



HAL
open science

High Photoinitiating Efficiency of Benzothioxanthene-based Oxime Esters in Photopolymerization via Photocleavage and/or Single Electron Transfer under Visible Light and Sunlight

Yijun Zhang, Bin Song, Zheng Liu, Adel Noon, Céline Dietlin, Fabrice Morlet-Savary, Michael Schmitt, Didier Gigmes, Frédéric Dumur, Jacques Lalevée

► **To cite this version:**

Yijun Zhang, Bin Song, Zheng Liu, Adel Noon, Céline Dietlin, et al.. High Photoinitiating Efficiency of Benzothioxanthene-based Oxime Esters in Photopolymerization via Photocleavage and/or Single Electron Transfer under Visible Light and Sunlight. *Angewandte Chemie International Edition*, 2024, 63 (35), pp.e202405337. 10.1002/anie.202405337 . hal-04681586

HAL Id: hal-04681586

<https://hal.science/hal-04681586v1>

Submitted on 29 Aug 2024

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.

High Photoinitiating Efficiency of Benzothioxanthene-based Oxime Esters in Photopolymerization via Photocleavage and/or Single Electron Transfer under Visible Light and Sunlight

Yijun Zhang,^[a,b] Bin Song,^[a,b] Zheng Liu,^[c] Adel Noon,^[a,b] Céline Dietlin,^[a,b] Fabrice Morlet-Savary,^[a,b] Michael Schmitt,^[a,b] Didier Gigmes,^[c] Frédéric Dumur,^{*,[c]} Jacques Lalevée^{*,[a,b]}

[a] Dr. Yijun Zhang, Bin Song, Adel Noon, Céline Dietlin, Dr. Fabrice Morlet-Savary, Dr. Michael Schmitt, Prof. Dr. Jacques Lalevée
Institut de Science des Matériaux de Mulhouse (IS2M-CNRS UMR 7361)

Université de Haute-Alsace

68100 Mulhouse, France

E-mail: Jacques.lalevee@uha.fr

[b] Dr. Yijun Zhang, Bin Song, Adel Noon, Céline Dietlin, Dr. Fabrice Morlet-Savary, Dr. Michael Schmitt, Prof. Dr. Jacques Lalevée

Université de Strasbourg

E-mail: Jacques.lalevee@uha.fr

[c] Zheng Liu, Prof. Dr. Didier Gigmes, Prof. Dr. Frédéric Dumur

Institut de Chimie Radicalaire (ICR-CNRS, UMR 7273)

Aix-Marseille Université

13397 Marseille, France

E-mail: frederic.dumur@univ-amu.fr

[*] Corresponding Authors

Prof. Dr. Jacques Lalevée ; Prof. Dr. Frédéric Dumur

Abstract: In this work, six benzothioxanthene-based oxime esters were employed as photoinitiators for photopolymerization with visible light (LED) and sunlight. Their abilities to behave as Type I photoinitiators by means of a photocleavage mechanism of oxime esters but also in multicomponent photoinitiating system with an iodonium salt (through an electron transfer mechanism) were both explored with the different structures. Due to their broad absorption spectra tailing up to 600 nm, photoinitiating properties of the benzothioxanthene-based oxime esters were systematically tested under excitation with low-intensity LED light at wavelengths of 405 nm and 450 nm. Additionally, to the polymerization tests done under artificial light, different benzothioxanthene-based oxime esters were also investigated as solar photoinitiators and displayed a high reactivity in France (Western Europe) even in winter conditions. For the best candidates i.e. the most reactive structures, direct laser write experiments were carried out, evidencing the interest of these structures.

Introduction

In recent years, photopolymerization has received more and more interests from academics and industrials for the production of various polymeric materials.^[1, 2] According to the free radical photopolymerization (FRP) mechanism, free radical photoinitiators can be classified as Type I (photocleavage) and as Type II (hydrogen abstraction) initiators.^[3-8] Benefiting from the ongoing efforts for developing visible light photoinitiating systems, numerous photoinitiating systems of innovative compositions have been developed in recent years, consisting of a

photoinitiator absorbing light and optionally additives enabling to generate the initiating species. In these systems, a single electron transfer (SET) event can be observed between photoinitiators and additives (electron donor vs. electron acceptor), and active species can be generated during this process to initiate photopolymerization.^[9-11] In this field, the most popular approach consists in using an electron-rich photosensitizer that will promote in the excited state a photoinduced electron transfer towards an electron-deficient onium salt (most of the time an iodonium salt), that will be reduced, generating an unstable structure that will immediately decompose and generate the desired initiating radicals.^[12, 13]

Oxime esters (OXEs), as Type I photoinitiators, have been extensively studied due to their easiness of synthesis starting from cheap and commercially available reagents, their remarkable thermal stabilities and finally the facile tunability of the absorption maxima of OXEs by a careful selection of the chromophores.^[14-17] Concerning the working principle of oxime esters, upon excitation with light, a homolytic cleavage of the N-O bond can occur, enabling to generate iminyl and acyloxy/aryloxy radicals. Subsequent to the bond cleavage, a decarboxylation reaction can occur on the acyloxy/aryloxy radicals, generating alkyl/aryl radicals.^[18-20] This decarboxylation step is important for the reactivity of oxime esters since no radical recombination can occur subsequent to the decarboxylation reaction, improving the reactivity of oxime esters. Besides, all oxime esters do not exhibit the same reactivity upon photoexcitation. Among the main factors impacting the reactivity of oxime esters, the molar absorption coefficient that can negatively impact the photoinitiating efficiency if too high. In this

case, an inner filter effect can take place, which refers to the restriction of light propagation within the polymerization system caused by the light absorption of photoinitiator during photopolymerization, thus affecting the efficient utilization and transmission of light energy.^[21, 22] When the molar absorption coefficient of photoinitiator is high, the photoinitiator has a strong ability to absorb light, which result in the predominate absorption of light energy by the photoinitiator rather than an efficient utilization for photopolymerization. This behavior leads to the efficient utilization of light energy only on the surface layer of photopolymerization system, preventing sufficient penetration into the deeper layers, thus limiting the depth and efficiency of photopolymerization.^[23] Parallel to this, the excited state involved in the N-O cleavage is also important (bond breaking from the singlet or the triplet excited state upon light excitation ($\Delta H_{\text{Cleavage } S_1}$ or $\Delta H_{\text{Cleavage } T_1} > 0$).^[24-26] And finally, the reactivity of the radicals formed by homolytic cleavage of the N-O bond and the ability of acyloxy/aryloxy radicals to decarboxylate in order to generate more reactive radicals.^[27] In light of these considerations (molar extinction coefficient, energy level of the excited state, ability of the aryloxy/acyloxy radical to decarboxylate or not), further studies need to be conducted in order to find the best compromise between these three main parameters.

N-(alkyl)benzothioxanthene-3,4-dicarboximide also named benzothioxanthene (BTXI) is a sulfur-containing rylene-imide dye, which is well-known to be an excellent fluorophore and which is extensively used in bioimaging.^[28] Parallel to this application in bioimaging, BTXI and its derivatives are also commonly used as light-emitting materials for organic light-emitting devices (OLEDs),^[29, 30] but also as semi-conductors for organic field effect transistors (OFETs) due to their electron-rich structures.^[31, 32] Because BTXI has good light absorption properties in the visible region with an absorption band extending from 400 nm to ca. 510 nm,^[33] BTXI and its derivatives have the potential to become interesting photoinitiators for visible light photopolymerization. In order to develop monocomponent systems, BTXI can be easily chemically modified as oxime esters. As reported in the literature,^[33, 34] the Highest Occupied Molecular Orbital (HOMO) energy level of BTXI with -5.94 eV is close to the Lowest Unoccupied Molecular Orbital (LUMO) energy level of *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod) with -5.71 eV, indicating the possibility of a favorable electron transfer between BTXI and Iod in the excited state.

Parallel to the search for new chromophores enabling to improve both the polymerization speed as well as the function conversions of monomers, photopolymerization under sunlight is also an active research field considering that sunlight is the cheapest light source available on Earth, exhibiting a broad emission spectrum which is perfectly adapted for photoinitiators possessing a broad absorption spectrum. In this aim, benzothioxanthene-based oxime esters are appropriate candidates for such investigations. Interestingly, only few oxime esters activable under sunlight have been reported in the literature and carbazole or naphthoquinone derivatives have recently been developed by our groups.^[2, 5]

In this work, six benzothioxanthene-based oxime esters (BTXIOXEs) were designed and synthesized as Type I

photoinitiators (see Figure 1) with excellent light absorption properties in the visible range from 400 to ca. 525 nm. When tested as type I photoinitiators, good initiating performances could be observed in thin samples. However, their molar extinction coefficients negatively impacted their photoinitiating efficiency for thick samples, with function conversions that were clearly far from that obtained in thin films. In this regard, we hypothesized that combining BTXIOXEs with an iodonium salt could allow to form two-component photoinitiating systems and generate activate radicals for initiating free radical photopolymerization *via* the sensitization of the iodonium salt upon exposure with a LED@405nm, a LED@450nm and sunlight, respectively.

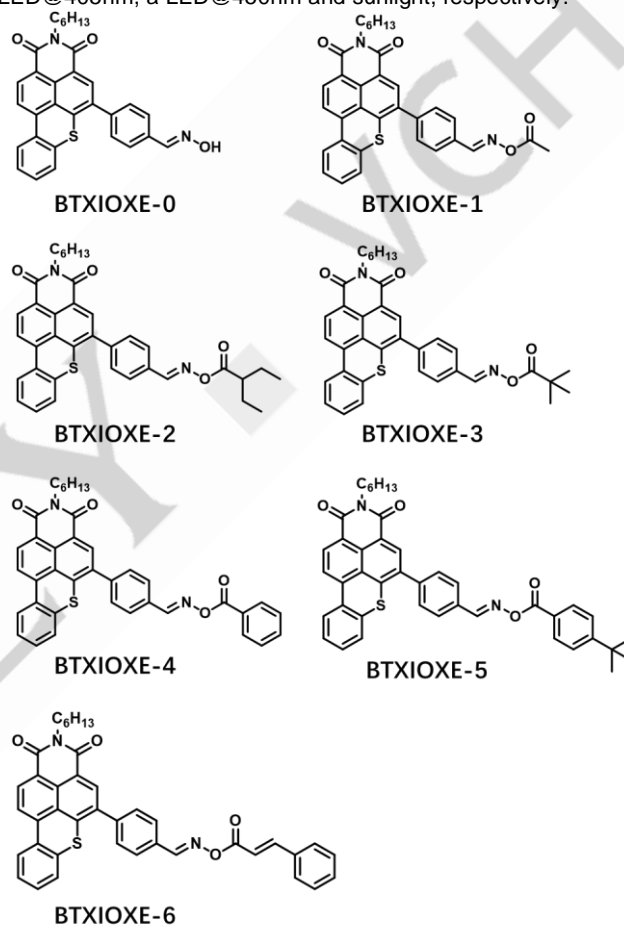


Figure 1. Chemical structures of BTXIOXE-1 to BTXIOXE-6.

Results and Discussion

Theoretical calculations

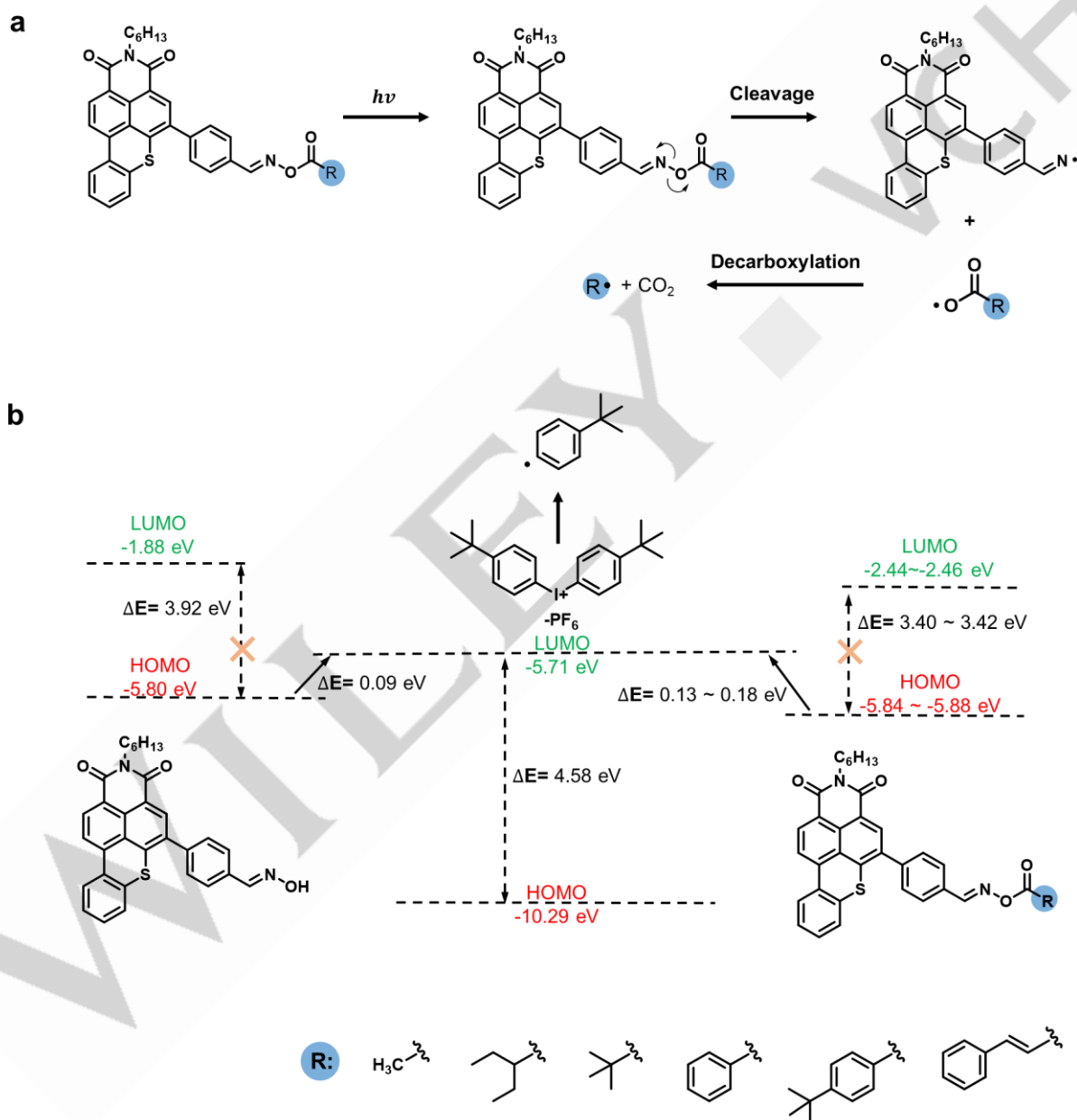
In order to investigate the photoinitiating ability of BTXIOXEs from the theoretical viewpoint, molecular modeling was first performed on the different structures. Energy levels and contour plots of the HOMO, LUMO, LUMO-1 and LUMO-2 of BTXIOXEs were calculated, as shown in Scheme S1 and Table S1. The frontier orbitals of BTXIOXEs are mainly distributed on the benzothioxanthene core with low contribution of the oxime ester groups (see HOMO in Scheme S1). Their LUMO almost distributes on the benzothioxanthene core, while LUMO-1 is on oxime ester moiety. Therefore, an intermolecular chargefrom

RESEARCH ARTICLE

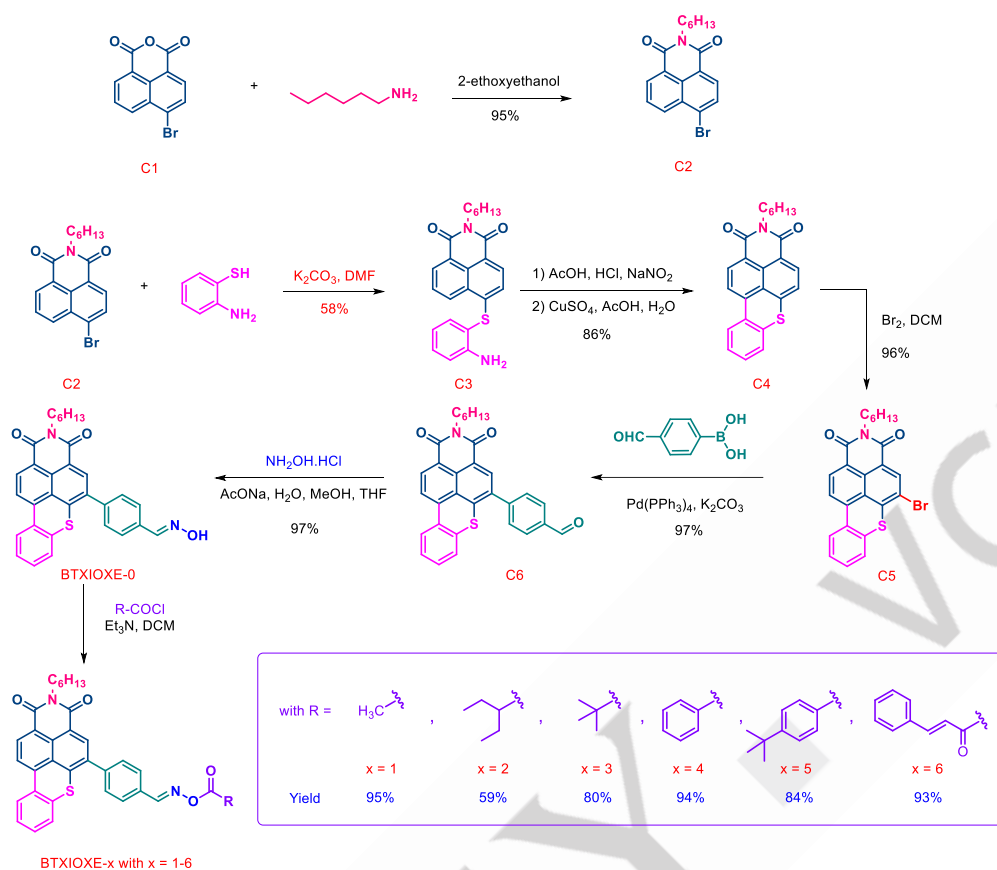
HOMO to LUMO-1 can be clearly observed which indicates the possibility of cleavage in LUMO-1. In addition, these compounds exhibit differences in their LUMO-1 values due to their differences in their structures. To further evaluate the possibility of cleavage, bond dissociation energies of the N-O bond (BDE) and energies of the triplet excited-states (E_{T1}) were calculated and are listed in Table S1. The singlet excited-state energies (E_{S1}) of BTXIOXEs were calculated by Equation S2. As shown in Table S1, enthalpies of the cleavage process of the N-O bond at the singlet excited-state and the triplet excited-state ($\Delta H_{\text{Cleavage } S1} < 0$ and $\Delta H_{\text{Cleavage } T1} > 0$) indicate that the N-O bond cleavage of BTXIOXEs is favorable from the singlet excited-states (see Scheme 1.a).

Therefore, these compounds can be used as Type I photoinitiators.

Molecular modeling also indicates that the LUMO energy of *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod) (-5.71 eV) is close to the HOMO energies of BTXIOXEs (-5.84 ~ -5.89 eV) (see Table S1). Therefore, electrons of the HOMO level of BTXIOXE can be easily transferred to Iod upon light irradiation. Subsequent to the photoinduced electron transfer, Iod is reduced, resulting in the decomposition of the unstable radical, generating *tert*-butylbenzene radicals and iodobenzene (see Scheme 1.b). Therefore, the feasibility of an α -cleavage with these structures is theoretically proven.



Scheme 1. Proposed mechanism of α -cleavage and sensitization of an iodonium salt.



Scheme 2. Synthetic routes to BTXIOXE-1 to BTXIOXE-6.

Synthesis of the different dyes

After theoretical calculations proved the feasibility of these compounds to act as photoinitiators but also as photosensitizer in electron transfer reactions, we synthesized the different unreported structures. Details are presented in the "BTXIOXE Synthesis" section of SI.

The six oxime esters BTXIOXE-1 to BTXIOXE-6 were synthesized in seven steps starting from the commercially available 4-bromo-1,8-naphthalic anhydride and according to the procedure reported in the Scheme 2. In first step, the amide C2 was formed by reaction of 4-bromo-1,8-naphthalic anhydride C1 and hexylamine, enabling to furnish the compound C1 in 95% yield. By reaction with 2-aminothiophenol under basic conditions, the intermediate C3 could be formed in 58% yield. After ring closure, C4 was halogenated with bromine, enabling to generate C5 in 96% yield. By mean of a metal-catalyzed cross-coupling reaction with 4-formylphenylboronic acid, C6 could be obtained in high yield i.e. 97%. The oxime BTXIOXE-0 was prepared using hydroxylamine hydrochloride and sodium acetate as the reagents in a mixture of three solvents (deionized water, tetrahydrofuran (THF) and methanol (1 : 10 : 1 vol%)). Finally, oxime esters BTXIOXE-1 to-BTXIOXE-6 were obtained using the appropriate acid chloride and triethylamine as the base. The six oxime esters were obtained with reaction yields ranging between 59% for BTXIOXE-2 and 95% for BTXIOXE-1.

Optical properties of the different dyes

Optical properties of BTXIOXEs were examined by UV-Visible spectroscopy (see Figure 2) and their photophysical characteristics are listed in Table 1. As shown in Figure 2, BTXIOXE-0 presents a high molar extinction coefficient, while BTXIOXEs show obviously lower molar extinction coefficients, which could be attributed to the introduction of different OXE groups. It is interesting to be observed that all BTXIOXEs show a broad absorption band extending from ca. 400 nm to ca. 520 nm, indicating their potential to be utilized as visible light sensitive photoinitiators. As a novel series of oxime esters, the maximum absorption wavelength values of BTXIOXEs can be 478 nm, which is higher than that of many oxime esters reported before.^[18, 25, 35] This indicates their higher absorbance towards specific wavelengths of visible light, such as 450 nm.

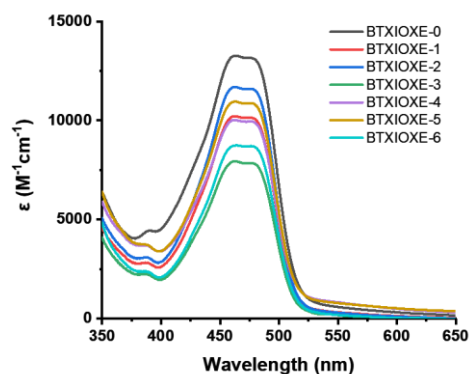


Figure 2. UV-Visible absorption spectra of BTXIOXEs (concentration: 4×10^{-5} M) in dichloromethane (DCM) at room temperature.

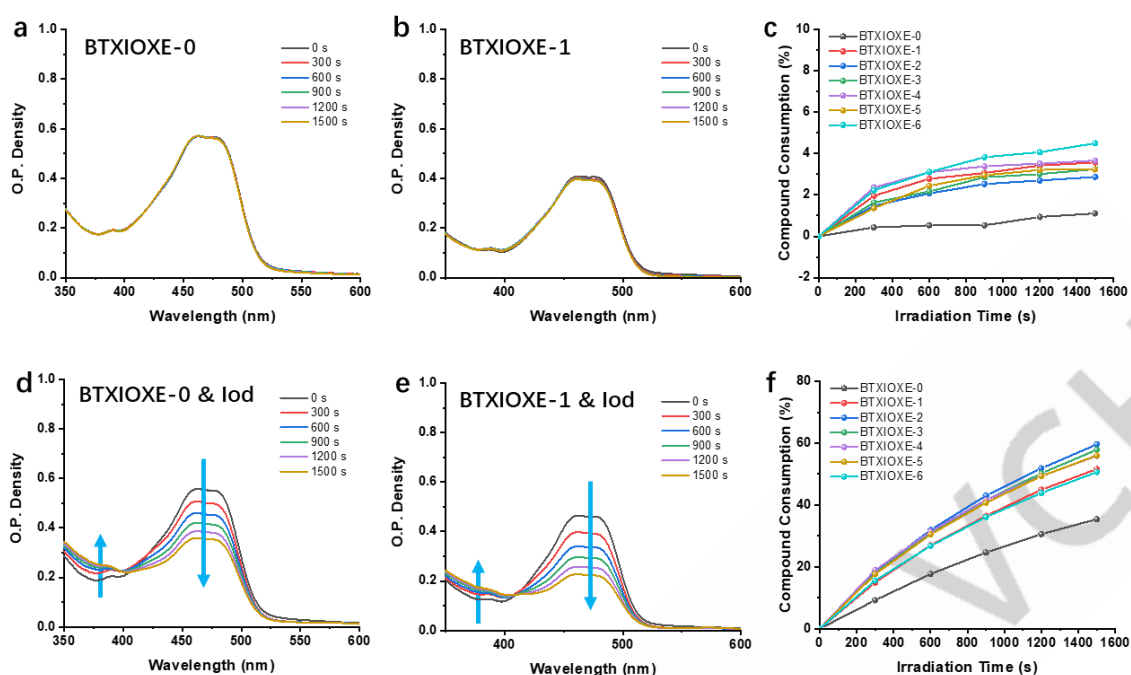


Figure 3. Steady-state photolysis of photoinitiating systems in DCM upon LED@405nm irradiation ($110 \text{ mW}\cdot\text{cm}^{-2}$) at room temperature: (a) BTXIOXE-0, (b) BTXIOXE-1, (d) BTXIOXE-0/Iod, (e) BTXIOXE-1/Iod, (c) compound consumption of BTXIOXEs, and (f) compound consumption of BTXIOXEs with Iod.

Photolysis experiments were also performed to investigate the photochemical behavior of these compounds upon irradiation with a LED@405nm ($110 \text{ mW}\cdot\text{cm}^{-2}$) and a LED@450nm ($70 \text{ mW}\cdot\text{cm}^{-2}$). When BTXIOXEs were used as shown in Figure 3, the consumption of BTXIOXE-0 is only at 1.1%, showing no cleavage after 1500 s of irradiation with a LED@405nm. Meanwhile, the consumptions of other BTXIOXEs are all higher than BTXIOXE-0 (see Figures 3 and S1), which can be confidently assigned to their self-decomposition i.e. the α -cleavage of the OXE groups. The similar situation also can be observed when a LED@450nm was used as light source for photolysis experiments (see Figure S2). According to the results of molecular modeling (see Table S1), BTXIOXE-0, without an oxime ester functional group, has the highest LUMO-1 value of -1.39 eV resulting in lowest consumption in photolysis, while BTXIOXE-6 with a LUMO-1 value of -1.92 eV shows the higher consumption under the irradiation of either LED@405 nm or LED450 nm, compared to other BTXIOXEs. For other BTXIOXEs, their LUMO-1 values range from -1.66 eV to -1.72 eV , with a similar consumption in photolysis process (see Table S2). For BTXIOXE-1 to BTXIOXE-3 with alkyl carboxylate, their LUMO values are very close approximately -1.66 or -1.67 eV . On the other hand, aryl carboxylate BTXIOXE-4 and BTXIOXE-5, have lower LUMO-1 values of -1.75 eV and -1.71 eV . These five BTXIOXEs have similar LUMO-1 values, which result in similar consumptions (2.9%–3.6% LED@405nm, 2.2%–4.9% LED@450nm) during photolysis process. In our previous work about phenothiazines based oxime esters,^[36] the α -cleavage of the oxime ester group could be observed which is contributed to that HOMO and LUMO both mainly distributed on oxime ester moiety resulting in an obvious photolysis under LED@405nm irradiation. But the situation of BTXIOXEs in this work is different. The LUMO of BTXIOXEs almost distributed on the benzothioxanthene core,

and LUMO-1 is on oxime ester moiety, which results in a competition during charge transfer from HOMO to LUMO or LUMO-1. Due to the lower energy gap between HOMO and LUMO, the charge transfer mainly occurs on LUMO, which is impossible to produce radicals for photoinitiating. Few charge transfer happens from HOMO to LUMO-1, the main process of radical generation, resulting in a slower photolysis or low consumption.

Table 1. The photochemical data at room temperature: extinction coefficient at 405 nm $\epsilon_{405\text{nm}}$, absorption maximum λ_{max} , extinction coefficient ϵ_{max} , Stern-Volmer quenching constant (K_{sv}), fluorescence decay time t_0 and quenching rate constant k_q for BTXIOXEs.

	$\epsilon_{405\text{nm}}$ [$\text{M}^{-1}\text{cm}^{-1}$]	λ_{max} [nm]	ϵ_{max} [$\text{M}^{-1}\text{cm}^{-1}$]	$K_{\text{sv}}^{\text{Iod}}$ [M^{-1}]	t_0 [ns]	k_q [$10^9 \text{ Lmol}^{-1}\text{s}^{-1}$]
BTXIOXE-0	4800	478	11400	25	7.8	3.2
BTXIOXE-1	2800	478	8100	25	8.0	3.1
BTXIOXE-2	3100	478	9200	27	8.1	3.3
BTXIOXE-3	2000	478	7800	22	8.2	2.7
BTXIOXE-4	3500	478	7900	24	8.1	2.9
BTXIOXE-5	3600	478	8700	23	8.0	2.9
BTXIOXE-6	1700	478	8600	22	8.0	2.7

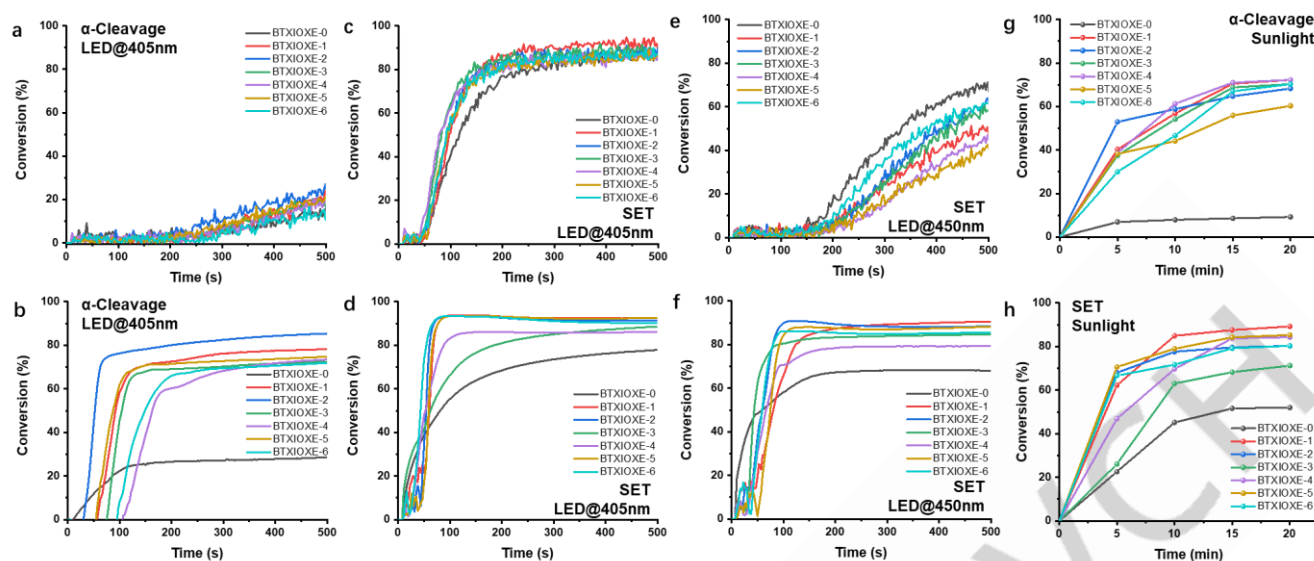


Figure 4. Photopolymerization of PEGDA containing different photoinitiating systems: (a) thick samples containing BTXIOXEs under LED@405nm, (b) thin samples (laminated) containing BTXIOXEs under LED@405nm, (c) thick samples containing BTXIOXEs/Iod under LED@405nm, (d) thin samples containing BTXIOXEs/Iod under LED@405nm, (e) thick samples containing BTXIOXEs/Iod under LED@450nm, (f) thin samples (laminated) containing BTXIOXEs/Iod under LED@450nm, (g) thin samples (laminated) containing BTXIOXE under sunlight, and (h) thin samples (laminated) containing BTXIOXE/Iod under sunlight. The concentration of BTXIOXE and BTXIOXE/Iod were controlled at 2.0×10^{-6} mol and $2.0 \times 10^{-6}/4.0 \times 10^{-6}$ (mol/mol) in 1 g PEGDA, respectively. The LED was switched on at $t = 10$ s during for the RT-FTIR experiments a to f.

When Iod was utilized as an electron acceptor, all BTXIOXEs showed a significant photolysis process as shown by their UV-Visible absorption spectra, and their consumptions reached up 60% after 1500 s of irradiation, suggesting an efficient intermolecular electron transfer process between BTXIOXE and Iod which is consistent to the conclusions established by the molecular modeling. Moreover, a similar tendency of photolysis process upon irradiation of LED@450nm was observed (see Figure S2).

Stern-Volmer quenching constant (K_{sv}), Lifetime (t_0) and quenching constant (k_q) were characterized (see Figure S3, S4) and their results are listed in Table 1. Upon introduction of the oxime ester groups in BTXIOXE-0 leading to BTXIOXE-1 to BTXIOXE-6, the excited state lifetimes (8.0-8.2 ns) are slightly longer than that of the parent BTXIOXE-0 (7.8 ns), and their K_{sv}^{Iod} are similar. Depart from these, most of their quenching rate constants are slightly smaller, compared to BTXIOXE-0 as well. Therefore, the fluorescence properties of these compounds are similar. As shown in Figure S5, the cross the intersection without unit of normalized fluorescence emission spectra and the normalized UV visible absorption spectra was used to calculate the E_{s1} of each BTXIOXE to estimate their possibility of α -cleavage which has been discussed in "2.1 Theoretical calculations" section.

Photoinitiating properties of the different oxime esters BTXIOXE-1 to BTXIOXE-6

Photopolymerization of poly(ethylene glycol) diacrylate (PEGDA) ($M_w \approx 600$) was evaluated by RT-FTIR, and photopolymerization profiles are presented in Figure 4. The procedure itself is described in the supporting information. When

used as type I photoinitiators, BTXIOXEs (concentration in the range of 2×10^{-6} mol in 1 g PEGDA, see SI) showed good initiating performances in thin samples ($\sim 25 \mu\text{m}$, laminated = reduced oxygen rediffusion) upon LED@405nm irradiation and acrylate function conversions (FCs) ranging between 71 and 85% could be determined. Conversely, a poor photoinitiating efficiency was clearly detected for thick samples (1.4 mm), which is directly related to their high molar extinction coefficients that hinders the light penetration in depth. For comparison, formulations containing the BTXIOXE/Iod (concentration 2×10^{-6} mol : 4×10^{-6} mol in 1 g PEGDA, see SI) systems were examined upon irradiation with a LED@405nm. As listed in Table S3, all formulations showed an improved FC (85-89%). For thin samples, the PEGDA resin containing BTXIOXE-1/Iod, BTXIOXE-2/Iod, BEOXE-5/Iod and BTXIOXE-6/Iod, showed the highest FCs with values of 92, 91, 92 and 90%, respectively. These results indicate that the two-component BTXIOXE/Iod systems can be a good strategy to improve the photoinitiating efficiency of these oxime esters. When a LED@450nm was utilized as the light source, the different formulations showed only a moderate improvement of the polymerization efficiency in thick samples, with FCs ranging between 42 and 66%, and conversions ranging between 68 and 90% in thin samples. Therefore, when BTXIOXEs were used as Type I photoinitiators, good photoinitiating efficiencies were observed for thin samples, whereas the BTXIOXE/Iod systems proved to be a better photoinitiating system for thick samples. At the same time, these results clearly demonstrate that if a photoinitiator with high molar absorption coefficient is used for photopolymerization, an efficient way to avoid or weaken the influence of inner filter effect on photopolymerization, is to reduce the thickness of samples (for example, the significantly improved FC reducing thickness from 1.4 mm to $\sim 25 \mu\text{m}$ in this

work), or to use other additives to form a more efficient photoinitiating system to improve the photoinitiating efficiency, such as using Iod as electron acceptor or amine as hydrogen donor.

Different from artificial light sources (i.e., LED), the emission of sunlight is broader than that of LEDs, but the solar intensity is also lower, which means that numerous photoinitiators cannot be efficient upon sunlight exposure although they are reported as efficient structures for LEDs. In previous studies,^[37, 38] for all wavelengths emitted by the solar disk, the reduced total hemispherical radiation $H(t)$ - $D(t)$ and diffused sky radiation $D(t)$ on a horizontal surface in winter are in the range of 15-40 $\text{mW}\cdot\text{cm}^{-2}$ and 5.0 $\text{mW}\cdot\text{cm}^{-2}$, respectively, which are nearly 3 times lower than that of the maximal hemispherical radiation possible under optimal conditions on the surface of Earth. According to the ASTM G173-03 reference spectrum analysis, sun irradiation in the 280-400 nm range is reduced to 0.5-1.4 $\text{mW}\cdot\text{cm}^{-2}$. Because of the low intensity of sunlight, photopolymerization time could be elongated from several hours up to several days.^[39, 40] According to the excellent light absorption properties of BTXIOXE-1-BTXIOXE-6, photopolymerizations (thin sample, ~25 μm , laminated = reduced oxygen rediffusion) under light irradiation *via* α -cleavage and SET were performed, respectively (see Figures 4.g and 4.h). The weather report of Mulhouse (France, winter) is shown in Figure S6. When BTXIOXEs were used as Type I photoinitiators, their FCs were 30-53% ($t = 5$ min) and then increased up to 60-72% ($t = 20$ min) (see Table S4). When the BTXIOXE/Iod systems were used, FCs of BTXIOXE-1/Iod and BTXIOXE-2/Iod increased up to 62% and 68% rapidly ($t = 5$ min), and then their FCs were 89% and 80% ($t = 20$ min). For the other systems, their FCs ($t = 20$ min) were 80-85%, except for BTXIOXE-3/Iod (FC= 71%, $t = 20$ min). The same operation was performed on trimethylolpropane triacrylate (TMPTA) as well and the results were presented in Figure S8 and Table S5. As BTXIOXE-1-BTXIOXE-6 were used as Type I photoinitiators, their FCs of TMPTA are 36-52% ($t = 20$ min). For BTXIOXE/Iod systems, FCs of TMPTA can be 61-68% ($t = 20$ min). Their performances under sunlight are even comparable with some oxime esters used under LED@405nm irradiation reported before, such as OEC4 (FC< 40%, coumarin-based),^[24] 2-S (46%, coumarin-based),^[25] BC-OXEs ($\leq 50\%$, bicarbazole-based),^[18] MMM, MME, MMP MPE (< 45%, substituted stilbene-based).^[41]

In the past few years, many oxime esters have been reported as photoinitiators,^[14, 15, 41-43] but only few works claimed that these oxime esters can have a good photoinitiating performance upon sunlight exposure when they were used as type I photoinitiators alone or used with other additives to form photoinitiating systems (such as Iod and ethyl dimethylaminobenzoate (EDB)).^[2, 5, 44] A TMPTA conversion of 15% and 9% were determined respectively, when carbazole-fused coumarin based oxime esters were used as type I photoinitiators ($2.0 \times 10^{-5} \text{ mol}\cdot\text{g}^{-1}$) in our previous work.^[2] In the other work about naphthoquinone-based oxime esters, the TMPTA conversion of 62% could be determined after 40 min of sunlight exposure using a three-component OXE-1/Iod/EDB (0.1wt%/0.2wt%/0.2wt%).^[5] Compared to these oxime esters, BTXIOXEs in this work indicate their excellent photoinitiating performance for TMPTA polymerization under sunlight. Therefore, these photoinitiators

amply indicate their high photoinitiating efficiencies under visible light or sunlight irradiation.

As reported in our previous works, if OXEs can initiate photopolymerization, the generation of CO_2 can be detected on the RT-FTIR curves and the photochemical mechanism of initiation can thus be verified.^[5] As shown in Figure S8, appearance of a CO_2 peak could be detected at 2337 cm^{-1} on the IR spectrum during photopolymerization, evidencing the occurrence of a decarboxylation process during photopolymerization. In order to get a deeper insight into the intermolecular interaction existing between BTXIOXE and Iod, the photochemical mechanism was also investigated by electron spin resonance spin trapping (ESR-ST). As shown in Figure S9, ESR-ST was performed on BTXI, and signals issued from BTXI could be evidenced and used as reference. As shown in Figure 5.a, the smaller signal (9.7%) with a hyperfine coupling constant $\alpha_N = 14.3$ G and $\alpha_H = 2.1$ G can be confidently assigned to the formation of phenyl radical adducts issued from the cleavage of Iod.^[45, 46] The second signal (90.3%) with a hyperfine coupling constant $\alpha_N = 5.4$ G can be assigned to the nitroxide radical, which is also related to the benzothioxanthene core. The same phenomena could be observed on BTXIOXE-2 (see Figure 5.b). Therefore, the photoinitiating mechanism of this SET process is consistent with that proposed in Scheme 1.

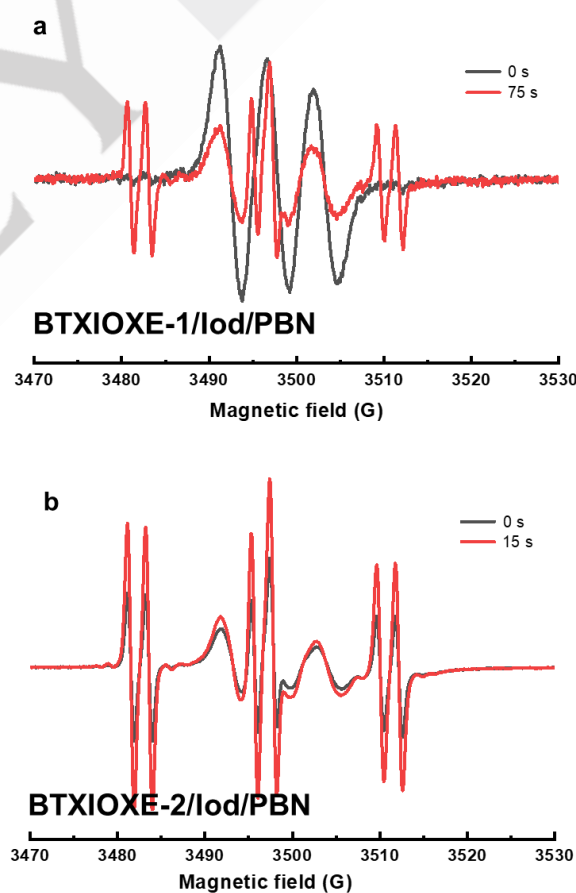


Figure 5. ESR spectrum of different initiating systems containing N-tert-butyl- α -phenylnitron (PBN) upon irradiation of LED@405nm: (a) BTXIOXE-1/Iod/PBN and (b) BTXIOXE-2/Iod/PBN.

Direct laser write experiments

The two-component BTXIOXE-1/Iod and BTXIOXE-2/Iod systems were chosen to be model photoinitiating systems for direct laser write (DLW) experiments using PEGDA as the monomer, due to their favorable photoinitiation performances upon irradiation with a LED@405nm. The letters “IS2M” and “PM2P” were manufactured *via* DLW, respectively, which are the abbreviations of “Institut de Science des Matériaux de Mulhouse” and “(Photo)chimie Moléculaire et (Photo)Polymérisation”. As shown in Figure 6, the surface of these letters all have good resolutions and the route of the laser write can be clearly detected from the SEM pictures.

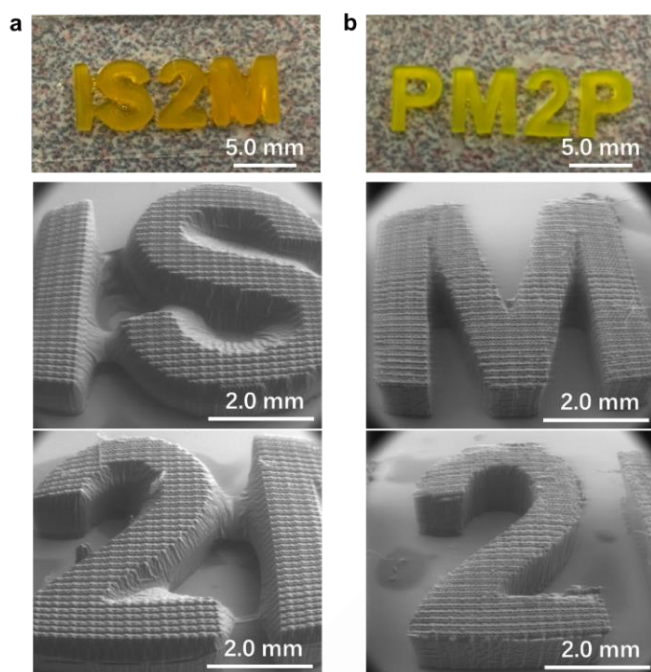


Figure 6. Digital images and SEM images for different formulations (a) BTXIOXE-1/Iod/PEGDA and (b) BTXIOXE-2/Iod/PEGDA.

Conclusion

In this work, six new benzothioxanthene-based oxime esters were successfully designed and synthesized. None of them has been previously reported in the literature. Photopolymerization experiments of polyethylenglycol diacrylate ($M_w \approx 600$) were carried out to systematically investigate the photoinitiating efficiencies of BTXIOXEs as monocomponent systems, but also as photosensitizers for the two-component BTXIOXEs/Iod systems. In addition, we proved that these compounds all have excellent photoinitiating performance under sunlight (“low” light intensity) *via* both α -cleavage and single electron transfer. This work clearly demonstrates the significant impact of the molar extinction coefficient on the photoinitiating ability of oxime esters. In the present case, choice of benzothioxanthene as the chromophore revealed the resulting oxime esters to be unable to act as efficient photoinitiators in thick films due to their exceptionally high molar extinction coefficients

and the resulting inner filter effect. Depending on the desired application, a good balance between molar extinction coefficient and reactivity has thus to be found in order to develop high performance photoinitiators optimized for the application.

Supporting Information

The authors have cited additional references within the Supporting Information.^[34]

Acknowledgements

The authors thank the Agence Nationale de la Recherche for fundings provided by the ANR PhotoFlat. Bin Song and Zheng Liu acknowledge the financial support from Chinese Scholarship Council (CSC) for their Ph.D. studies. The molecular modelling in this work was performed using HPC resources of the Mesocentre of the University of Strasbourg and the HPC resources from GENCI-IDRIS (Grant 2023-AD010812313R2/Jean_Zay).

Keywords: Oxime Esters; Photocleavage; Photochemistry, Single Electron Transfer; Photopolymerization; Visible Light and Sunlight

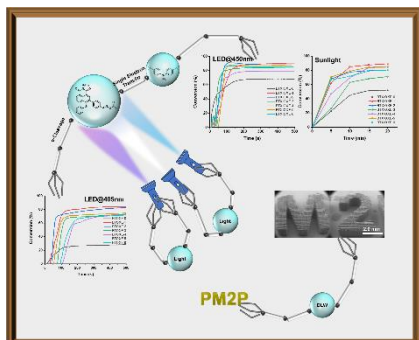
Reference

- [1] G. Zhu, J. Zhang, J. Huang, Y. Qiu, M. Liu, J. Yu, C. Liu, Q. Shang, Y. Hu, L. Hu, Y. Zhou, *Chem. Eng. J.* **2023**, 452, 139401-139411.
- [2] Y. Zhang, Z. Liu, T. Borjigin, B. Graff, F. Morlet-Savary, M. Schmitt, D. Gimes, F. Dumur, J. Lalevée, *Green Chem.* **2023**, 25, 6881-6891.
- [3] D. Zhu, P. Wagner, P. Xiao, *Ind. Eng. Chem. Res.* **2021**, 60, 8733-8742.
- [4] X. Peng, D. Zhu, P. Xiao, *Eur. Polym. J.* **2020**, 127, 109569-109576.
- [5] Y. Zhang, B. Song, C. Dietlin, F. Morlet-Savary, M. Schmitt, F. Dumur, J. Lalevée, *Ind. Eng. Chem. Res.* **2024**, 63, 3962-3974.
- [6] C. G. Bailey, M. D. Nothling, L. L. Fillbrook, Y. Vo, J. E. Beves, D. R. McCamey, M. H. Stenzel, *Angew. Chem. Int. Ed. Engl.* **2023**, 62, e202301678-e202301684.
- [7] Y. Zhu, D. Xu, Y. Zhang, Y. Zhou, Y. Yagci, R. Liu, *Angew. Chem. Int. Ed. Engl.* **2021**, 60, 16917-16921.
- [8] S. M. Müller, S. Schlögl, T. Wiesner, M. Haas, T. Griesser, *ChemPhotoChem* **2022**, 6, e202200091-e202200102.
- [9] F. Dumur, *Eur. Polym. J.* **2023**, 193, 112120-112142.
- [10] X. He, Y. Shao, Y. Pang, J. Wang, M. Liu, Y. Xin, Y. Zou, *Polym. Chem.* **2023**, 14, 1543-1553.
- [11] Y. Bao, *Macromol. Rapid Comm.* **2022**, 43, 2200202-2200216.
- [12] H. Chen, T. Borjigin, C. Regeard, P. Xiao, F. Dumur, J. Lalevée, *Small* **2023**, 19, 2300772-2300783.
- [13] T. Borjigin, J. Feng, M. Schmitt, D. Zhu, F. Morlet-Savary, P. Xiao, J. Lalevée, *Green Chem.* **2024**, 26, 277-286.
- [14] D. E. Fast, A. Lauer, J. P. Menzel, A.-M. Kelterer, G. Gescheidt, C. Barner-Kowollik, *Macromolecules* **2017**, 50, 1815-1823.
- [15] W. J. Lee, H. S. Kwak, D.-r. Lee, C. Oh, E. K. Yum, Y. An, M. D. Halls, C.-W. Lee, *Chem. Mater.* **2021**, 34, 116-127.
- [16] C. Elian, N. Sanosa, N. Bogliotti, C. Herrero, D. Sampedro, D.-L. Versace, *Polym. Chem.* **2023**, 14, 3262-3269.
- [17] W. Liao, M. Jin, *Prog. Org. Coat.* **2024**, 189, 108290-108298.
- [18] R. Zhou, H. Pan, D. Wan, J.-P. Malval, M. Jin, *Prog. Org. Coat.* **2021**, 157, 106306-106314.

- [19] S. Liu, N. Giacoletto, M. Schmitt, M. Nechab, B. Graff, F. Morlet-Savary, P. Xiao, F. Dumur, J. Lalevée, *Macromolecules* **2022**, *55*, 2475-2485.
- [20] A. Noon, F. Hammoud, B. Graff, T. Hamieh, J. Toufaily, F. Morlet-Savary, M. Schmitt, T. T. Bui, A. Rico, F. Goubard, S. Péralta, F. Dumur, J. Lalevée, *Adv. Mater. Technol.* **2023**, *8*, 2300205-2300218.
- [21] P. Garra, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, *Polym. Chem.* **2017**, *8*, 7088-7101.
- [22] J. Jakubiak, A. Sionkowska, L.-Å. Lindén, J. F. Rabek, *J. Therm. Anal. Calorim.* **2001**, *65*, 435-443.
- [23] R. Liu, H. Chen, Z. Li, F. Shi, X. Liu, *Polym. Chem.* **2016**, *7*, 2457-2463.
- [24] W. Qiu, P. Hu, J. Zhu, R. Liu, Z. Li, Z. Hu, Q. Chen, K. Dietliker, R. Liska, *ChemPhotoChem* **2019**, *3*, 1090-1094.
- [25] W. Qiu, M. Li, Y. Yang, Z. Li, K. Dietliker, *Polym. Chem.* **2020**, *11*, 1356-1363.
- [26] F. Hammoud, N. Giacoletto, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gigmes, F. Dumur, J. Lalevée, *Mater. Chem. Front.* **2021**, *5*, 8361-8370.
- [27] R. Li, H. Guo, X. Luo, Q. Wang, Y. Pang, S. Li, S. Liu, J. Li, B. Strehmel, Z. Chen, *Angew. Chem. Int. Ed. Engl.* **2024**, e202404454-e202404460.
- [28] A. L. Dauphin, J. M. Andrés Castán, J. Yu, P. Blanchard, N. Sojic, H. S. Ahn, B. Walker, C. Cabanetos, L. Bouffier, *ChemElectroChem* **2022**, *9*, 202200967-202200974.
- [29] P. Josse, K. Morice, D. P. Sanchez, T. Ghanem, J. Boixel, P. Blanchard, C. Cabanetos, *New J. Chem.* **2022**, *46*, 8393-8397.
- [30] J. M. A. Castán, C. Amruth, P. Josse, L. A. Galan, P. S. Marqués, M. Allain, O. Maury, T. Le Bahers, P. Blanchard, C. Monnereau, G. C. Welch, C. Cabanetos, *Mater. Chem. Front.* **2022**, *6*, 1912-1919.
- [31] P. Josse, S. Li, S. Dayneko, D. Joly, A. Labrunie, S. Dabos-Seignon, M. Allain, B. Siegler, R. Demadrille, G. C. Welch, C. Risko, P. Blanchard, C. Cabanetos, *J. Mater. Chem. C* **2018**, *6*, 761-766.
- [32] J. M. Andrés Castán, S. Abidi, T. Ghanem, S. Touihri, P. Blanchard, G. C. Welch, Y. Zagranyski, J. Boixel, B. Walker, P. Josse, C. Cabanetos, *Colorants* **2022**, *2*, 22-30.
- [33] M. Deiana, P. Josse, C. Dalinot, A. Osmolovskiy, P. S. Marques, J. M. A. Castan, L. Abad Galan, M. Allain, L. Khrouz, O. Maury, T. Le Bahers, P. Blanchard, S. Dabos-Seignon, C. Monnereau, N. Sabouri, C. Cabanetos, *Commun. Chem.* **2022**, *5*, 142-152.
- [34] D. Wang, P. Garra, J. P. Fouassier, B. Graff, Y. Yagci, J. Lalevée, *Polym. Chem.* **2019**, *10*, 4991-5000.
- [35] W. Wang, M. Jin, H. Pan, D. Wan, *Prog. Org. Coat.* **2021**, *151*, 106019-106030.
- [36] Y. Zhang, F. Morlet-Savary, M. Schmitt, B. Graff, A. Rico, M. Ibrahim-Ouali, F. Dumur, J. Lalevée, *Dyes Pigm.* **2023**, *215*, 111202-111214.
- [37] M. Schmitt, F. Heib, *RSC Adv.* **2014**, *4*, 17639-17647
- [38] M. Schmitt, *Nanoscale* **2015**, *7*, 9532-9544.
- [39] F. Dumur, *Eur. Polym. J.* **2023**, *189*, 111988-112008.
- [40] M. Tehfe, F. Louradour, J. Lalevée, J.-P. Fouassier, *Appl. Sci.* **2013**, *3*, 490-514.
- [41] S. Chen, M. Jin, J.-P. Malval, J. Fu, F. Morlet-Savary, H. Pan, D. Wan, *Polym. Chem.* **2019**, *10*, 6609-6621.
- [42] X. Guo, W. Wang, D. Wan, M. Jin, *Eur. Polym. J.* **2021**, *156*, 110617-110627.
- [43] X. Wu, S. Gong, Z. Chen, J. Hou, Q. Liao, Y. Xiong, Z. Li, H. Tang, *Dyes Pigm.* **2022**, *205*, 110556-111565.
- [44] J. Feng, Y. Zhang, F. Morlet-Savary, M. Schmitt, J. Zhang, P. Xiao, F. Dumur, J. Lalevée, *Small* **2024**, e2400230-e2400243.
- [45] E. Hola, F. Morlet-Savary, J. Lalevée, J. Ortyl, *Eur. Polym. J.* **2023**, *189*, 111971-111983.
- [46] W. Liao, Q. Liao, Y. Xiong, Z. Li, H. Tang, *J. Photochem. Photobiol. A Chem.* **2023**, *435*, 114297-114308.

RESEARCH ARTICLE

Entry for the Table of Contents



Good light absorption property facilitates an efficient photopolymerization reaction. In this work, six different benzothioxanthene-based oxime esters (BTXIOXEs) demonstrate their efficient photoinitiating performances under visible light and sunlight, following photocleavage and/or single electron transfer processes, which offers a strategy for developing novel oxime ester-based photoinitiators under visible light and sunlight.