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Recent Advances on Pyrene-Based Photoinitiators of Polymerization

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Abstract

Photoinitiators of polymerization activable under low light intensity and in the visible range are actively researched by both the academic and industrial communities. To efficiently harvest light and initiate a polymerization process, polyaromatic structures are ideal candidates. In this field, pyrene can be cited as a relevant example. Over the years, a wide range of Type I and Type II photoinitiators have been developed, ranging from push-pull dyes to polyaromatic structures, ferrocenium, ketones, chromones or acridinediones. In this review, an overview of the different pyrene-based photoinitiators reported to date is presented. Especially, a structure-performance relationship will be established with benchmark photoinitiators, evidencing all the interests of this polyaromatic structure.

Keywords

Photoinitiator; pyrene; photopolymerization; LED; visible light

1. Introduction

During the past decades, photoinitiating systems that can be activated under low light intensity and in the visible region have been the focus of numerous research efforts. Face to the traditional UV photoinitiators which are at the origin of numerous safety concerns with regards to the use of UV light and the different drawbacks that are classically listed such as the necessity to use high intensity light sources, the use of expensive setups also at the origin of an excessive electricity consumption,[1,2] alternatives to these traditional photoinitiators are thus actively researched.[3] Thanks to the recent development of energy-efficient and affordable lighting technologies such as Light-Emitting Diodes (LEDs) and fluorescence bulbs, a new generation of photoinitiators adapted to these new light sources of low light intensity is currently under development. Considering that the absorption spectra of the benchmark UV photoinitiators are too difficult to redshift towards the visible range as it would require a hard synthetic work (a shift of approximately 100-150 nm is required to get a sufficient

absorption in the near visible range), the traditional UV photoinitiators can't thus be used as a basis for the elaboration of visible light photoinitiators. Consequently, chemical structures never studied in the context of photopolymerization have recently emerged as potential candidates for visible-light photoinitiation. Indeed, it clearly appeared that the development of visible light photoinitiators activable under low light intensity could only proceed through the search of new structures, ensuring an increase of their photochemical reactivity in the visible range. Considering the novelty of the approach as visible light photoinitiators activable under low light intensity are only developed since a decade, this is a research field which is at present almost devoid of any investigation. Besides, in this decade, a wide range of structures have nonetheless been examined, as exemplified with chalcones **1**,[4] chromones **2**,[5-7] perylenes **3**,[8-10] diketopyrrolopyrroles **4**,[11-13] acridine-1,8-diones **5**,[14,15] naphthalimides **6**,[16-26] iodonium salts **7**,[27-29] squaraines **8**, bodipys **9** and porphyrins **10**,[30,31] benzophenones **11**,[32-35] push-pull dyes **12**,[36-43] coumarines **13**,[44-45] pyridinium derivatives **14**,[46] 2,3-diphenylquinoxaline derivatives **15**,[47] dihydroxyanthraquinones **16**,[48] carbazoles **17**,[51-53] helicenes **18**,[54,55] thioxanthenes **19**,[56,57] camphorquinones **20**,[58,59] acridones **21**[60,61] and cyclohexan-1-one **22**[62-64] (See Figure 1).

Photoinitiators of polymerization are actively researched due to the different advantages photopolymerization exhibits over the traditional thermal polymerization. Among the main advantages of this technology, a spatial and a temporal control can be obtained so that this old polymerization technique initially developed for coating applications in the 60's has known a revival of interest for 3D and 4D printing applications.[65-67] High polymerization speeds and high final monomer conversions can also be achieved with short reaction times, enabling to produce tack-free polymers.[68] As other appealing feature, photopolymerization can be carried out at room temperature, what is of crucial importance, especially for dental applications.[69,70] Sunlight can also be used as a cheap and inexhaustible energy source, making photopolymerization a green approach to generate polymers.[71] Especially, the possibility to polymerize with sunlight is of prime importance for outdoor applications such as paints drying, etc.... As other appealing feature, photopolymerization can also be carried out without solvents, enabling to drastically reduce the amount of released volatile organic

compounds (VOC).[72-77] If visible light photoinitiators are presently so popular, this is also related to the cure depth which is directly correlated to the wavelength of irradiation.[78]

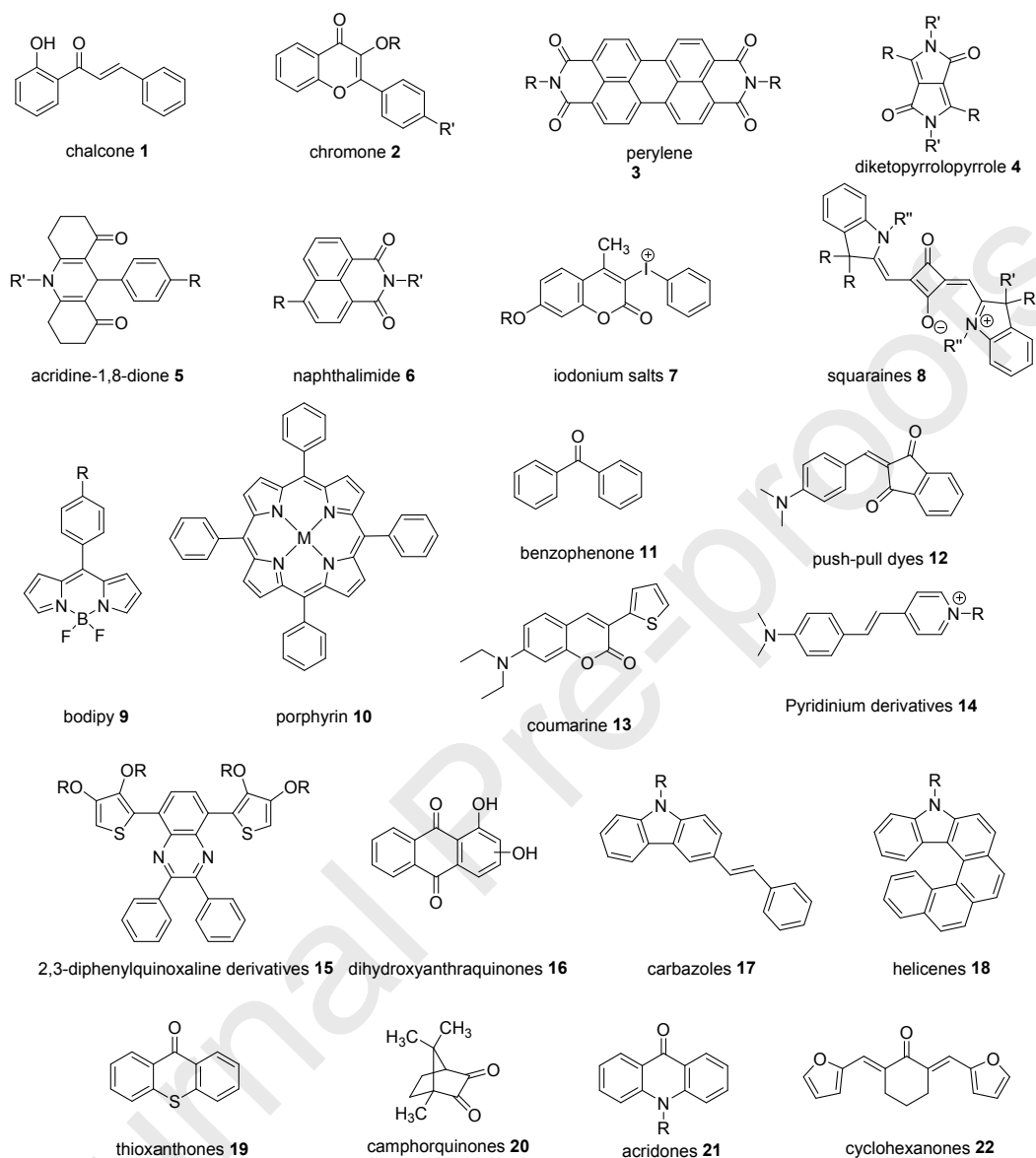


Figure 1. Different families of compounds (1-22) recently examined as visible light photoinitiators of polymerization activable under low light intensity.

As evidenced in the Figure 2 for a polystyrene latex with an average diameter of 112 nm, the light penetration can range between 600 μm in the UV range to 5 cm in the near-infrared region, revolutionizing the scope of applications of photopolymerization. Notably, under long wavelength irradiation, the access to thick and filled samples is rendered possible.[79,80] In understanding the light penetration dependence in photocurable resins, different parameters have been identified such as the photoinitiator concentration (internal

filter effects), the refractive index of monomers or the light scattering by heterogeneous mixtures.[81,82]

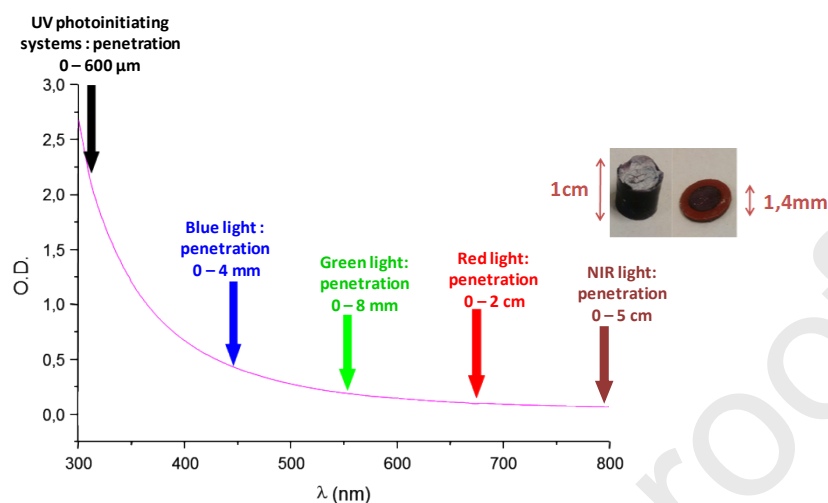


Figure 2. Light penetration inside a polystyrene latex with an average diameter of 112 nm. Inset: examples of polymerized resins containing fillers. Reproduced with permission from Bonardi et al. [78]. Copyright 2018 American Chemical Society.

Parallel to the performances obtained with these different dyes, a new approach recently applied to photopolymerization has notably motivated the development of new photoinitiators, namely the photoredox catalysis. Indeed, photoredox catalysis initially developed for organic chemistry[83-93] has rapidly been extended to the photopolymerization area, so that the photoinitiator could behave as a photocatalyst, when combined with the suitable additives.[94-96] As a consequence of this, a drastic reduction of the photoinitiator content can be obtained, addressing the extractability issue.[97-103]

Among polyaromatic structures, pyrene which is composed of four aromatic rings fused together belongs to the family of Polycyclic Aromatic Hydrocarbons (PAHs) which is the subject of interdisciplinary research in the fields of chemistry, physics, materials science, and biology.[104-107] Concerning more specifically pyrene, this compound has notably been extensively studied for the design of photoluminescent materials,[108,109] pyrene exhibiting a photoluminescence quantum yield of 0.68 in the solid state.[110,111] However, as commonly observed for planar polyaromatic structures, pyrene exhibits a strong tendency to dimerize at high concentration, adversely affecting its solubility in most of the common organic compounds.[112-120] To rationalize this, several empirical and semi-empirical models have

been proposed in the literature.[121] Parallel to this, the fluorescence of pyrene is often admixed with that of excimers, resulting from the dimerization of pyrene.[122-124] To overcome this drawback, *tert*-butyl groups are often introduced at the 2,7-positions of pyrene but this compound remains relatively expensive so that the search of simple substitution method of the pyrene is still an active research field.[125] Nonetheless, pyrene remains an interesting building block for the design of photoinitiators due to its long excited state lifetime (50-90 ns),[126,127] its easiness of functionalization with simple reactions such as bromination, Vilsmeier-Haak or Friedel and Crafts acylation reactions (See Figure 3).[128] Photophysical properties of pyrenes have been extensively in the literature, with numerous studies reported in the 70's so that it constitutes a solid background for the design of visible light photoinitiators.[129] Access to azapolyacenes is also possible with pyrene, by oxidation of the adjacent aromatic rings, enabling to prepare pyrene-diones or pyrene-tetraones.[130]

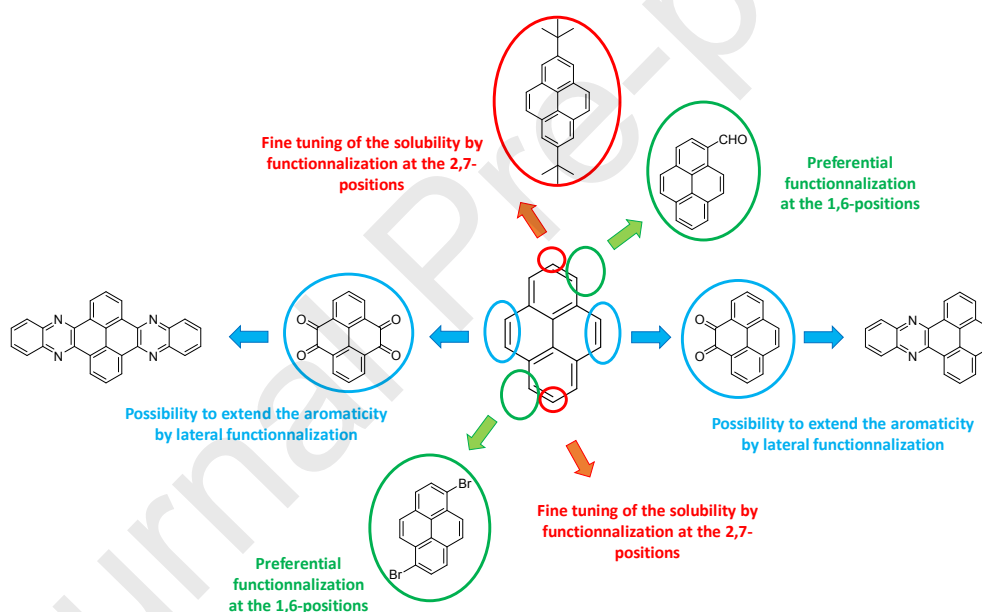
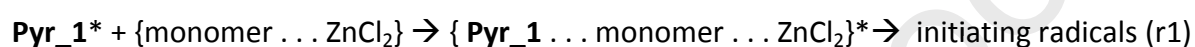


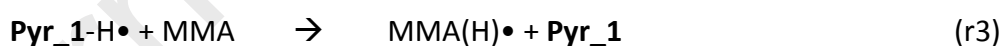
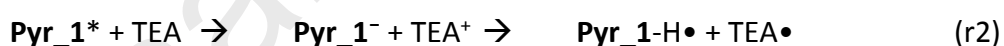
Figure 3. The different possible chemical modifications of the pyrene core.

Historically, 1-(bromoacetyl)pyrene (**Pyr_2**) which is a derivative of pyrene (**Pyr_1**) has been extensively studied by Daswal and coworkers as a UV-photoinitiator for the copolymerization of styrene with *n*-butyl acrylate,[131] methyl methacrylate[132] or acrylonitrile in solution (See Figure 4).[133] In these different studies, modification of the substitution pattern of pyrene was determined as strongly influencing the reactivity of the pyrene.[134] Thus, during the free radical polymerization (FRP) of *n*-butyl acrylate, if **Pyr_1** proved to be ineffective in initiating the FRP of acrylates, incorporation of an acetyl group in

Pyr_3 and then of a bromoacetyl group in **Pyr_2** markedly accelerated the polymerization rate of *n*-butyl acrylate. However, the arsonium salt of **Pyr_3** i.e. **Pyr_4** proved to be a less efficient photoinitiator than **Pyr_3**, evidencing the crucial role of the substitution pattern on the photoreactivity. Besides, in earlier works, the possibility to initiate the FRP of acrylonitrile, styrene or methyl methacrylate was demonstrated by mixing **Pyr_1** with different Lewis acids such as ZnCl₂, Zn(OAc)₂ or Zn(NO₃)₂.^[135] In this last case, the formation of a complex between the monomer, **Pyr_1** and the Lewis acid was postulated as being at the origin of the radicals responsible of the photoinitiation process (See r1). However, the nature of the radicals formed by mean of the charge transfer was not discussed in this work.



In other studies, the photopolymerization of different monomers with UV light was obtained by formation of charge transfer complexes between **Pyr_1** and triethylamine (TEA) (See r2).^[136] Considering that **Pyr_1** was not consumed during the polymerization process, two plausible mechanisms were proposed to support the high polymerization efficiency while regenerating **Pyr_1** (see r3 and r4). It was notably suggested that the initiating radicals could be produced from the interaction of methyl methacrylate (MMA) with the (**Pyr_1**⁻,TEA⁺) ion pair and/or the hydroropyrenyl radicals. Besides, the experimental data were insufficient to allow a discrimination between the two possible processes.



A few years later, time-resolved absorption spectroscopy experiments revealed the interaction of the pyrene anion **Pyr_1**⁻ with the monomer to be responsible of the generation of radicals, according to equations (r5 and r6).^[137]



In 2002, a new approach consisting in using pyrene as a photosensitizer for onium salts was proposed.^[138] Cationic polymerization initiated with onium salts is a well-established

procedure in industry but this process still suffers from a slower polymerization rate compared to that of the free radical polymerization. Additionally, absorption of onium salts is strongly centered in the UV region so that no polymerization can be initiated with a visible light. This drawback could be overcome by photosensitization with electron-rich polyaromatic compounds even if these polyaromatic structures often exhibit a low solubility in monomers of interest for cationic photopolymerizations.[139,140] If several mechanisms exist, the most efficient one consists in the photosensitization of the onium salts by electron transfer (See r7-r10).[141,142]



Face to the solubility issue, Crivello and coworkers developed a series of pyrene-based photosensitizers exhibiting a higher compatibility with monomers and alkyl chains than the previous ones and polymerizable groups were also attached to **Pyr_5-Pyr-7** for the covalent linkage to the polymer networks (See Figure 4).

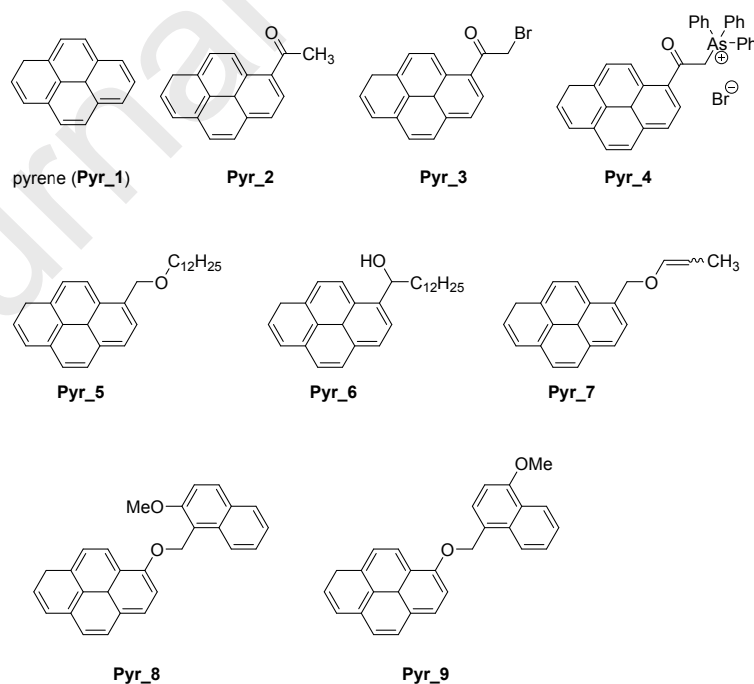
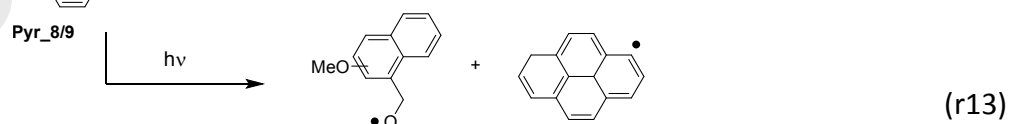
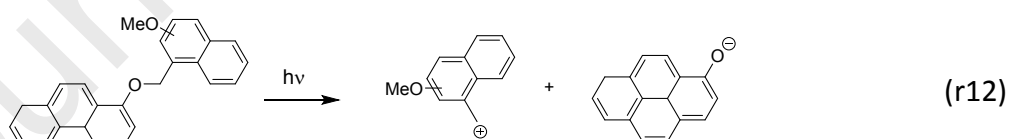
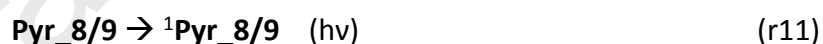


Figure 4. Chemical structures of **Pyr_1-Pyr_9**.

If the control experiments without photosensitizers **Pyr_5-Pyr-7** revealed the higher reactivity of the photosensitized resins for the cationic polymerization of epoxides even under UV light irradiation, polymerization with direct exposure to sunlight was rendered possible for the photosensitized resins, evidencing the benefits of the two-component systems (dyes/iodonium salt). In 2014, the concept of charge transfer used to generate initiating species was extended to intramolecular charge transfer and in this aim, two derivatives **Pyr_8** and **Pyr_9** were designed and synthesized.[143] Analysis of the photoproducts obtained by photolysis of **Pyr_8** and **Pyr_9** in different solvents revealed the photodecomposition to preferentially afford a methoxynaphthalen-1-ylmethyl carbocation/pyrenyloxanion pair instead of an methoxynaphthalen-1-ylmethoxy radical/pyrenyl radical pair (see r11-r13). Especially, the methoxynaphthalen-1-ylmethyl carbocation was determined as being the initiating species for both the polymerization of styrene and cyclohexene oxide. Control experiments carried out in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) revealed the monomer conversion to remain unaffected, demonstrating that the polymerization of styrene was occurring according to an ionic mechanism and not by a radical process. Despite the substitution of **Pyr_8** and **Pyr_9** with naphthalene groups, the two compounds only presented intense absorption bands close to the visible region so that the different polymerization experiments could only be carried out with a 500 W high-pressure Hg lamp.



In this review, an overview of the different photoinitiators comprising a pyrene unit and used as photoinitiators/photosensitizers under visible light and low-light intensity is presented. In a general way, the questions which have been solved with the development of these pyrene-based photoinitiators were first getting high polymerization efficiencies while

adapting their structures to the currently available light sources. To evidence the remarkable photoinitiating abilities of the newly developed pyrene-based photoinitiators/ photosensitizers, comparisons with reference compounds will be established.

2. Pyrenes as photoinitiators of polymerization

2.1. Trifunctional photoinitiators

As evidenced in the introduction section, absorption of **Pyr_1** is strongly centered in the UV region and the different chemical modifications done in **Pyr_2-Pyr_9** were insufficient to redshift their absorptions towards the visible range. These photoinitiators are also small molecules so that their migratability inside the polymer network can be a major issue for numerous applications.[144-146] In 2012, Lalevée and coworkers developed an original strategy to increase the molar extinction coefficient of **Pyr_10** while addressing the migratability issue by attaching three pyrene units to the truxene core while creating an oligomeric structure.[147] By summing up the contributions of both the pyrenes units and truxene,[148] a broad absorption band ranging from 330 nm to 415 nm could be determined in acetonitrile, with a long tail extending until 500 nm. This absorption spectrum drastically differs from that of **Pyr_1** which is severely limited, not extending beyond 380 nm. Enhancement of the light absorption properties of **Pyr_10** relative to that of **Pyr_1** relies on an efficient coupling of the molecular orbitals of the peripheral pyrene units with that of the truxene core, resulting in a higher delocalization of the molecular orbitals and a redshifted absorption. By using the appropriate spacer in **Pyr_10**, a compound worthwhile for both the cationic polymerization (CP) of epoxides and the free radical polymerization (FRP) of acrylates was obtained. Fluorescence quenching experiments revealed **Pyr_10** to promote a fast decomposition of diphenyl iodonium (Ph_2I^+) by electron transfer, an interaction rate constant of $2 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ being determined. By adding *tris*(trimethylsilyl)silane ($(\text{TMS})_3\text{Si-H}$) to the previous two-component system, formation of silyl radicals ($(\text{TMS})_3\text{Si}\cdot$) by hydrogen abstraction with the phenyl radicals $\text{Ph}\cdot$ was clearly demonstrated, possibly initiating a FRP process. Parallel to this, $(\text{TMS})_3\text{Si}\cdot$ can be easily oxidized by Ph_2I^+ or **Pyr_10⁺**, generating silylium cations capable to initiate the Free Radical Promoted Cationic Polymerization (FRPCP) of epoxides (See Figure 5). Therefore, the three-component system

(**Pyr_10**/Ph₂I⁺/(TMS)₃Si-H) constitutes a unique dual initiating system for generating interpenetrated networks (IPNs).

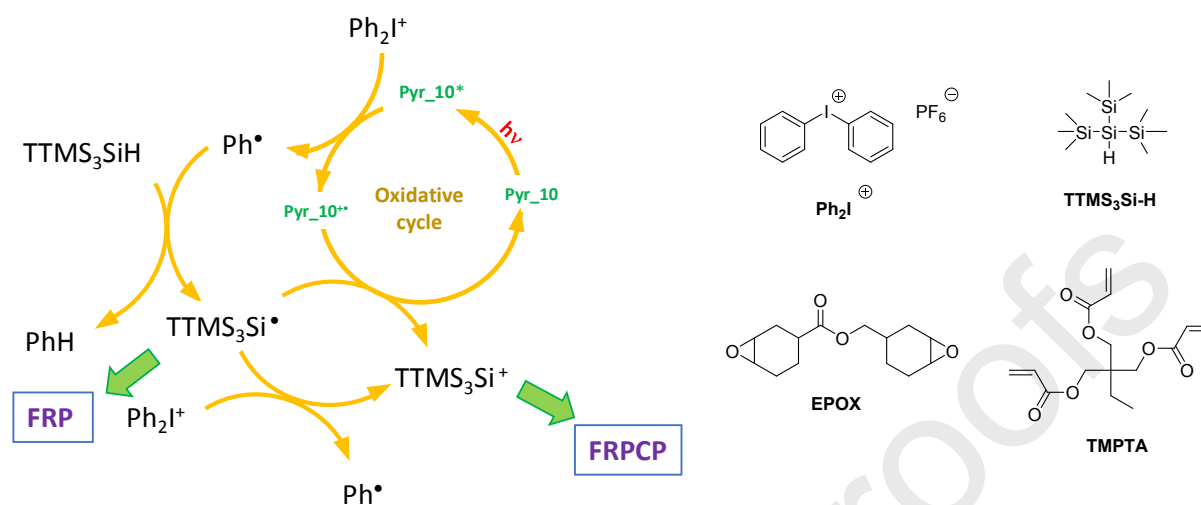


Figure 5. The catalytic cycle involved in the generation of radical and cationic initiating species with **Pyr_10**.

While examining the FRPCP of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX), the three-component system **Pyr_10**/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w) could furnish a final monomer conversion of 70% within 100s upon irradiation with a halogen lamp under air whereas a monomer conversion of only 45% was obtained with the two-component system **Pyr_10**/Ph₂I⁺ (0.2%/2% w/w) in the same conditions. Conversely, no polymerization could be obtained with the three component system **Pyr_1**/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w), consistent with previous results reported in the literature.[149] While using a reference photocatalyst i.e. Ir(piq)₃ for the three component system Ir(piq)₃/(TMS)₃Si-H/Ph₂I⁺ (0.2%/3%/2% w/w), a final monomer of 35% was obtained after 800 s of irradiation under air, far from the 70% obtained with **Pyr_10**. The high reactivity of the three component systems comprising silanes is largely related to the unique ability of silanes to convert the different peroxy radicals formed in the reaction medium by addition of oxygen onto the propagating radicals into new reactive silyl radicals.[150-156] High efficiencies could be maintained upon irradiation of the resins with a blue LED bulb or a laser diode at 405 nm, conversions of 57 and 37% were respectively obtained for the CP of EPOX. Similarly, the remarkable efficiencies of the two and three-component systems were also demonstrated during the FRP of trimethylolpropane triacrylate (TMPTA), conversions of 25

and 55% being obtained after 300s of irradiation with a halogen lamp. Finally, the hybrid cure of a TMPTA/EPOX blend (50/50 w/w) could provide a tack-free polymer within a few minutes, with acrylate and epoxy conversions of 75% and 55% respectively.

In the search for new architectures aiming at optimizing the electronic coupling between the central core and the peripheral pyrenes, several strategies were developed to prepare trifunctional photoinitiators, as exemplified with **Pyr_11** possessing a triazine central core (See Figure 6).[157]

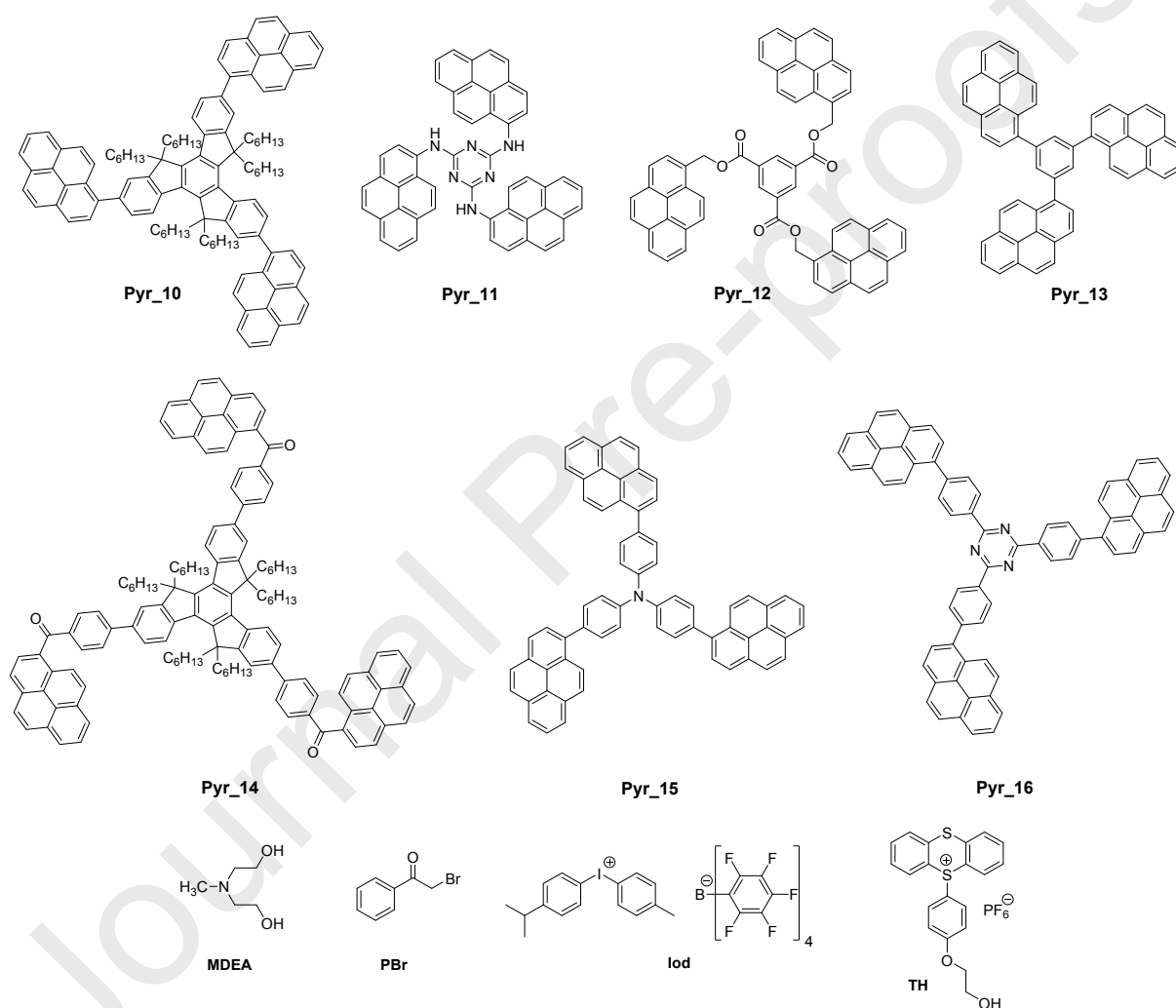
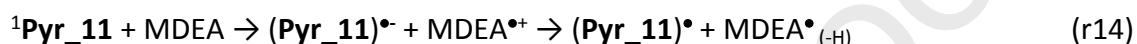


Figure 6. Chemical structures of organophotocatalysts **Pyr_10-Pyr_16** and co-initiators.

Here again, a high rate constant of interaction ($1.2 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$) between **Pyr_11** and Ph_2I^+ was found, evidencing the efficiency of the electron transfer from **Pyr_11** to the iodonium salt. If the absorption of **Pyr_11** was more limited than that of **Pyr_10** as the absorption spectrum was not extending beyond 400 nm, the three-component system **Pyr_11**/ $(\text{TMS})_3\text{Si-H}/\text{Ph}_2\text{I}^+$ (1%/3%/2% w/w) could efficiently promote the FRPCP of EPOX (80%

after 200s of irradiation with a Xe–Hg lamp ($\lambda > 300$ nm)) or the FRP of TMPTA (80% after 400s of irradiation with the same light source). The same holds true when using *N*-methyl diethanolamine (MDEA) as the co-initiator for **Pyr_11**. Thanks to the high rate constant of interaction of $2 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$, the triazine derivative/MDEA (1%/5% w/w) combination was also a good initiating system, enabling to reach a final conversion higher than 70% after 400s for TMPTA, upon exposure of the resin to a Xe-Hg lamp ($\lambda > 300$ nm) in laminate. In this last case, efficiency of the photoinitiating system was assigned to the generation of α -aminoalkyl radicals according to the equation r14. These radicals are well known to be very efficient structures for the addition on acrylates.[158]



Pyr_11 could also initiate alone the FRP of TMPTA even if the polymerization process was less efficient (55% of conversion after 400s) (See Figure 7). In this last case, photoinitiation was ascribed to a hydrogen abstraction reaction between ${}^*\text{Pyr}_{11}$ and TPMTA, producing an initiating radical $\text{TMPTA}(-\text{H})^{\bullet}$, according to the following equation r15.

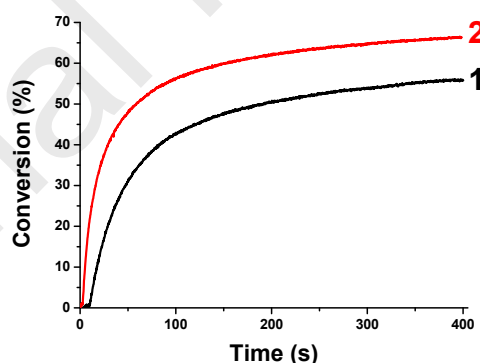
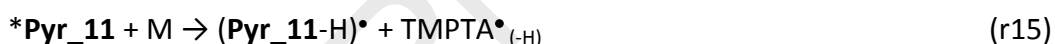
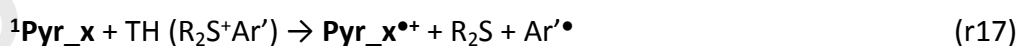


Figure 7. Photopolymerization profiles of TMPTA upon irradiation with a Xe-Hg lamp ($\lambda > 300$ nm; $I = 66 \text{ mW/cm}^2$) in laminate (1) **Pyr_11** (1% w/w) and (2) **Pyr_11**/MDEA (1%/5% w/w). Reproduced with permission from Tehfe et al. [147]. Copyright 2012 American Chemical Society.

In 2013, a more extended study was carried out on five trifunctional organophotocatalysts **Pyr_12-Pyr_16** varying by the nature of the central core (See Figure 6).[159] To determine the influence of the central core on the photoinitiating abilities, four different co-initiators were examined, namely, iodonium salts, sulfonium salts, alkyl halides

and amines (See Figure 7). As the first finding, except for **Pyr_12** and **Pyr_13** for which absorption maxima located at 350 nm were determined for the two compounds due to the lack of conjugation between the pyrene end-groups with the central benzene ring for **Pyr_12** and the twisted structure of **Pyr_13** interrupting the π -conjugation, **Pyr_14-Pyr-16** showed broader absorption spectra extending until 450 nm. The highest molar extinction coefficient was found for **Pyr_14** ($13 \times 10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$ at 353 nm) (See Table 1). All trifunctional organophotocatalysts showed high rate constants of interaction with the four co-initiators, ensuring an efficient production of initiating radicals. To illustrate this, rate constants of 1.5×10^{10} , 9×10^9 , 1×10^{10} and $3.7 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$ were respectively determined for the **Pyr_13**/PBr, **Pyr_13**/MDEA, **Pyr_13**/Iod and **Pyr_13**/TH combinations, (where PBr, Iod and TH stands for phenacyl bromide, [methyl-4-phenyl(methyl-1-ethyl)-4-phenyl]iodonium tetrakis(pentafluorophenyl)borate and (4-hydroxyethoxyphenyl)thianthrenium hexafluorophosphate) demonstrating that the electron transfer between **Pyr_13** and the co-initiators was under diffusion control. Comparison of the polymerization profiles obtained for the polymerization of EPOX using the two-component system **Pyr_x** ($x = 12-16$)/Iod (0.2%/2% w/w) under air revealed the fastest polymerization rate and the highest final monomer conversion to be obtained with the **Pyr_13**/Iod couple. Final conversions of 80% were obtained upon irradiation with a Xe-Hg lamp after 200s, far from the 50% conversion obtained with the **Pyr_1**/Iod couple. Good conversions were also obtained with the two-component systems **Pyr_x** ($x = 12-16$)/TH (0.2%/2% w/w), furnishing similar monomer conversions. Based on the equations r16 and r17, reactions of the photosensitizer **Pyr_x** with co-initiators furnished in both case radical cations $\text{Pyr}_x^{\bullet+}$ that can initiate the CP of epoxides.



Besides, a structure-performance relationship could not be established with this series, three parameters being concomitantly involved in the photoinitiation process: 1) the light absorption properties, 2) the rate constants of interaction between the dyes and the co-initiators 3) the ability of $\text{Pyr}_x^{\bullet+}$ to initiate the CP process.

Unexpectedly, storage stability of the resin based on the **Pyr_15**/Iod couple was relatively limited, a complete polymerization of the resin being observed after 24 hours in the

dark and at room temperature. As evidenced by electron spin resonance (ESR) experiments, formation of radical cations could be detected in the resin even without irradiation. Except for **Pyr_15**, all the other dyes furnished stable formulations that could be kept for weeks in the dark. While examining the possibility to carry out the FRP of TMPTA only in the presence of **Pyr_x** ($x = 12-16$), a polymerization process could be evidenced but the inhibition time was relatively long and the final conversions low. When combined with MDEA or PBr, the two-component systems **Pyr_x** ($x = 12-16$)/MDEA or the **Pyr_x** ($x = 12-16$)/PBr shortened the inhibition times jointly with an improvement of the final monomer conversions. Surprisingly, no modification of the monomer conversions was observed while using the three-component systems **Pyr_x** ($x = 12-16$)/MDEA/PBr, the polymerization profiles almost superimposing that obtained with the two-component systems. Besides, in the case of the three-component systems, a catalytic behavior was expected, the two additives MDEA and PBr being involved both in the oxidative and the reductive cycles (See Figure 8). In fact, the ESR experiments revealed the contribution of the reductive cycle to be marginal in the overall generation of radicals, supporting the absence of improvement of the TMPTA conversion with the three-component systems.

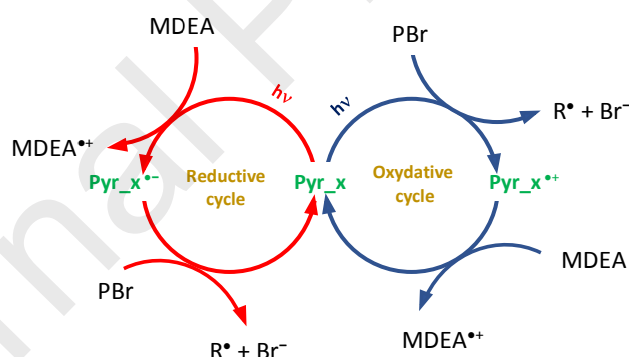


Figure 8. The oxidative and the reductive cycles coexisting in the three-component system **Pyr_x** ($x = 12-16$)/MDEA/PBr.

2.2. Bifunctional photoinitiators

Parallel to the trifunctional photoinitiators **Pyr_10-Pyr_16**, the design of bifunctional photoinitiators was also examined as the reduction of the polyaromaticity can potentially address the solubility issue in the photocurable resins. If this last point was not especially addressed with the series of organophotocatalysts **Pyr_17-Pyr_21**, comparison of the photoinitiating ability of **Pyr_17-Pyr_21** revealed these properties to be similar to that of the

previous series **Pyr_12-Pyr_16** (See Figure 9).[159] Besides, stabilities of the epoxide resins prepared with **Pyr_17-Pyr_21** were far behind that of the previous series since a thermal polymerization was observed with most of the two-component systems **Pyr_x (x = 19-21)**/Iod (1%/2% w/w).

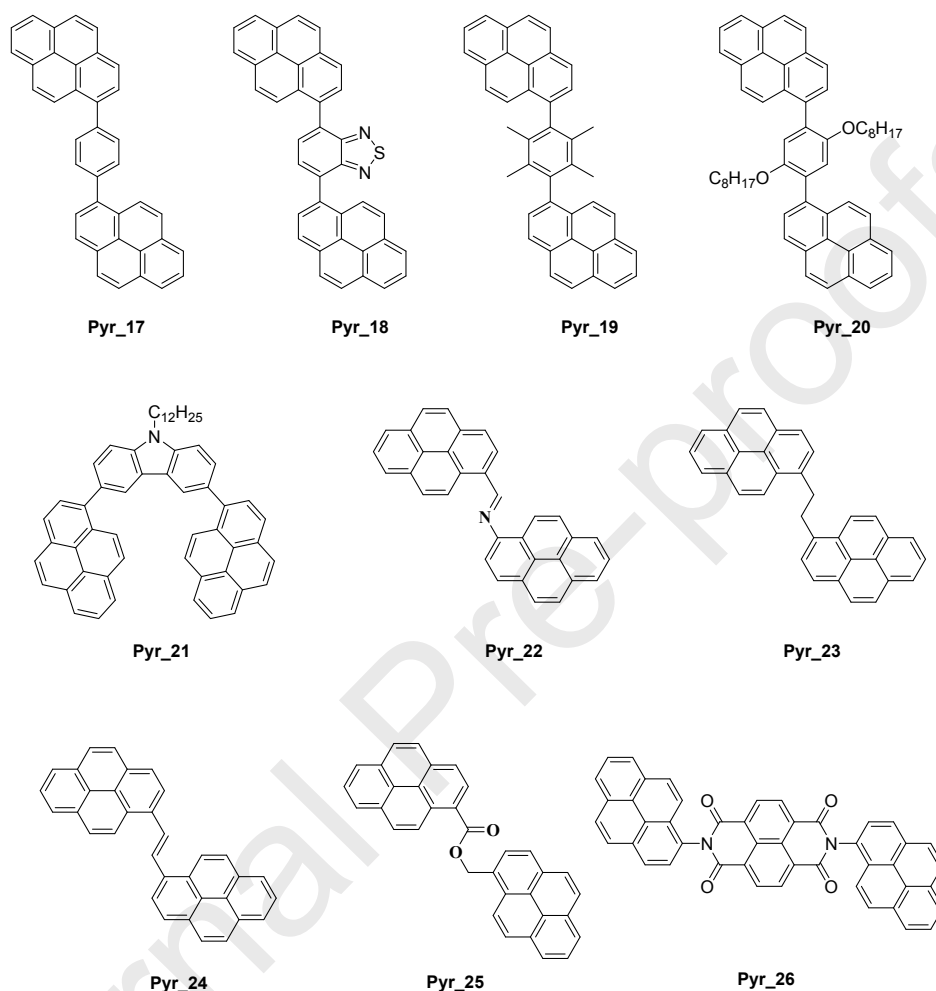


Figure 9. Chemical structures of pyrene-based photoinitiators **Pyr_17-Pyr_26**.

In the **Pyr_17-Pyr_21** series, carbon-carbon bonds between aromatic rings have been used to connect the pyrene groups to the central aromatic rings. By the formation of a biaryl structure, a strong torsion is automatically introduced into the molecule due to the steric hindrance generated by the presence of consecutive aromatic rings.[160-162] To overcome this drawback, a spacer can be introduced and the connection of pyrenes by mean of flexible linkages was examined for this purpose (see Figure 9).[163] Benefits of this strategy were immediate since the absorption spectra of **Pyr_22** and **Pyr_24** which possess conjugated spacers could extend until 480 nm for **Pyr_24** and 540 nm for **Pyr_22**, with molar extinction coefficients of 28 000 and 44 000 $M^{-1}.cm^{-1}$ for **Pyr_24** and **Pyr_22** respectively. By separating

the two pyrene units with a spacer, the π -conjugation between pyrene could be restored, red-shifting the absorption. Conversely, the lack of electronic communication in **Pyr_23** and **Pyr_25** furnished two dyes of more limited absorptions (not extending beyond 450 nm) and with smaller molar extinction coefficients ($10\,000$ and $4\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ for **Pyr_22** and **Pyr_25** respectively). Consequently, these new photoinitiators **Pyr_22-Pyr_25** allowed the use of long wavelength excitations (halogen lamp, laser diode at 457 nm or Xe–Hg lamp) for photopolymerization processes whereas **Pyr_1** was inefficient in these conditions, this compound not absorbing beyond 380 nm. In the presence of the three-component **Pyr_x**/ Ph_2I^+ / $(\text{TMS})_3\text{Si-H}$ or **Pyr_x**/TH/ $(\text{TMS})_3\text{Si-H}$ systems, excellent polymerization profiles of EPOX could be obtained with **Pyr_23** and **Pyr_24**, tack-free polymers being obtained in 540 s with a laser diode at 457 nm or an halogen lamp under air. Conversely, no FRPCP of EPOX could be initiated with **Pyr_25** and a thermal degradation of the formulation based on **Pyr_22** was evidenced as occurring within a few seconds. Instability of **Pyr_22** in resins can be confidently assigned to the imine group introduced between the two pyrene groups, giving rise to hydrolysis processes. Notably, imines are well-known in organic chemistry to be highly sensitive to the protic character of the reaction media.[164] **Pyr_22** and **Pyr_23** proved to be versatile photoinitiators since hybrid cure experiments involving both a CP and a FRP process could be successfully carried out under air. Thus, the photopolymerization of a TMPTA/EPOX blend, TMPTA/DVE-3 blend (where DVE-3 stands for triethyleneglycol divinyl ether) or DVE-3/EPOX blends could furnish tack-free coatings within ten minutes upon irradiation with a laser diode at 457 nm (See Figure 10).

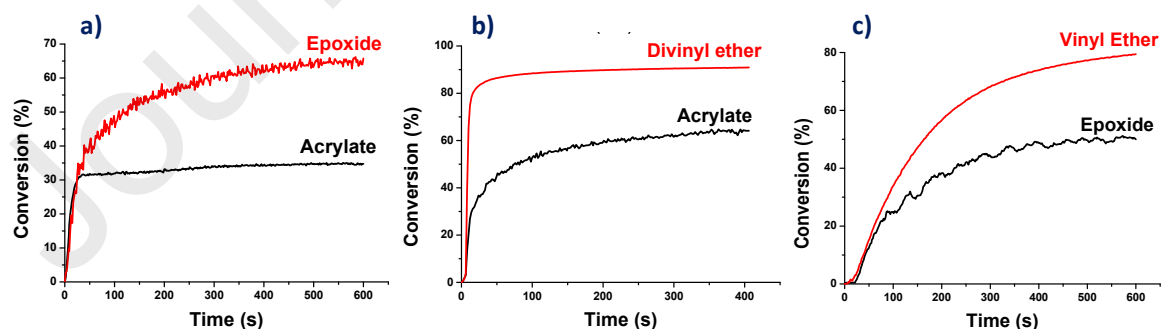


Figure 10. Photopolymerization profiles of different monomer blends (50%/50%) using the three-component system **Pyr_24**/ Ph_2I^+ / $(\text{TMS})_3\text{Si-H}$ (0.2%/3%/2% w/w) upon irradiation with a laser diode at 457 nm a) polymerization of a TMPTA/EPOX blend under air; b) polymerization of a TMPTA–DVE-3 blend in laminate; c) polymerization of an EPOX/DVE-3 blend in laminate. Adapted from ref. [163] with permission from The Royal Society of Chemistry.

In 2014, Lalevée and coworkers tried to develop a series of photoinitiators based on the naphthalene scaffold.[165] Unfortunately, solubility of the photoinitiators in resins was the major issue of this series as exemplified with **Pyr_26** (see Figure 9). No polymerization processes could be initiated with this compound due to its poor solubility in monomers.

2.3. Push-pull dyes

Push-pull dyes which are composed of electron donors connected to electron acceptors by mean of a conjugated or a none-conjugated spacer is an easy way to design dyes strongly absorption in the visible range but also exhibiting high molar extinction coefficients.[166-171] Considering that pyrene-1-carboxaldehyde is commercially available and that pyrene is an electron-rich group, pyrene therefore constitutes an excellent candidate for the design of push-pull chromophores.[172-177] Interest for push-pull dyes is also sustained by the easiness of synthesis, most of these compounds being obtained by a Knoevenagel reaction. It has to be noticed that this condensation reaction is an old reaction as this procedure was developed as soon as 1896 by Knoevenagel for the synthesis of the first push-pull dyes based on benzaldehyde as the electron donor.[178] Besides, the different studies done by Lalevée and coworkers have rapidly revealed that the molar extinction coefficient was not the only parameter governing the photoinitiating ability. To illustrate this, **Pyr_27** and **Pyr_28** are two dyes characterized by broad absorption bands extending until 470 nm (See Figure 11).[163] However, all polymerization tests (CP and FRP) failed albeit excellent light absorption in the visible range. Attempt to rationalize this unexpected behavior was carried out with another dye i.e. **Pyr_29**. [179] The absorption of **Pyr_29** was relatively broad, with a charge transfer band extending from 300 to 550 nm. An absorption maximum located at 464 nm and a molar extinction coefficient of $21\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ could also be determined for **Pyr_29**, allowing an efficient matching of its absorption with the light source emission spectra (halogen lamp and laser diodes emitting at 405, 457, 473, 532 nm). To get a deeper insight into the optical properties of **Pyr_29**, the solvatochromism was examined with different empirical polarity scales such as the Dimroth–Reichardt's,[180] Kamlet–Taft's,[181] Catalan's,[182] Lippert–Mataga's,[183] Bakhshiev's,[184] Kawski–Chamma–Viallet's,[185] McRae's,[186] and Suppan's scales.[187] Interestingly, linear correlations could be obtained

with the Bakhshiev's, Kawski–Chamma–Viallet's, Lippert–Mataga, McRae's and Suppan's polarity scales, with strong negative slopes.

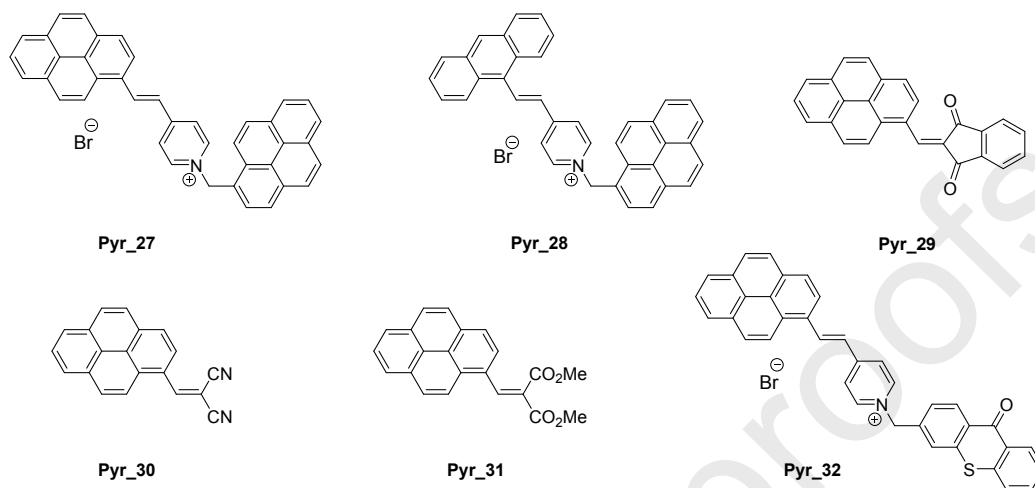
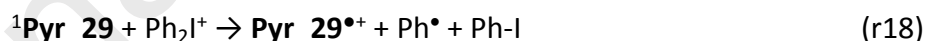


Figure 11. Chemical structures of push-pull dyes **Pyr₂₇-Pyr₃₅**.

Negative slopes obtained with the different plots are indicative of a significant charge redistribution upon photoexcitation. Chen tested as a photoinitiator, no ring opening polymerization of EPOX could occur with this compound. In fact, photolysis experiments revealed the UV-visible absorption spectrum of the **Pyr₂₉/Ph₂I⁺** solution to remain unchanged, indicative of a back-electron transfer regenerating **Pyr₂₉** (see r18). As a result of this, decomposition of the iodonium salt was ineffective and no FRP or CP could occur.



These results were confirmed the same year by another study devoted to **Pyr₃₀** and **Pyr₃₁**.^[188] Here again, the two dyes were inefficient for photopolymerization due to the back-electron transfer, impeding the formation of radicals. Finally, polymerization processes could be initiated with **Pyr₃₂** possessing a thioxanthone end group.^[189] Photolysis of the **Pyr₃₂/Ph₂I⁺** solution revealed the photolysis to be extremely slow, consistent with the results obtained with **Pyr₂₉-Pyr₃₁**. By laser flash photolysis, excitation of **Pyr₃₂** and analyses of the transient species revealed the maximum absorption wavelengths of these transient species to superimpose that of the thioxanthone triplet states.^[190] Consequently, photoinitiating ability of **Pyr₃₂** was assigned to the contribution of the thioxanthone moiety and not to originate from the push-pull part attached to it. Finally, push-pull dyes that could

really initiate a polymerization process were reported in 2013. As specificity, **Pyr_33-Pyr_35** are not neutral dyes by cationic structures (see Figure 12).[46] In this last case, photolysis process of the **Pyr_x (x = 33-35)/Ph₂I⁺** solution was extremely fast since a complete bleaching of the solution was observed within 40s. However, photoinitiating abilities of **Pyr_33-Pyr_35** cannot be assigned to the presence of the pyridinium groups. Indeed, numerous neutral push-pull dyes have been reported as efficient photoinitiators subsequently to this work.[191,192] Considering the minor structural modifications existing between **Pyr_27** and **Pyr_33**, **Pyr_32** and **Pyr_34/Pyr_35** and the difference of photoinitiating abilities evidenced between these different structures, the extensive works done by several research groups concerning the structural modifications of a selected structure (push-pull dyes, benzophenones, thioxanthenes, porphyrins, metal complexes, etc...) is totally justified.

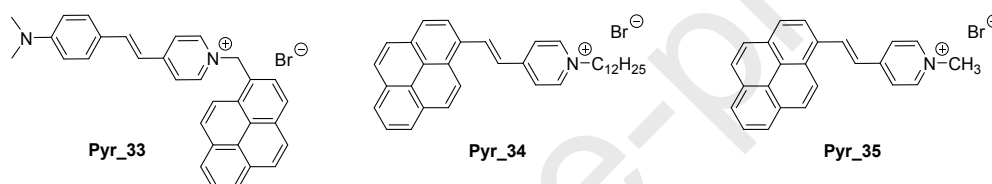


Figure 12. Chemical structures of push-pull dyes **Pyr_33-Pyr_35**.

2.4. Benzophenone and thioxanthone derivatives

Benzophenone is a well-known UV photoinitiator of polymerization and various strategies have been developed to redshift its absorption towards the visible range. In this aim, substitution of the benzophenone core with various chromophores,[193,196] its incorporation in high molecular weight arrangements such as difunctional [197,199] and trifunctional [200] structures, oligomers,[201] dendrimers[202] and even polymers[203-206] have been examined. By mean of a strong coupling of the molecular orbitals within the compounds, new chromophores that no longer resembles that of benzophenone were obtained. To modify the absorption properties of benzophenone, several strategies were developed.

As the first approach, the covalent linkage of pyrene introduced as substituents of benzophenone was proposed, as exemplified with **Pyr_36** [163] or **Pyr_37** [32]. But the same strategy was also used to prepare thioxanthone derivatives such as **Pyr_38** (See Figure 13). By

mean of the strong coupling between benzophenone and pyrene, a 170-fold enhancement of the molar extinction coefficient of **Pyr_37** compared to that of benzophenone could be obtained ($\lambda_{\max} = 348 \text{ nm}$ ($26\,000 \text{ M}^{-1}\cdot\text{cm}^{-1}$) for **Pyr_37** vs. $\lambda_{\max} = 335 \text{ nm}$ ($150 \text{ M}^{-1}\cdot\text{cm}^{-1}$ for benzophenone)). Conversely, a 7-fold enhancement of the molar extinction coefficient was only observed for **Pyr_38** compared to isopropylthioxanthone ($\lambda_{\max} = 357 \text{ nm}$ ($32\,000 \text{ M}^{-1}\cdot\text{cm}^{-1}$) for **Pyr_38** vs. $\lambda_{\max} = 383 \text{ nm}$ ($4\,700 \text{ M}^{-1}\cdot\text{cm}^{-1}$ for isopropylthioxanthone))

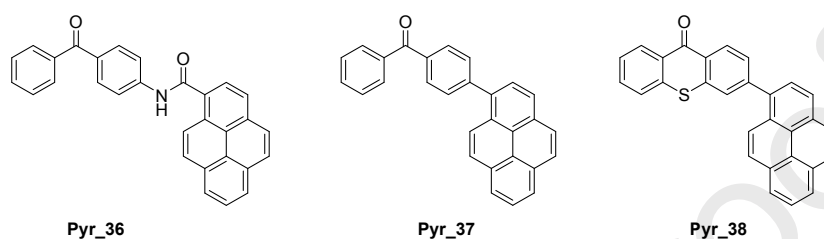


Figure 13. Chemical structure of pyrene-based photoinitiators **Pyr_36-Pyr_38**.

Comparison of the photoinitiating ability of **Pyr_37** with that of **Pyr_22-Pyr_25** and **Pyr_36** revealed **Pyr_37** to outperform these different photoinitiators. Besides, **Pyr_37** was less efficient than the trifunctional photoinitiator **Pyr_10** previously mentioned. Several points can be evoked to support the remarkable performances of **Pyr_37**: a high molar extinction coefficient and a high rate constant of interaction with Ph_2I^+ ($1.6 \times 10^{10} \text{ M}^{-1}\cdot\text{s}^{-1}$). Nevertheless, the lower solubility of **Pyr_37** in monomers than **Pyr_10** also support the lower photoinitiating efficiencies. Besides, with regards to the synthesis of **Pyr_10** and **Pyr_37**, **Pyr_37** is clearly more appealing than **Pyr_10**. Indeed, **Pyr_37** can be synthesized in a single step from commercially available reagents contrarily to **Pyr_10** which requires a multistep synthesis. Considering that the enhancement of the monomer conversion remains low (a few percent), going from **Pyr_37** to **Pyr_10**, easiness of synthesis is another parameter that should also be considered, especially for industrial applications.

As a second approach, a series of benzophenone derivatives in which one of the benzene rings has been replaced by a pyrene group has been proposed (See Figure 14).[189] By mean of this strategy, the molar extinction coefficients of **Pyr_39-Pyr_44** could be greatly improved compared to that of benzophenone but remained in the same order than that of pyrene. To illustrate this, compared to benzophenone which exhibits an absorption coefficient

of $120 \text{ M}^{-1}\cdot\text{cm}^{-1}$ at 340 nm (its absorption maximum), absorption coefficients of 8×10^3 , 5×10^3 , 1.8×10^3 , 1.1×10^3 , 4.4×10^3 and $25 \times 10^3 \text{ M}^{-1}\cdot\text{cm}^{-1}$ were determined for **Pyr_39-Pyr_44**, corresponding to an enhancement of the absorption by a factor 67, 42, 15, 9, 27 and 208 respectively. Huge enhancement of the molar extinction coefficient of **Pyr_44** can be assigned to the push-pull effect existing in this dye and resulting from the dimethylamino group. Conversely, if the dimethoxy group in **Pyr_41** is also an electron-donating group, its lower electron-donating ability than that of the dimethylamino group is clearly evidenced, a 15-fold enhancement of the molar extinction coefficient being only obtained.

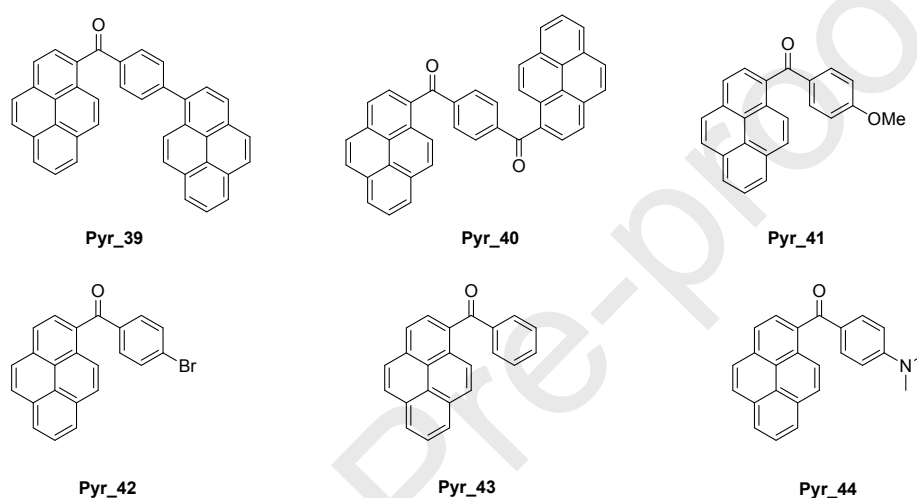


Figure 14. Chemical structure of pyrene-based photoinitiators **Pyr_39-Pyr_44**.

As positive point, absorptions of **Pyr_39-Pyr_44** could extend until 425 nm, therefore redshifted by about 25 nm compared to that of benzophenone and 50 nm compared to that of pyrene (**Pyr_1**) (See Figure 15). Detection of an absorption in the visible range can be assigned to the concomitant enhancement of the molar extinction coefficients for **Pyr_39-Pyr_44** and the replacement of a benzene ring by the pyrene moiety. Interestingly, analyses of the results obtained during the steady state photolysis experiments of the **Pyr_x** ($x = 39-44$)/Iod couples and the transient species detected upon excitation of **Pyr_x** ($x = 39-44$) in the laser flash photolysis experiments revealed that both the singlet and the triplet states of **Pyr_39-Pyr_44** could be involved in the formation of radicals by photodecomposition of the iodonium salt (see equation r19).



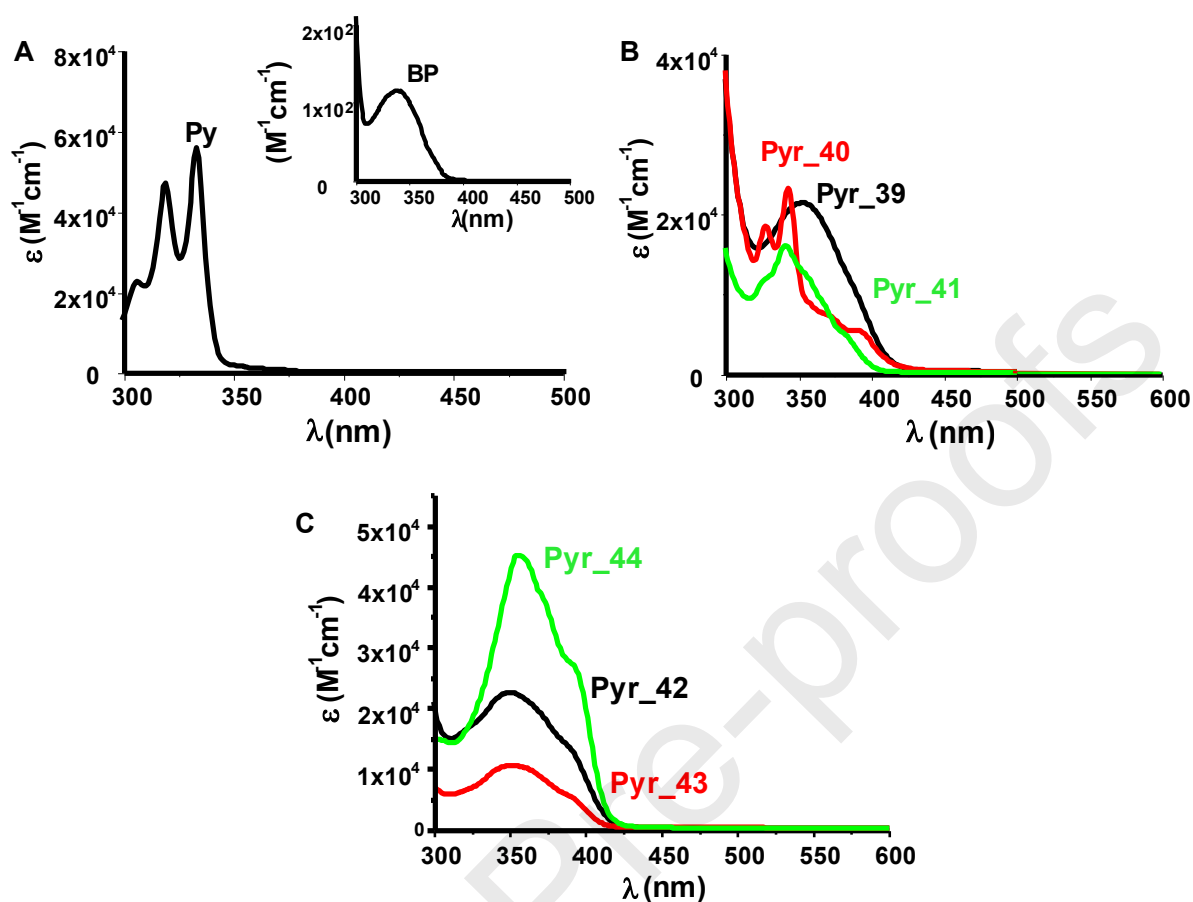


Figure 15. UV-visible absorption spectra of a) pyrene and benzophenone in acetonitrile; b) Pyr_39-Pyr_41 in toluene; c) Pyr_42-Pyr_44 in toluene. Reprinted from ref. [189], Copyright 2013, with permission from Elsevier

These dyes proved also to be versatile photoinitiators as it could produce radicals in oxidative processes (see equation r19) but also in reductive processes when combined with MDEA (see equation r20).



Radical polymerization of TMPTA using the two-component systems **Pyr_x** (**x = 39-44**)/MDEA (1%/2% w/w) upon irradiation with a Xe-Hg lamp in laminate was efficient since final conversions ranging from 54% for **Pyr₄₀** to 73% for **Pyr₄₁** were obtained. The following efficiency order of **Pyr₄₂** > **Pyr₄₄** > **Pyr₄₃** > **Pyr₄₂** > **Pyr₄₀** > **Pyr₃₉** was determined, demonstrating that the benzophenone derivatives benefiting from a push-pull effect could

outperform the others. Considering that an excess of amine used as additive is introduced in the resin, photopolymerization of TMPTA could also be carried out under air, even if lower final monomer conversions were obtained as a result of the oxygen inhibition. Upon a halogen lamp irradiation under air, excellent polymerization profiles could be obtained for the FRPCP of EPOX with the two-component system **Pyr_x** (**x = 39-44**)/Iod (1%/2% w/w). However, the order of reactivity was greatly modified compared to that observed during the FRP of TMPTA. Thus, the highest monomer conversions were obtained with **Pyr_43** and **Pyr_39** (> 70% conversion) whereas the lowest ones were determined with **Pyr_41** (40% conversion) and **Pyr_44** (20% conversion after 400 s). In fact, during the CP of EPOX, the worse candidates were **Pyr_41** and **Pyr_44** whereas these latter were the best photoinitiators for the FRP of TMPTA. In fact, counter-performances determined for **Pyr_41** and **Pyr_44** during the CP of EPOX can be assigned to the low photoinitiating ability of their corresponding radical cations **Pyr_41^{•+}** and **Pyr_44^{•+}**.

2.5. Acridinediones and chromones

Acridinediones are structures well-known in the literature to absorb in the near UV and the visible range. Consequently, these compounds have notably been reported as photoinitiators operating in the UV range,[207,208] or as fluorescent probes for the monitoring of free radical polymerization processes.[209] Acridinediones are also extremely stable structures, these compounds being used as laser dyes.[210-215] In 2013, the unique pyrene-based acridinedione **Pyr_45** was reported (See Figure 16).[216] From a photophysical point of view, replacement of the phenyl ring in **23** by a pyrene in **Pyr_45** resulted in a 2-fold enhancement of the molar extinction coefficient (15 404 M⁻¹.cm⁻¹ at 348 nm vs. 6 900 M⁻¹.cm⁻¹ at 355 nm for **23**). However, the shape of the absorption spectrum of **Pyr_45** drastically differs from that of **23**, resembling that of pyrene. Upon the Xe-Hg lamp exposure (56 mW/cm²), a high final monomer conversion was obtained for the polymerization of EPOX (around 59% after 800 s) with the two-component system **Pyr_45**/Iod (3%/2%, w/w). These performances remained unchanged with the three-component system **Pyr_45**/Iod/NVK (3%/2%/3%, w/w/w), the conversion peaking at 60%. These results are remarkable considering that no polymerization was detected with **23** irrespective of the conditions used and once again highlights the crucial role of the substituent on the photoinitiating ability. Finally, irradiation with a LED at 405 nm (12 mW/cm²) furnished the honorable conversion of 28% with the two-

component system **Pyr_45**/Iod (3%/2%, w/w), demonstrating the high reactivity of the photoinitiating system. The rate constant of interaction of the $^1\text{Pyr}_45/\text{Ph}_2\text{I}^+$ system determined by fluorescence quenching experiments revealed the interaction to be diffusion-controlled ($3 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$). By transient absorption spectroscopy, the interaction rate constants of the $^3\text{Pyr}_45/\text{Ph}_2\text{I}^+$ system was determined as being $6.6 \times 10^6 \text{ M}^{-1}\cdot\text{s}^{-1}$ so that only the singlet states pathway was operative to produce radicals. In fact, the decisive role of pyrene in the photoinitiating efficiency of **Pyr_45** for the CP of EPOX was determined as originating from the location of the radical cation onto the pyrene moiety and not on the acridinedione moiety. This point was clearly evidenced while comparing the performance of **Pyr_45** with that of the other acridinediones examined in this work.

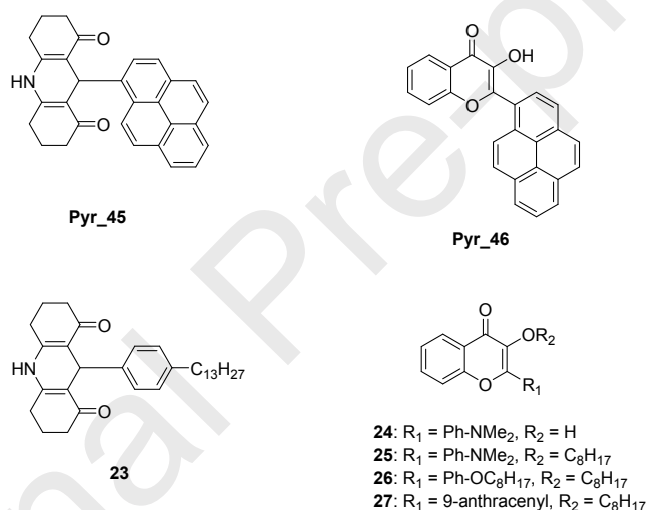


Figure 16. Chemical structures of **Pyr_45** and **Pyr_46** and **23-27**.

As other structure that slightly differ from benzophenone and which is also encountered in the photopolymerization field is chromones. Indeed, interaction of chromones with amines is capable to generate α -aminoalkyl radicals upon UV light exposure and this point is well-documented in the literature.[217-222] Comparison of the absorption properties of **Pyr_46** with that of the **24-27** series designed for comparison revealed **Pyr_46** to exhibit the most redshifted absorption of the series. To illustrate this, absorption maxima located at 394, 377, 325 and 385 nm were respectively determined for the **24-27** series, far from the absorption maximum of **Pyr_46** (431 nm). By theoretical calculations, a location of the HOMO

and the LUMO energy levels onto the pyrene and the carbonyl group of the chromone was determined and supports the red-shifted absorption of **Pyr_46**. On the opposite, a bigger HOMO-LUMO gap was determined for **27**, resulting from a less efficient charge transfer between the anthracenyl and the ketone groups as a result of the twisted structure of **27**. Here again, photolysis experiments revealed the S_1 pathway to be the main route for the **Pyr_46**/ Ph_2I^+ interaction. ESR spin trapping (ESR-ST) experiments carried out with the three-component system **Pyr_46**/MDEA/PBr showed the phenacyl radical to be the only species detected upon irradiation of the solution. It thus confirmed the $^1\text{Pyr}_46$ /MDEA interaction to produce a highly reactive **Pyr_46** $^{\bullet-}$ immediately reacting with phenacyl bromide (See r21 and r22).



However, photopolymerization of TMPTA with the three component system **Pyr_46**/MDEA/R-Br (0.5%/4%/3% w/w) furnished a moderate monomer conversion, lower than 30% after 300 s of irradiation with an halogen lamp and far behind that obtained with **24** (60% of conversion). A similar behavior was observed during the FRPCP of EPOX with another three-component system **Pyr_46**/ Ph_2I^+ /NVK (0.5%/3%/3% w/w). Here again, upon irradiation with a laser diode at 457 nm, **24** could outperform **Pyr_46**, furnishing final conversions of 65 and 45% respectively. If the **25**/ Ph_2I^+ /NVK system exhibited an efficiency better than the reference system BAPO/ Ph_2I^+ /NVK system, a lower efficiency was found for **Pyr_46**.

2.6. Phenazine derivatives

Phenazines are at the basis of numerous dyes used as light-absorbing materials for photovoltaic applications.[223] This family of compounds is also used in the photopolymerization area. Notably, phenazines have been used as additives for FRP processes,[224,225] as photosensitizers for onium salts in CP processes.[226-228] Recently, benzo[2,3-*b*]phenazines have also been reported as photosensitizers for FRP and CP while using high intensity irradiation sources.[229] In 2014, a pyrene-based phenazine **Pyr_47** that can be activated under low-light intensity and in the visible range was reported (See Figure 17).[230]

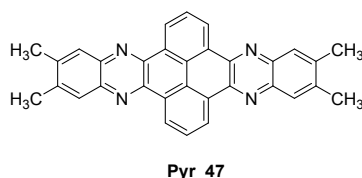


Figure 17. Chemical structure of **Pyr_47**.

By extending the π -conjugation with two phenazine moieties, absorption of **Pyr_47** could extend until 440 nm. Photoreactivity of the three-component system **Pyr_47**/MDEA/P-Br was good since a final conversion of 60% within 400s could be obtained under low light intensity while using a LED at 405 nm. Similarly, a good monomer conversion was obtained during the ring opening polymerization of EPOX, peaking at 50% **Pyr_47**/Ph₂I⁺/NVK (0.5%/3%/3% w/w) upon irradiation with a halogen lamp.

2.7. Photochrome-based photoinitiators

Dyes which are used as photoinitiators of polymerization are most of the time only used to initiate the polymerization process and their behaviors in the photopolymerized film subsequent to the polymerization process are rarely examined. When photocatalytic systems are employed, dyes are regenerated so that their inherent properties (photoluminescence, photochromism, thermochromism, etc...) can be maintained. At present, only few photoinitiators have been used to bring additional properties to the polymer films. One of the most obvious property that can be furnished by photoinitiators is undoubtedly photoluminescence, most of the photoinitiators being photoluminescent. But other specific properties can be provided by the photoinitiators such as antibacterial properties [231,232] or modification of the mechanical properties of polymers. In this last field, polyoxometalates are candidates of choice by their fully inorganic structures and their behavior when introduced in polymers is comparable to that to fillers.[233,235] To the best of our knowledge, no photochromes have been reported before 2013 as photoinitiators. But use of such structures as photoinitiators is counterintuitive considering that light can induce a photoisomerization of the dye, totally modifying its absorption spectrum. In this case, the discoloration of the dye or shift of its absorption in a completely different part of the visible range can render these structures totally ineffective for photoinitiation. In fact, to be usable in photopolymerization, the photochrome which is selected as the photoinitiators should be capable to photoisomerize slowly so that its absorption remains almost unchanged during the

polymerization time. This challenge was addressed in 2013 with a pyrene derivative, namely 2,7-di-*tert*-butyldimethyldihydropyrene **Pyr_48**. More specifically, **Pyr_48** was examined as a panchromatic photoinitiator, its absorption extending from 200 to 700 nm (See Figure 18).[236] Panchromatic photoinitiators are actively researched in photopolymerization as these compounds exhibit an almost constant sensitivity to light over a wide range of absorption and thus do not require a specific wavelength for photoinitiation.[237-240] While coming back to **Pyr_48**, this photochrome can be converted to its open form by irradiation with visible light whereas the closed form can be obtained upon irradiation in the UV range.[241-246]

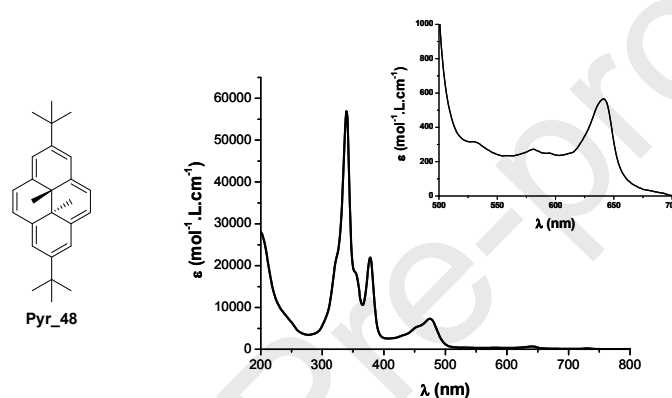


Figure 18. Chemical structure of **Pyr_48** and UV-visible absorption spectrum of **Pyr_48** in acetonitrile. Reprinted with permission from Ref. [236]. Copyright © 2013 John Wiley & Sons, Inc.

Considering that **Pyr_48** is panchromatic, polymerization processes could be initiated with seven different LEDs (365, 395, 405, 457, 473, 532 and 635 nm). While using the three-component system **Pyr_48**/Iod/NVK (1%/2%/3%, w/w), final conversions ranging between 60 % (LED at 532 nm) to 95% (LED at 365 nm) could be determined (See Figure 19), demonstrating the versatility of this photochrome.

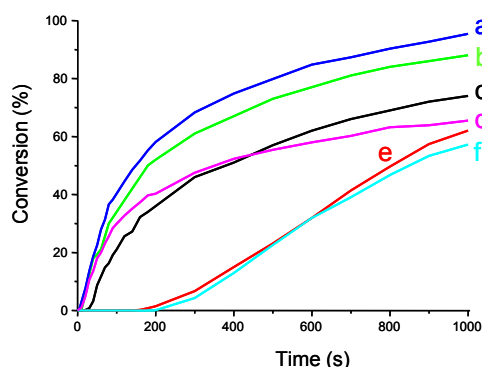


Figure 19. Polymerization profiles of EPOX under air using the three-component system **Pyr_48**/Iod/NVK (1%/2%/3%, w/w) upon irradiation with a) a laser diode at 473 nm (70 mW/cm²), b) a laser diode at 457 nm (60 mW/cm²), c) a halogen lamp, d) a laser diode at 635 nm (10 mW/cm²), e) a laser diode at 405 nm (4.2 mW/cm²), f) a laser diode at 532 nm (5 mW/cm²) Reprinted with permission from Ref. [236]. Copyright © 2013 John Wiley & Sons, Inc.

Differences of final monomer conversions are directly related to the molar extinction coefficients of **Pyr_48** at the considered LED emission but also to the intensity of the light absorbed at these different wavelengths, which drastically differs from a wavelength to another one (See Figure caption of Figure 19). Among the most interesting findings, photochromic behavior of **Pyr_48** could be maintained in the polymer film, evidencing that this property well-known for **Pyr_48** in solution could still exist in the solid state (See Figure 20). If a partial consumption of **Pyr_48** during the photopolymerization process could nevertheless be evidenced (see curves a) and b)), irradiation of the polymer film with a Xe-Hg lamp could regenerate **Pyr_48** in the closed form.

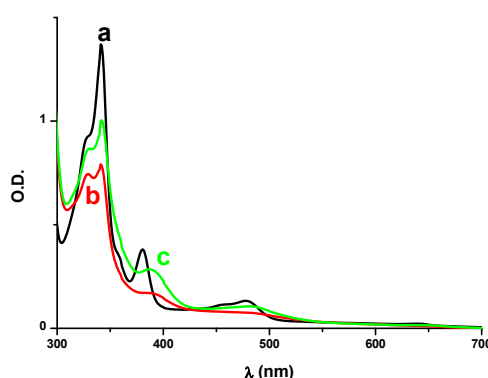


Figure 20. UV-visible spectra of a **Pyr_48**-containing EPOX film: (a) before irradiation; (b) after 1000 s of irradiation with a diode laser at 635 nm; (c) after a subsequent UV irradiation (Xe-

Hg lamp; 30 s) of the synthesized polymer in (b). Reprinted with permission from Ref. [236]. Copyright © 2013 John Wiley & Sons, Inc.

2.8. Type I photoinitiators

Photoinitiators can be separated into two well-distinct classes of structures, namely, those which are cleavable compounds (Type I photoinitiators) and those which are uncleavable compounds (Type II photoinitiators). In the two cases, radicals usable for FRP, CP and FRPCP are produced. Besides, contrarily to Type II photoinitiators that can be used in catalytic amount while using the adapted photoinitiating system, Type I photoinitiators are consumed during the polymerization process as a result of an irreversible homolytic cleavage upon photoexcitation. In this field, Type I photoinitiators based on pyrene are scarce and only one example has been reported in the literature (i.e. **Pyr_49**), under the form of a mixture of two isomers (See Figure 21).[32]

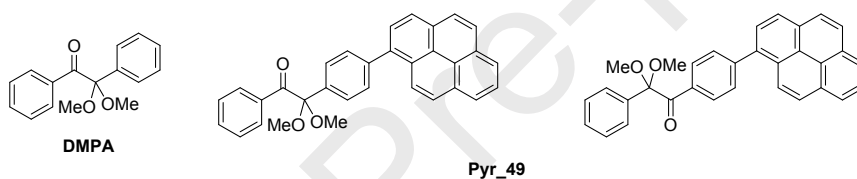
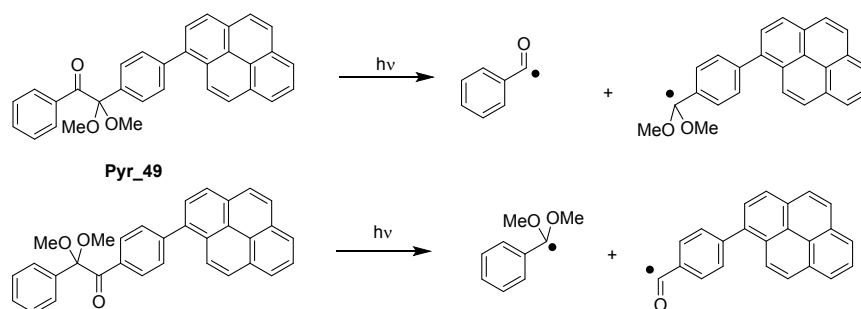


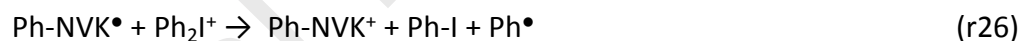
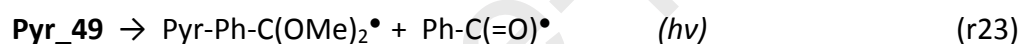
Figure 21. Chemical structures of DMPA and pyrene-based DMPA (**Pyr_49**)

Considering that pyrene is directly connected to 2,2'-dimethoxy-2-phenylacetophenone (DMPA) which is a UV photoinitiator,[247] the combination of the two partners only resulted in a moderate orbital coupling between both due to the biaryl linkage so that the absorption of **Pyr_49** could not extend beyond 420 nm. The fast bleaching of **Pyr_49** upon irradiation with a Xe-Hg lamp revealed the light-harvesting ability of pyrene in these structures. Despite the presence of two regioisomers in **Pyr_49**, a unique signal was detected during the ESR-spin trap experiments, indicating that the radicals formed upon irradiation were not affected by the presence of the pyrene moiety (See Scheme 1).



Scheme 1. The two possible cleavage for **Pyr_49**.

The possibility to convert the two radicals $\text{Pyr-Ph-C(OMe)}_2^\bullet$ and $\text{Ph-C(OMe)}_2^\bullet$ into the two cations Pyr-Ph-C(OMe)_2^+ and Ph-C(OMe)_2^+ was demonstrated, these radicals being easily oxidized with an iodonium salt. Upon addition of NVK to the previous system, Ph^\bullet can add onto NVK, producing Ph-NVK^\bullet that can also be oxidized as Ph-NVK^+ . Overall, the following mechanism could be proposed to support the high efficiency of **Pyr_49** in CP and FRP (see r23-r27).

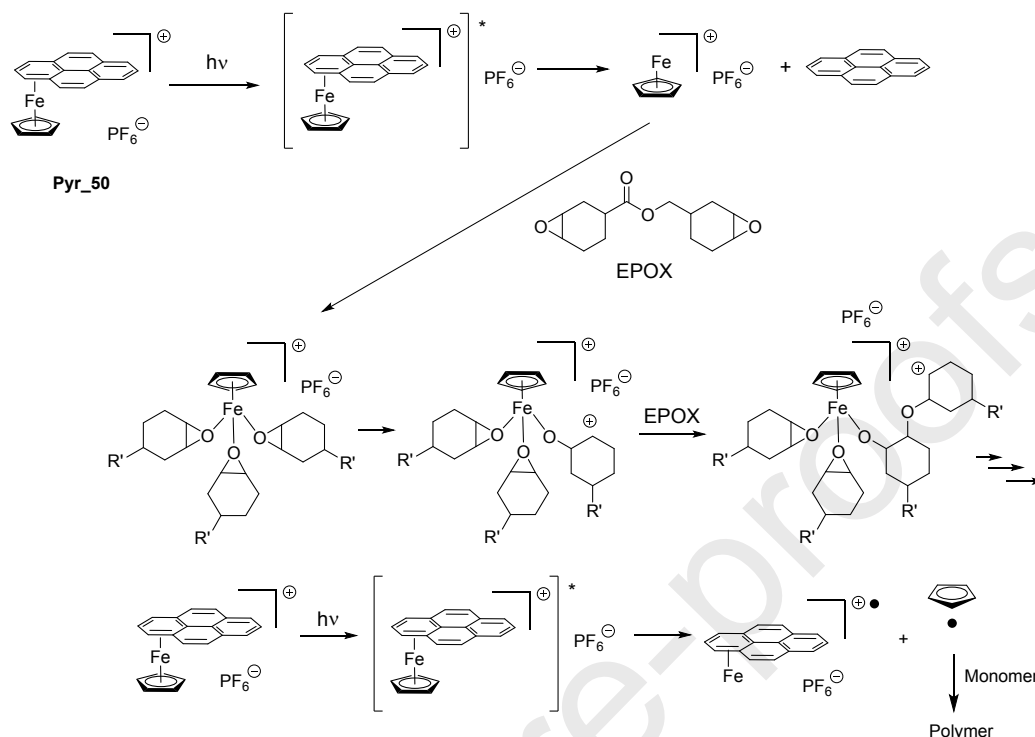


Finally, comparison of **Pyr_49** with **Pyr_37** and **Pyr_38** revealed the photoinitiating performances of **Pyr_49** to be on par with that of **Pyr_37** and **Pyr_38**. Considering that **Pyr_49** requires more synthetic steps than **Pyr_37** and **Pyr_38** to be obtained and that the performances are similar, **Pyr_49** is from this point of view a less interesting candidate than **Pyr_37** and **Pyr_38**.

2.9. Ferrocenium derivatives.

Ferrocenium are well-known cationic photoinitiators of polymerization[248-253] and these structures have attracted a great deal of interest by their facile access from cheap precursors.[254-257] Especially, ferrocenium can be prepared from ferrocene by ligand exchange following the procedure reported by Nesmeyanov and co-workers.[258,259] The high efficiency of these cationic photoinitiators for the CP of EPOX is directly related to the

mechanism involved in the polymerization process. Notably, the first step consisting in a ligand release, generating a strong Lewis acid (See Scheme 2).[260]



Scheme 2. Mechanism suggested to support the photoinitiating ability of pyrene-based ferrocenium salt **Pyr₅₀**.

Subsequently, three epoxide units can coordinate to the Lewis acid, activating the ring-opening of epoxides. Parallel to this, dissociation of the cyclopentadienyl-Fe bond can also produce a radical that can act as a free radical photoinitiator. In 2016, an interesting ferrocenium comprising a pyrene ligand (**Pyr₅₀**) was reported.[261] The absorption of this compound was relatively broad and the molar extinction coefficients of **Pyr₅₀** at 385, 405, 455 and 520 nm are respectively of 2300, 860, 770 and 180 M⁻¹.cm⁻¹. Considering that 405 nm constitutes an interesting irradiation wavelength notably for dental and 3D-printing applications, photoinitiating ability of **Pyr₅₀** was examined at this wavelength and mono-component, two-component **Pyr₅₀/iod** (0.2%/2% w/w) and three-component systems **Pyr₅₀/iod/NVK** (0.2%/2%/3% w/w) were studied. Logically, an improvement of the monomer conversions was observed going from the mono to the three-component systems at 405 nm, the conversion increasing from 25 to 31 and 56% respectively after 800s of irradiation. The mechanism sustaining the efficiency improvement by going from the mono to the three

component systems are identical to those previously reported in this review. In addition to the initiation of a CP, **Pyr_50** was also examined as a free radical photoinitiator for TMPTA. Still while using the same three-component system **Pyr_50**/iod/NVK (0.2%/2%/3% w/w) and upon irradiation with the LED at 405 nm for 800s, a final monomer of 60% was obtained, comparable to the conversion obtained with **Pyr_45** or **Pyr_48**.

Table 1. Summary of the photophysical properties of Pyr_1-Pyr_50.

Compound	$\lambda_{\max}^{(1)}$ (nm)	$\epsilon_{\max}^{(1)}$ (L.mol ⁻¹ . cm ⁻¹)	$\lambda_{\text{em}}^{(1)}$ (nm)	$E_{\text{ox}}^{(1)}$ (V/SCE)	Reference
Pyr_1	240	8.4×10^4	-		132
Pyr_3	288, 366	-	-		131
Pyr_4	278, 348	-	-		134
Pyr_5	264 275 312 325 341	25 560 49 430 11 990 29 670 46 010	-		138
Pyr_6	264 297 312 325 341	27 780 4 890 13 180 31 070 46 160	-		138
Pyr_10	360	-	-		147
Pyr_11	348	38 000	-		157
Pyr_12	344	-	380	0.8	159
Pyr_13	351	-	393	0.9	159
Pyr_14	353	-	404	0.7	159
Pyr_15	365	-	441	0.9	159
Pyr_16	367	-	440	-	159
Pyr_17	351	-	423	0.6	159
Pyr_18	344	-	530	0.7	159
Pyr_19	346	-	428	0.8	159
Pyr_20	347	-	425	0.9	159
Pyr_21	346	-	409	-	159
Pyr_22	420 ⁽²⁾	40 000	-	-	163
Pyr_23	325 ⁽²⁾ 350 ⁽²⁾	8 000 11 000	-	-	163
Pyr_24	420 ⁽²⁾	28 000	-	-	163
Pyr_25	360 ⁽²⁾	4 000	-	-	163
Pyr_26	360 ⁽³⁾ 380 ⁽³⁾	-	-	-	165
Pyr_27	460 ⁽²⁾	6 000	-	-	163
Pyr_28	340 ⁽²⁾	11 000	-	-	163
Pyr_29	464	21 000	-	1.34	179
Pyr_30	434	20 130	518	1.5	188
Pyr_31	366	21 700	443	1.4	188
Pyr_32	452 ⁽²⁾	-	600	-	189

Pyr_33	495	23 000	-	-	46
Pyr_34	450	7 600	-	0.7	46
Pyr_35	440	28 000	-	-	46
Pyr_36	356 ⁽²⁾	18 000	-	-	163
Pyr_37	335 ⁽⁴⁾	26 000	-	-	32
Pyr_38	357 ⁽⁴⁾	32 000	-	-	32
Pyr_39	353 ⁽²⁾	23 000	439	0.7	189
Pyr_40	342 ⁽²⁾	24 000	395	0.7	189
Pyr_41	340 ⁽²⁾	16 000	396	0.9	189
Pyr_42	350 ⁽²⁾	24 000	418	0.7	189
Pyr_43	360 ⁽²⁾	10 000	420	0.7	189
Pyr_44	360 ⁽²⁾	45 000	414	0.7	189
Pyr_45	348	15 404	-	1.23	216
Pyr_46	431	16 000	-	0.65	5
Pyr_47	422	26 000	-	0.67	230
Pyr_48	339	56 900	-	0.54	236
	378	21950			
	474	7350			
	641	650			
Pyr_49	345	35 000	-	0.87	32
Pyr_50	450	1 000	-	-	261

Values determined ⁽¹⁾ in acetonitrile, ⁽²⁾ in toluene, ⁽³⁾ in acetone, ⁽⁴⁾ in acetonitrile/toluene (50/50).

Conclusion

During the past decades, pyrene derivatives have been the focus of numerous researches and fifty pyrene-based photoinitiators have been developed. If difunctional and trifunctional photoinitiators proved to be the best candidates for FRP and CP, mitigate results have been obtained while developing push-pull dyes based on pyrene as the electron donor. By chemical engineering, a few examples for pyridinium salts (**Pyr_34** and **Pyr_35**) were however capable to initiate a CP, FRPCP or FRP. This approach i.e. the design of push-pull dyes is however the most straightforward route to produce pyrene derivatives with strong absorptions in the visible range. Finally, structures such as chromones or acridinediones have only been scarcely studied, despites promising results. Clearly, Type I photoinitiators based on pyrene have been the less studied than their Type II analogues, only one example based on DMPA being reported to date. Even if the design of such Type I photoinitiators required an extensive synthetic work as it consists in the chemical modification of benchmark structures, it opens the way towards the recycling of efficient UV-photoinitiators, updated to become activable under visible light.

Declaration of competing interest

The author declares no conflict of interest.

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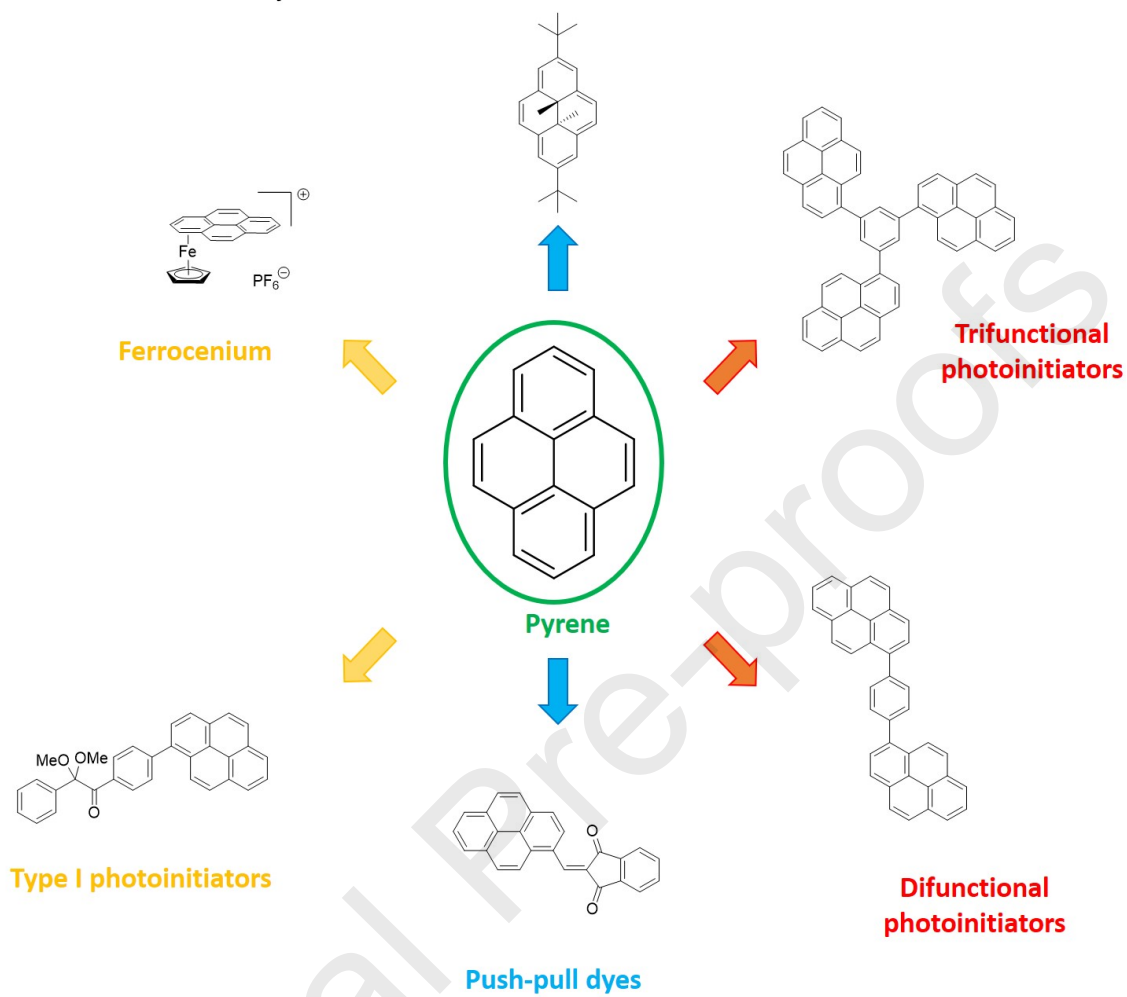
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Graphical abstract

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Conflicts of interest

The authors declare no conflict of interest.

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