (2001) 8–18. [https://doi.org/10.1016/S1011-1344\(01\)00198-1](https://doi.org/10.1016/S1011-1344(01)00198-1).
- [20] F.R. de Gruijl, Skin cancer and solar UV radiation, *Eur. J. Cancer*. 35 (1999) 2003–2009. [https://doi.org/10.1016/S0959-8049\(99\)00283-X](https://doi.org/10.1016/S0959-8049(99)00283-X).
- [21] 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>.
- [22] C. Noè, M. Hakkarainen, M. Sangermano, Cationic UV-Curing of Epoxidized Biobased Resins, *Polymers*. 13 (2021) 89. <https://doi.org/10.3390/polym13010089>.
- [23] 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>.
- [24] 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>.
- [25] 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>.
- [26] 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).
- [27] 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>.
- [28] 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>.
- [29] H. Chen, G. Noirbent, Y. Zhang, K. Sun, S. Liu, D. Brunel, D. Gimes, 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>.
- [30] A. Bagheri, J. Jin, Photopolymerization in 3D Printing, *ACS Appl. Polym. Mater.* 1 (2019) 593–611. <https://doi.org/10.1021/acscapm.8b00165>.
- [31] J. Lalevée, S. Telitel, P. Xiao, M. Lepeltier, F. Dumur, F. Morlet-Savary, D. Gimes, 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>.

- [32] W. Tomal, H.C. Kiliçlar, 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>.
- [33] A.H. Bonardi, F. Dumur, T.M. Grant, G. Noirbent, D. Gimes, 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>.
- [34] P. Garra, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gimes, J.-P. Fouassier, J. Lalevée, Photopolymerization processes of thick films and in shadow areas: a review for the access to composites, *Polym. Chem.* 8 (2017) 7088–7101. <https://doi.org/10.1039/C7PY01778B>.
- [35] M.-A. Tehfe, F. Dumur, E. Contal, B. Graff, F. Morlet-Savary, D. Gimes, 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>.
- [36] S. Telitel, F. Dumur, T. Faury, B. Graff, M.-A. Tehfe, D. Gimes, 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>.
- [37] N. Uchida, H. Nakano, T. Igarashi, T. Sakurai, Nonsalt 1-(arylmethoxy)pyrene photoinitiators capable of initiating cationic polymerization, *J. Appl. Polym. Sci.* 131 (2014) 40510. <https://doi.org/10.1002/app.40510>.
- [38] 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>.
- [39] M.-A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, D. Gimes, 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>.
- [40] 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>.
- [41] M.-A. Tehfe, F. Dumur, N. Vilà, B. Graff, C.R. Mayer, J.P. Fouassier, D. Gimes, 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>.
- [42] S. Telitel, F. Dumur, D. Gimes, 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>.
- [43] M.-A. Tehfe, J. Lalevée, S. Telitel, E. Contal, F. Dumur, D. Gimes, 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>.
- [44] H. Mokbel, F. Dumur, J. Lalevée, On demand NIR activated photopolyaddition reactions, *Polym. Chem.* 11 (2020) 4250–4259. <https://doi.org/10.1039/D0PY00639D>.

- [45] 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>.
- [46] V. Launay, F. Dumur, D. Gigmes, 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>.
- [47] 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>.
- [48] 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>.
- [49] 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>.
- [50] 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>.
- [51] A.-H. Bonardi, F. Bonardi, G. Noirbent, F. Dumur, D. Gigmes, C. Dietlin, J. Lalevée, Free-radical polymerization upon near-infrared light irradiation, merging photochemical and photothermal initiating methods, *J. Polym. Sci.* 58 (2020) 300–308. <https://doi.org/10.1002/pol.20190079>.
- [52] H. Mokbel, G. Noirbent, D. Gigmes, F. Dumur, J. Lalevée, Towards new NIR dyes for free radical photopolymerization processes, *Beilstein J. Org. Chem.* 17 (2021) 2067–2076. <https://doi.org/10.3762/bjoc.17.133>.
- [53] F. Dumur, Recent Advances on Anthracene-based Photoinitiators of Polymerization, *Eur. Polym. J.* (2022) 111139. <https://doi.org/10.1016/j.eurpolymj.2022.111139>.
- [54] 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>.
- [55] 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>.
- [56] 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>.
- [57] 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>.
- [58] 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>.
- [59] 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>.
- [60] 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>.
- [61] 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>.
- [62] 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>.
- [63] 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>.
- [64] 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>.
- [65] 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>.
- [66] 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>.
- [67] 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) 1269.
<https://doi.org/10.3390/catal11111269>.
- [68] 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>.
- [69] 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>.
- [70] 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>.
- [71] 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>.
- [72] 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>.
- [73] 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>.
- [74] H. Mokbel, J. Toufaily, T. Hamieh, F. Dumur, D. Campolo, D. Gigmes, 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>.
- [75] S. Villotte, D. Gigmes, 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>.
- [76] 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>.
- [77] 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>.
- [78] 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).
- [79] L.I. Jun, L.I. Miaozhen, 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.
- [80] N. Zivic, P.K. Kuroishi, F. Dumur, D. Gigmes, 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>.
- [81] 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>.
- [82] 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>.
- [83] 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>.
- [84] 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>.
- [85] 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>.
- [86] 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>.
- [87] 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>.
- [88] 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>.
- [89] 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>.
- [90] M. Abdallah, T.-T. Bui, F. Goubard, D. Theodosopoulou, F. Dumur, A. Hijazi, J.-P. Fouassier, J. Lalevée, Phenothiazine derivatives as photoredox catalysts for cationic and radical photosensitive resins for 3D printing technology and photocomposite synthesis, *Polym. Chem.* 10 (2019) 6145–6156. <https://doi.org/10.1039/C9PY01265F>.
- [91] 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>.
- [92] Y. Zhang, F. Morlet-Savary, M. Schmitt, B. Graff, A. Rico, M. Ibrahim-Ouali, F. Dumur, J. Lalevée, Photoinitiation behavior of phenothiazines containing two oxime ester functionalities (OXEs) in free radical photopolymerization and 3D printing application, *Dyes Pigments*. 215 (2023) 111202. <https://doi.org/10.1016/j.dyepig.2023.111202>.
- [93] A. Noon, F. Hammoud, B. Graff, T. Hamieh, J. Toufaily, F. Morlet-Savary, M. Schmitt, T.-T. Bui, A. Rico, F. Goubard, S. Peralta, F. Dumur, J. Lalevée, Photoinitiation Mechanisms of Novel Phenothiazine-Based Oxime and Oxime Esters Acting as Visible Light Sensitive Type I and Multicomponent Photoinitiators, *Adv. Mater. Technol.* n/a (2023) 2300205. <https://doi.org/10.1002/admt.202300205>.
- [94] 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>.
- [95] 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>.
- [96] 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>.
- [97] 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>.
- [98] 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>.
- [99] 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>.
- [100] 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>.
- [101] 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>.
- [102] 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>.
- [103] 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>.
- [104] 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>.
- [105] 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>.
- [106] J. Li, X. Zhang, S. Ali, M.Y. Akram, J. Nie, X. Zhu, The effect of polyethylene glycol diacrylate 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>.
- [107] 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>.
- [108] 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>.
- [109] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gigmes, 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>.
- [110] 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>.
- [111] A. Al Mousawi, F. Dumur, P. Garra, J. Toufaily, T. Hamieh, B. Graff, D. Gignes, 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>.
- [112] A. Al Mousawi, D.M. Lara, G. Noirbent, F. Dumur, J. Toufaily, T. Hamieh, T.-T. Bui, F. Goubard, B. Graff, D. Gignes, 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>.
- [113] 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>.
- [114] 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>.
- [115] 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>.
- [116] 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>.
- [117] 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>.
- [118] 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>.
- [119] 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>.
- [120] 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.* 172 (2022) 111218. <https://doi.org/10.1016/j.eurpolymj.2022.111218>.
- [121] 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>.

- [122] 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>.
- [123] 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.* 307 (2022) 2200082. <https://doi.org/10.1002/mame.202200082>.
- [124] 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>.
- [125] 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>.
- [126] F. Dumur, Recent Advances on Furan-Based Visible Light Photoinitiators of Polymerization, *Catalysts*. 13 (2023). <https://doi.org/10.3390/catal13030493>.
- [127] 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>.
- [128] 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>.
- [129] 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>.
- [130] M.-A. Tehfe, F. Dumur, B. Graff, D. Gigmes, 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>.
- [131] P. Garra, D. Brunel, G. Noirbent, B. Graff, F. Morlet-Savary, C. Dietlin, V.F. Sidorkin, F. Dumur, D. Duché, D. Gigmes, 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>.
- [132] 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>.
- [133] 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>.
- [134] 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>.

- [135] 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>.
- [136] 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>.
- [137] 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>.
- [138] 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>.
- [139] 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>.
- [140] 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>.
- [141] 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>.
- [142] 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>.
- [143] 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>.
- [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, 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>.
- [146] 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>.
- [147] 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>.
- [148] 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>.
- [149] 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>.
- [150] 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>.
- [151] 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>.
- [152] 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>.
- [153] 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>.
- [154] 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>.
- [155] 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>.
- [156] 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>.
- [157] 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) 2752. <https://doi.org/10.3390/ijms24032752>.
- [158] 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>.

- [159] 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<::AID-APMC1>3.0.CO;2-2](https://doi.org/10.1002/(SICI)1522-9505(19990901)270:1<::AID-APMC1>3.0.CO;2-2).
- [160] 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>.
- [161] 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>.
- [162] 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>.
- [163] 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>.
- [164] 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>.
- [165] Z. Kucybała, I. Pyszka, J. Pączkowski, 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.* 7 (2000) 1559–1567. <https://doi.org/10.1039/B000583P>.
- [166] 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>.
- [167] 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>.
- [168] 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>.
- [169] 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>.
- [170] F. Dumur, Recent Advances on Quinoxaline-Based Photoinitiators of Polymerization, *Catalysts.* 13 (2023). <https://doi.org/10.3390/catal13040718>.
- [171] 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>.
- [172] 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>.

- [173] 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>.
- [174] 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>.
- [175] 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>.
- [176] 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>.
- [177] 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>.
- [178] M. Rajeshirke, M.C. Sreenath, S. Chitrabalam, I.H. Joe, N. Sekar, Enhancement of NLO Properties in OBO Fluorophores Derived from Carbazole–Coumarin Chalcones Containing Carboxylic Acid at the N-Alykl Terminal End, *J. Phys. Chem. C*. 122 (2018) 14313–14325. <https://doi.org/10.1021/acs.jpcc.8b02937>.
- [179] 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>.
- [180] M. Rahal, B. Graff, J. Toufaily, T. Hamieh, G. Noirbent, D. Gigmes, 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>.
- [181] F. Hammoud, N. Giacoletto, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gigmes, 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>.
- [182] 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>.
- [183] 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>.
- [184] 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>.
- [185] 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>.
- [186] 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>.
- [187] 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>.
- [188] 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>.
- [189] 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>.
- [190] 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>.
- [191] 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>.
- [192] 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>.
- [193] 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>.
- [194] 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>.
- [195] 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>.
- [196] 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>.
- [197] 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>.
- [198] 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>.
- [199] 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>.

- [200] 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.* 223 (2022) 2100450. <https://doi.org/10.1002/macp.202100450>.
- [201] 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.* 47 (2023) 5330–5337. <https://doi.org/10.1039/D2NJ05996G>.
- [202] 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>.
- [203] 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>.
- [204] Y. Xu, G. Noirbent, D. Brunel, Z. Ding, D. Gigmes, 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>.
- [205] 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>.
- [206] H. Chen, G. Noirbent, S. Liu, D. Brunel, B. Graff, D. Gigmes, 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>.
- [207] 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>.
- [208] 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>.
- [209] M. Ibrahim-Ouali, F. Dumur, Recent Advances on Chalcone-based Photoinitiators of Polymerization, *Eur. Polym. J.* 158 (2021) 110688. <https://doi.org/10.1016/j.eurpolymj.2021.110688>.
- [210] H. Chen, G. Noirbent, S. Liu, Y. Zhang, K. Sun, F. Morlet-Savary, D. Gigmes, 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>.
- [211] 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) 1395. <https://doi.org/10.3390/polym13183195>.
- [212] M.-A. Tehfe, F. Dumur, P. Xiao, M. Delgove, B. Graff, J.-P. Fouassier, D. Gigmes, 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>.
- [213] 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>.
- [214] 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.* 166 (2022) 111042. <https://doi.org/10.1016/j.eurpolymj.2022.111042>.
- [215] 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>.
- [216] 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>.
- [217] 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>.
- [218] 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>.
- [219] 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>.
- [220] 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>.
- [221] F. Dumur, Recent Advances on Glyoxylates and Related Structures as Photoinitiators of Polymerization, *Macromol.* 3 (2023) 149–174. <https://doi.org/10.3390/macromol3020010>.
- [222] G. Noirbent, Y. Xu, A.-H. Bonardi, S. Duval, D. Gigmes, J. Lalevée, F. Dumur, New Donor-Acceptor Stenhouse Adducts as Visible and Near Infrared Light Polymerization Photoinitiators, *Molecules.* 25 (2020). <https://doi.org/10.3390/molecules25102317>.
- [223] P. Xiao, W. Hong, Y. Li, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmes, 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>.
- [224] P. Xiao, W. Hong, Y. Li, F. Dumur, B. Graff, J.P. Fouassier, D. Gigmes, 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>.
- [225] A. Al Mousawi, P. Garra, X. Sallenave, F. Dumur, J. Toufaily, T. Hamieh, B. Graff, D. Gigmes, 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>.
- [226] 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>.
- [227] 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>.
- [228] 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>.
- [229] 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>.
- [230] F. Dumur, Recent advances on naphthoquinone-based photoinitiators of polymerization, *Eur. Polym. J.* 193 (2023) 112120. <https://doi.org/10.1016/j.eurpolymj.2023.112120>.
- [231] F. Dumur, Recent advances on Anthraquinone-based photoinitiators of polymerization, *Eur. Polym. J.* 191 (2023) 112039. <https://doi.org/10.1016/j.eurpolymj.2023.112039>.
- [232] 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>.
- [233] 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>.
- [234] 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>.
- [235] 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>.
- [236] 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>.
- [237] 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>.

- [238] 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>.
- [239] 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>.
- [240] 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>.
- [241] 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>.
- [242] M.-A. Tehfe, D. Gigmes, F. Dumur, D. Bertin, F. Morlet-Savary, B. Graff, J. Lalevée, J.-P. Fouassier, Cationic photosensitive formulations based on silyl radical chemistry for green and red diode laser exposure, *Polym. Chem.* 3 (2012) 1899–1902. <https://doi.org/10.1039/C1PY00460C>.
- [243] 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>.
- [244] 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>.
- [245] 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>.
- [246] 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>.
- [247] 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>.
- [248] 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>.
- [249] 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>.

- [250] 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>.
- [251] 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>.
- [252] 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>.
- [253] 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>.
- [254] 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>.
- [255] 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>.
- [256] 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>.
- [257] 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>.
- [258] 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>.
- [259] 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>.
- [260] 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>.
- [261] 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>.
- [262] M. Bouzrati-Zerelli, N. Guillaume, F. Goubard, T.-T. Bui, S. Villotte, C. Dietlin, F. Morlet-Savary, D. Gigmes, J.P. Fouassier, F. Dumur, J. Lalevée, A novel class of photoinitiators with a thermally activated delayed fluorescence (TADF) property, *New J. Chem.* 42 (2018) 8261–8270. <https://doi.org/10.1039/C7NJ04394E>.
- [263] 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>.
- [264] J.P. Fouassier, F. Morlet-Savary, K. Yamashita, S. Imahashi, The role of the dye/iron arene complex/amine system as a photoinitiator for photopolymerization reactions, *Polymer*. 38 (1997) 1415–1421. [https://doi.org/10.1016/S0032-3861\(96\)00659-3](https://doi.org/10.1016/S0032-3861(96)00659-3).
- [265] F. Dumur, Recent Advances on Photoinitiating Systems Designed for Solar Photocrosslinking Polymerization Reactions, *Eur. Polym. J.* 189 (2023) 111988. <https://doi.org/10.1016/j.eurpolymj.2023.111988>.
- [266] F. Bella, R. Bongiovanni, Photoinduced polymerization: An innovative, powerful and environmentally friendly technique for the preparation of polymer electrolytes for dye-sensitized solar cells, *J. Photochem. Photobiol. C Photochem. Rev.* 16 (2013) 1–21. <https://doi.org/10.1016/j.jphotochemrev.2013.03.002>.
- [267] J. Lalevée, J.P. Fouassier, Recent advances in sunlight induced polymerization: role of new photoinitiating systems based on the silyl radical chemistry, *Polym. Chem.* 2 (2011) 1107–1113. <https://doi.org/10.1039/C1PY00073J>.
- [268] 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>.
- [269] W. Tomal, J. Ortyl, Water-Soluble Photoinitiators in Biomedical Applications, *Polymers*. 12 (2020) 1073. <https://doi.org/10.3390/polym12051073>.
- [270] T.N. Eren, T. Gencoglu, M. Abdallah, J. Lalevée, D. Avci, A water soluble and highly reactive bisphosphonate functionalized thioxanthone-based photoinitiator, *Eur. Polym. J.* 135 (2020) 109906. <https://doi.org/10.1016/j.eurpolymj.2020.109906>.
- [271] T.N. Eren, J. Lalevée, D. Avci, Bisphosphonic Acid-Functionalized Water-Soluble Photoinitiators, *Macromol. Chem. Phys.* 220 (2019) 1900268. <https://doi.org/10.1002/macp.201900268>.
- [272] 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>.
- [273] M.A. Lago, A.R.-B. de Quirós, R. Sendón, J. Bustos, M.T. Nieto, P. Paseiro, Photoinitiators: a food safety review, *Food Addit. Contam. Part A*. 32 (2015) 779–798. <https://doi.org/10.1080/19440049.2015.1014866>.
- [274] F. Hammoud, A. Hijazi, M. Schmitt, F. Dumur, J. Lalevée, A review on recently proposed oxime ester photoinitiators, *Eur. Polym. J.* 188 (2023) 111901. <https://doi.org/10.1016/j.eurpolymj.2023.111901>.
- [275] 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>.
- [276] P. Xiao, J. Zhang, F. Dumur, M.A. Tehfe, F. Morlet-Savary, B. Graff, D. Gigmes, J.P. Fouassier, J. Lalevée, Visible light sensitive photoinitiating systems: Recent progress in cationic and radical photopolymerization reactions under soft conditions, *Prog. Polym. Sci.* 41 (2015) 32–66. <https://doi.org/10.1016/j.progpolymsci.2014.09.001>.

- [277] A. Allushi, C. Kutahya, C. Aydogan, J. Kreutzer, G. Yilmaz, Y. Yagci, Conventional Type II photoinitiators as activators for photoinduced metal-free atom transfer radical polymerization, *Polym. Chem.* 8 (2017) 1972–1977. <https://doi.org/10.1039/C7PY00114B>.
- [278] Y.-C. Chen, Y.-T. Kuo, Photocuring Kinetic Studies of TMPTMA Monomer by Type II Photoinitiators of Different Weight Ratios of 2-Chlorohexaaryl Biimidazole (o-Cl-HABI) and N-Phenylglycine (NPG), *J. Photopolym. Sci. Technol.* 31 (2018) 487–492. <https://doi.org/10.2494/photopolymer.31.487>.
- [279] J. Kirschner, A. Baralle, B. Graff, J.-M. Becht, J.E. Klee, J. Lalevée, 1-Aryl-2-(triisopropylsilyl)ethane-1,2-diones: Toward a New Class of Visible Type I Photoinitiators for Free Radical Polymerization of Methacrylates, *Macromol. Rapid Commun.* 40 (2019) 1900319. <https://doi.org/10.1002/marc.201900319>.
- [280] J. Christmann, X. Allonas, C. Ley, A. Ibrahim, C. Croutxé-Barghorn, Triazine-Based Type-II Photoinitiating System for Free Radical Photopolymerization: Mechanism, Efficiency, and Modeling, *Macromol. Chem. Phys.* 218 (2017) 1600597. <https://doi.org/10.1002/macp.201600597>.
- [281] J. Kreutzer, K. Kaya, Y. Yagci, Poly(propylene oxide)-thioxanthone as one-component Type II polymeric photoinitiator for free radical polymerization with low migration behavior, *Eur. Polym. J.* 95 (2017) 71–81. <https://doi.org/10.1016/j.eurpolymj.2017.07.030>.
- [282] T. Urano, E. Ohno-Okumura, K. Sakamoto, S. Suzuki, T. Yamaoka, Effect of Ethyl group in Sensitization Mechanisms of Pyrromethene Dyes in Photopolymer Coating Layer, *J. Photopolym. Sci. Technol.* 13 (2000) 673–677. <https://doi.org/10.2494/photopolymer.13.673>.
- [283] P. Kaur, K. Singh, Recent advances in the application of BODIPY in bioimaging and chemosensing, *J. Mater. Chem. C.* 7 (2019) 11361–11405. <https://doi.org/10.1039/C9TC03719E>.
- [284] S. Cetindere, BODIPY Dyes for Biomedical Applications: Recent Advances, *Am. J. Biomed. Sci. Res.* 7 (2020) 93.
- [285] H. Klifout, A. Stewart, M. Elkhalfi, H. He, BODIPYs for Dye-Sensitized Solar Cells, *ACS Appl. Mater. Interfaces.* 9 (2017) 39873–39889. <https://doi.org/10.1021/acsami.7b07688>.
- [286] D. Madrid-Úsuga, A. Ortiz, J.H. Reina, Photophysical Properties of BODIPY Derivatives for the Implementation of Organic Solar Cells: A Computational Approach, *ACS Omega.* 7 (2022) 3963–3977. <https://doi.org/10.1021/acsomega.1c04598>.
- [287] B. Xie, L. Yin, J. Fan, C. Liu, Y. Li, Novel A- π -D- π -A-type BODIPY dyads as small-molecule donors for solution-processed organic solar cells, *J. Mater. Chem. C.* 10 (2022) 3248–3258. <https://doi.org/10.1039/D1TC04981J>.
- [288] G. Ulrich, A. Barsella, A. Boeglin, S. Niu, R. Ziessel, BODIPY-Bridged Push–Pull Chromophores for Nonlinear Optical Applications, *ChemPhysChem.* 15 (2014) 2693–2700. <https://doi.org/10.1002/cphc.201402123>.
- [289] N.P. Purayil, A.K. Satheesan, S. Edappadikkunnummal, C. Keloth, Coupling of the Tamm Plasmon to the BODIPY Fluorophore in Photonic Crystals for Nonlinear Optical Applications, *J. Phys. Chem. C.* 127 (2023) 1244–1250. <https://doi.org/10.1021/acs.jpcc.2c07579>.
- [290] M. Chapran, E. Angioni, N.J. Findlay, B. Breig, V. Cherpak, P. Stakhira, T. Tuttle, D. Volyniuk, J.V. Grazulevicius, Y.A. Nastishin, O.D. Lavrentovich, P.J. Skabara, An Ambipolar BODIPY Derivative for a White Exciplex OLED and Cholesteric Liquid

- Crystal Laser toward Multifunctional Devices, *ACS Appl. Mater. Interfaces*. 9 (2017) 4750–4757. <https://doi.org/10.1021/acsami.6b13689>.
- [291] D. Ma, G. Zhao, H. Chen, R. Zhou, G. Zhang, W. Tian, W. Jiang, Y. Sun, Creation of BODIPYs-based red OLEDs with high color purity via modulating the energy gap and restricting rotation of substituents, *Dyes Pigments*. 203 (2022) 110377. <https://doi.org/10.1016/j.dyepig.2022.110377>.
- [292] T. Nakamura, H. Sasabe, S. Abe, K. Kumada, R. Sugiyama, T. Hanayama, J. Kido, Highly efficient and stable green fluorescent OLEDs with high color purity using a BODIPY derivative, *Mol. Syst. Des. Eng.* (2023). <https://doi.org/10.1039/D3ME00029J>.
- [293] C.-L. Liu, Y. Chen, D.P. Shelar, C. Li, G. Cheng, W.-F. Fu, Bodipy dyes bearing oligo(ethylene glycol) groups on the meso-phenyl ring: tuneable solid-state photoluminescence and highly efficient OLEDs, *J. Mater. Chem. C*. 2 (2014) 5471–5478. <https://doi.org/10.1039/C4TC00720D>.
- [294] S. Kaga, S. Yapar, E.M. Gecici, R. Sanyal, Photopatternable “Clickable” Hydrogels: “Orthogonal” Control over Fabrication and Functionalization, *Macromolecules*. 48 (2015) 5106–5115. <https://doi.org/10.1021/acs.macromol.5b01536>.
- [295] G. Raffy, R. Bofinger, A. Tron, A.D. Guerzo, N.D. McClenaghan, J.-M. Vincent, 2D and 3D surface photopatterning via laser-promoted homopolymerization of a perfluorophenyl azide-substituted BODIPY, *Nanoscale*. 9 (2017) 16908–16914. <https://doi.org/10.1039/C7NR06848D>.
- [296] X. Wu, M. Belqat, B. Leuschel, G. Noirbent, F. Dumur, K. Mouglin, A. Spangenberg, Investigation of two-photon polymerized microstructures using fluorescence lifetime measurements, *Polym. Chem.* 13 (2022) 2902–2906. <https://doi.org/10.1039/D1PY01728D>.
- [297] T. Urano, E. Ohno-Okumura, K. Sakamoto, S. Suzuki, T. Yamaoka, N. Hara, K. Fukui, T. Karatsu, A. Kitamura, Substituent Effect in Sensitization Mechanisms of Pyrromethene Dyes in Solution, *J. Photopolym. Sci. Technol.* 13 (2000) 691–696. <https://doi.org/10.2494/photopolymer.13.691>.
- [298] O. García, A. Costela, I. García-Moreno, R. Sastre, Pyrromethene 567 Dye as Visible Light Photoinitiator for Free Radical Polymerization, *Macromol. Chem. Phys.* 204 (2003) 2233–2239. <https://doi.org/10.1002/macp.200300010>.
- [299] S. Noppakundiligrat, S. Suzuki, T. Urano, N. Miyagawa, S. Takahara, T. Yamaoka, Vis-sensitive photopolymer containing vinyl ether compound and pyrromethene dye, *Polym. Adv. Technol.* 13 (2002) 527–533. <https://doi.org/10.1002/pat.221>.
- [300] S. Blaya, P. Acebal, L. Carretero, A. Fimia, Pyrromethene-HEMA-based photopolymerizable holographic recording material, *Opt. Commun.* 228 (2003) 55–61. <https://doi.org/10.1016/j.optcom.2003.09.068>.
- [301] S. Suzuki, X. Allonas, J.-P. Fouassier, T. Urano, S. Takahara, T. Yamaoka, Interaction mechanism in pyrromethene dye/photoacid generator photosensitive system for high-speed photopolymer, *J. Photochem. Photobiol. Chem.* 181 (2006) 60–66. <https://doi.org/10.1016/j.jphotochem.2005.10.035>.
- [302] T. Mikulchik, S. Karuthedath, C.S.P. De Castro, A.A. Buglak, A. Sheehan, A. Wieder, F. Laquai, I. Naydenova, M.A. Filatov, Charge transfer mediated triplet excited state formation in donor–acceptor–donor BODIPY: Application for recording of holographic structures in photopolymerizable glass, *J. Mater. Chem. C*. 10 (2022) 11588–11597. <https://doi.org/10.1039/D2TC02263J>.

- [303] M.A. Filatov, Heavy-atom-free BODIPY photosensitizers with intersystem crossing mediated by intramolecular photoinduced electron transfer, *Org. Biomol. Chem.* 18 (2020) 10–27. <https://doi.org/10.1039/C9OB02170A>.
- [304] E. Bassan, A. Gualandi, P.G. Cozzi, P. Ceroni, Design of BODIPY dyes as triplet photosensitizers: electronic properties tailored for solar energy conversion, photoredox catalysis and photodynamic therapy, *Chem. Sci.* 12 (2021) 6607–6628. <https://doi.org/10.1039/D1SC00732G>.
- [305] J. Li, Y. Qian, L. Xie, Y. Yi, W. Li, W. Huang, From Dark TICT State to Emissive quasi-TICT State: The AIE Mechanism of N-(3-(benzo[d]oxazol-2-yl)phenyl)-4-tert-butylbenzamide, *J. Phys. Chem. C.* 119 (2015) 2133–2141. <https://doi.org/10.1021/jp5089433>.
- [306] Y. Qian, M. Cai, X. Zhou, Z. Gao, X. Wang, Y. Zhao, X. Yan, W. Wei, L. Xie, W. Huang, More than Restriction of Twisted Intramolecular Charge Transfer: Three-Dimensional Expanded #-Shaped Cross-Molecular Packing for Emission Enhancement in Aggregates, *J. Phys. Chem. C.* 116 (2012) 12187–12195. <https://doi.org/10.1021/jp212257f>.
- [307] O.I. Tarzi, X. Allonas, C. Ley, J.-P. Fouassier, Pyrromethene derivatives in three-component photoinitiating systems for free radical photopolymerization, *J. Polym. Sci. Part Polym. Chem.* 48 (2010) 2594–2603. <https://doi.org/10.1002/pola.24039>.
- [308] M. Bouzrati-Zerelli, M. Maier, C.P. Fik, C. Dietlin, F. Morlet-Savary, J.P. Fouassier, J.E. Klee, J. Lalevée, A low migration phosphine to overcome the oxygen inhibition in new high performance photoinitiating systems for photocurable dental type resins, *Polym. Int.* 66 (2017) 504–511. <https://doi.org/10.1002/pi.5262>.
- [309] 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>.
- [310] L. Gou, B. Opheim, C.N. Coretsopoulos, A.B. Scranton, Consumption of the molecular oxygen in polymerization systems using photosensitized oxidation of dimethylantracene, *Chem. Eng. Commun.* 193 (2006) 620–627. <https://doi.org/10.1080/00986440500193921>.
- [311] M. Höfer, N. Moszner, R. Liska, Oxygen scavengers and sensitizers for reduced oxygen inhibition in radical photopolymerization, *J. Polym. Sci. Part Polym. Chem.* 46 (2008) 6916–6927. <https://doi.org/10.1002/pola.23001>.
- [312] T. Li, Y. Chen, R. Liu, Z. Lu, T. Wang, X. Huang, Q. Zhang, A Visible-Light Curing system of Diphenyliodonium Salt/BODIPY dyes/Bisphenol-A Epoxy Resin Under Halogen Lamp, *IOP Conf. Ser. Earth Environ. Sci.* 300 (2019) 052016. <https://doi.org/10.1088/1755-1315/300/5/052016>.
- [313] M. Topa-Skwarczyńska, A. Świeży, D. Krok, K. Starzak, P. Niezgodna, B. Oksiuta, W. Wałczyk, J. Ortyl, Novel Formulations Containing Fluorescent Sensors to Improve the Resolution of 3D Prints, *Int. J. Mol. Sci.* 23 (2022). <https://doi.org/10.3390/ijms231810470>.
- [314] J. Kirschner, J.-M. Becht, J.E. Klee, J. Lalevée, A New Phosphine for Efficient Free Radical Polymerization under Air, *Macromol. Rapid Commun.* 41 (2020) 2000053. <https://doi.org/10.1002/marc.202000053>.
- [315] A. Stafford, D. Ahn, E.K. Raulerson, K.-Y. Chung, K. Sun, D.M. Cadena, E.M. Forrister, S.R. Yost, S.T. Roberts, Z.A. Page, Catalyst Halogenation Enables Rapid and Efficient Polymerizations with Visible to Far-Red Light, *J. Am. Chem. Soc.* 142 (2020) 14733–14742. <https://doi.org/10.1021/jacs.0c07136>.

- [316] J.C. Koziar, D.O. Cowan, Photochemical heavy-atom effects, *Acc. Chem. Res.* 11 (1978) 334–341. <https://doi.org/10.1021/ar50129a003>.
- [317] A.Y. Polykarpov, D.C. Neckers, Tetramethylammonium phenyltrialkylborates in the photoinduced electron transfer reaction with benzophenone. Generation of alkyl radicals and their addition to activated alkenes, *Tetrahedron Lett.* 36 (1995) 5483–5486. [https://doi.org/10.1016/0040-4039\(95\)01055-M](https://doi.org/10.1016/0040-4039(95)01055-M).
- [318] M. Jin, R. Zhou, M. Yu, H. Pan, D. Wan, D- π -a-type oxime sulfonate photoacid generators for cationic polymerization under UV–visible LED irradiation, *J. Polym. Sci. Part Polym. Chem.* 56 (2018) 1146–1154. <https://doi.org/10.1002/pola.28996>.
- [319] X. Sun, M. Jin, X. Wu, H. Pan, D. Wan, H. Pu, Bis-substituted thiophene-containing oxime sulfonates photoacid generators for cationic polymerization under UV–visible LED irradiation, *J. Polym. Sci. Part Polym. Chem.* 56 (2018) 776–782. <https://doi.org/10.1002/pola.28951>.
- [320] AllonasXavier, LalevéeJacques, FouassierJean-Pierre, TachiHideki, ShiraiMasamitsu, TsunookaMasahiro, Triplet State of O-Acyloximes Studied by Time-Resolved Absorption Spectroscopy, *Chem. Lett.* 29 (2004) 1090–1091. <https://doi.org/10.1246/cl.2000.1090>.
- [321] S. Chen, M. Jin, J.-P. Malval, J. Fu, F. Morlet-Savary, H. Pan, D. Wan, Substituted stilbene-based oxime esters used as highly reactive wavelength-dependent photoinitiators for LED photopolymerization, *Polym. Chem.* 10 (2019) 6609–6621. <https://doi.org/10.1039/C9PY01330J>.
- [322] G.A. Delzenne, U. Laridon, H. Peeters, Photopolymerization initiated by O-acyloximes, *Eur. Polym. J.* 6 (1970) 933–943. [https://doi.org/10.1016/0014-3057\(70\)90028-5](https://doi.org/10.1016/0014-3057(70)90028-5).
- [323] H. Kura, J. Tanabe, H. Oka, K. Kunimoto, A. Matsumoto, M. Ohwa, New oxime ester photoinitiators for color filter resists, *Radtech Rep.* 18 (2004) 30–35.
- [324] M. Bouzrati-Zerelli, J. Kirschner, C.P. Fik, M. Maier, C. Dietlin, F. Morlet-Savary, J.P. Fouassier, J.-M. Becht, J.E. Klee, J. Lalevée, Silyl Glyoxylates as a New Class of High Performance Photoinitiators: Blue LED Induced Polymerization of Methacrylates in Thin and Thick Films, *Macromolecules.* 50 (2017) 6911–6923. <https://doi.org/10.1021/acs.macromol.7b01370>.
- [325] S. Hu, X. Wu, D.C. Neckers, Methyl Phenylglyoxylate as a Photoinitiator, *Macromolecules.* 33 (2000) 4030–4033. <https://doi.org/10.1021/ma992100z>.
- [326] 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>.
- [327] J. Kirschner, M. Bouzrati-Zerelli, J.P. Fouassier, J.-M. Becht, J.E. Klee, J. Lalevée, Silyl glyoxylates as high-performance photoinitiators for cationic and hybrid polymerizations: Towards better polymer mechanical properties, *J. Polym. Sci. Part Polym. Chem.* 57 (2019) 1420–1429. <https://doi.org/10.1002/pola.29404>.
- [328] F. Dumur, Recent Advances on Diaryliodonium-Based Monocomponent Photoinitiating Systems, *Eur. Polym. J.* (2023) 112193. <https://doi.org/10.1016/j.eurpolymj.2023.112193>.
- [329] H. Gu, K. Ren, O. Grinevich, J.H. Malpert, D.C. Neckers, Characterization of Iodonium Salts Differing in the Anion, *J. Org. Chem.* 66 (2001) 4161–4164. <https://doi.org/10.1021/jo0015725>.
- [330] J. Iwaki, S. Suzuki, C. Park, N. Miyagawa, S. Takahara, T. Yamaoka, Sensitization Mechanism of the Anthracene Derivatives/Photoacid Generator Photoinitiating System,

- J. Photopolym. Sci. Technol. 17 (2004) 123–124.
<https://doi.org/10.2494/photopolymer.17.123>.
- [331] M. Jin, H. Xu, H. Hong, J.-P. Malval, Y. Zhang, A. Ren, D. Wan, H. Pu, Design of D- π -A type photoacid generators for high efficiency excitation at 405 nm and 800 nm, Chem. Commun. 49 (2013) 8480–8482. <https://doi.org/10.1039/C3CC43018A>.
- [332] M. Jin, H. Hong, J. Xie, J.-P. Malval, A. Spangenberg, O. Soppera, D. Wan, H. Pu, D.-L. Versace, T. Leclerc, P. Baldeck, O. Poizat, S. Knopf, π -conjugated sulfonium-based photoacid generators: an integrated molecular approach for efficient one and two-photon polymerization, Polym. Chem. 5 (2014) 4747–4755. <https://doi.org/10.1039/C4PY00424H>.
- [333] N. Klikovits, P. Knaack, D. Bomze, I. Krossing, R. Liska, Novel photoacid generators for cationic photopolymerization, Polym. Chem. 8 (2017) 4414–4421. <https://doi.org/10.1039/C7PY00855D>.
- [334] H. Kura, K. Fujihara, A. Kimura, T. Ohno, M. Matsumura, Y. Hirata, T. Okada, Initial step of anthracene-sensitized photoacid generation from diphenyliodonium hexafluorophosphate in an epoxy matrix studied by steady-state and laser-flash photolyses, J. Polym. Sci. Part B Polym. Phys. 39 (2001) 2937–2946. <https://doi.org/10.1002/polb.10051>.
- [335] N.A. Kuznetsova, G.V. Malkov, B.G. Gribov, Photoacid generators. Application and current state of development, Russ. Chem. Rev. 89 (2020) 173. <https://doi.org/10.1070/RCR4899>.
- [336] M.J. Plater, W.T. Harrison, R. Killah, Potential photoacid generators based on oxime sulfonates, J. Chem. Res. 43 (2019) 26–33. <https://doi.org/10.1177/1747519819831829>.
- [337] W. Zhou, S.M. Kuebler, K.L. Braun, T. Yu, J.K. Cammack, C.K. Ober, J.W. Perry, S.R. Marder, An Efficient Two-Photon-Generated Photoacid Applied to Positive-Tone 3D Microfabrication, Science. 296 (2002) 1106–1109. <https://doi.org/10.1126/science.296.5570.1106>.
- [338] K. Sambath, Z. Wan, Q. Wang, H. Chen, Y. Zhang, BODIPY-Based Photoacid Generators for Light-Induced Cationic Polymerization, Org. Lett. 22 (2020) 1208–1212. <https://doi.org/10.1021/acs.orglett.0c00118>.
- [339] J. Massue, D. Jacquemin, G. Ulrich, Boranils: Versatile Multifunctional Organic Fluorophores for Innovative Applications, Organics. 2 (2021) 365–375. <https://doi.org/10.3390/org2040020>.
- [340] A. Balcerak, J. Kabatc-Borcz, Z. Czech, M. Bartkowiak, Latest Advances in Highly Efficient Dye-Based Photoinitiating Systems for Radical Polymerization, Polymers. 15 (2023). <https://doi.org/10.3390/polym15051148>.
- [341] M.S.T. Gonçalves, Fluorescent Labeling of Biomolecules with Organic Probes, Chem. Rev. 109 (2009) 190–212. <https://doi.org/10.1021/cr0783840>.
- [342] N. Boens, V. Leen, W. Dehaen, Fluorescent indicators based on BODIPY, Chem. Soc. Rev. 41 (2012) 1130–1172. <https://doi.org/10.1039/C1CS15132K>.
- [343] G. Duret, R. Quinlan, P. Bissere, N. Blanchard, Boron chemistry in a new light, Chem. Sci. 6 (2015) 5366–5382. <https://doi.org/10.1039/C5SC02207J>.
- [344] A. Skotnicka, P. Czeleń, Substituted 2-Phenacylbenzoxazole Difluoroboranes: Synthesis, Structure and Properties, Molecules. 25 (2020). <https://doi.org/10.3390/molecules25225420>.
- [345] G. Wang, N.S. Hill, D. Zhu, P. Xiao, M.L. Coote, M.H. Stenzel, Efficient Photoinitiating System Based on Diaminoanthraquinone for 3D Printing of

- Polymer/Carbon Nanotube Nanocomposites under Visible Light, *ACS Appl. Polym. Mater.* 1 (2019) 1129–1135. <https://doi.org/10.1021/acsapm.9b00140>.
- [346] A. Balcerak, J. Kabatc, Recent progress in the development of highly active dyeing photoinitiators based on 1,3-bis(p-substituted phenylamino)squaraines for radical polymerization of acrylates, *Polym. Chem.* 13 (2022) 1787–1812. <https://doi.org/10.1039/D1PY01519B>.
- [347] Y. Wang, P. Spencer, X. Yao, Q. Ye, Effect of coinitiator and water on the photoreactivity and photopolymerization of HEMA/camphoquinone-based reactant mixtures, *J. Biomed. Mater. Res. A.* 78A (2006) 721–728. <https://doi.org/10.1002/jbm.a.30733>.
- [348] J. Kabatc, K. Kostrzewska, M. Kozak, A. Balcerak, Visible light photoinitiating systems based on squaraine dye: kinetic, mechanistic and laser flash photolysis studies, *RSC Adv.* 6 (2016) 103851–103863. <https://doi.org/10.1039/C6RA23060A>.
- [349] A. Balcerak, K. Iwińska, J. Kabatc, Novel 1,3-bis(p-substituted phenylamino)squaraine dyes. The synthesis and spectroscopic studies, *Dyes Pigments.* 170 (2019) 107596. <https://doi.org/10.1016/j.dyepig.2019.107596>.
- [350] J. Kabatc, K. Kostrzewska, K. Jurek, M. Kozak, A. Balcerak, Ł. Orzeł, New Squaraine-based two-component initiation systems for UV-blue light induced radical polymerization: Kinetic and time-resolved laser spectroscopy studies, *J. Polym. Sci. Part Polym. Chem.* 55 (2017) 471–484. <https://doi.org/10.1002/pola.28425>.
- [351] 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>.
- [352] S. Benedikt, J. Wang, M. Markovic, N. Moszner, K. Dietliker, A. Ovsianikov, H. Grützmacher, R. Liska, Highly efficient water-soluble visible light photoinitiators, *J. Polym. Sci. Part Polym. Chem.* 54 (2016) 473–479. <https://doi.org/10.1002/pola.27903>.