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Recent Advances on Visible Light Photoinitiators of Polymerization Based on Indane-1,3-dione and Related Derivatives

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Abstract

Photoinitiators that can operate under visible light and low light intensity are actively researched as this last generation of photoinitiators can address different issues raised by the traditional UV photoinitiators. Notably, the safety concern related to the use of UV light, the high energy consumption resulting from the use of UV irradiation setups, the low light penetration of UV light within the photocurable resins are three major concerns that visible light photoinitiators successfully address. Besides, the photoinitiating ability and the polymerization kinetic should remain high in order these new generations of photoinitiators to be capable to replace the traditional UV photoinitiators. Among the different scaffolds examined for the design of efficient visible light photoinitiators, indane-1,3-dione has been identified as a promising scaffold for the design of various structures. By the presence of the activated methylene group standing between the two ketone groups, this electron acceptor is an ideal candidate for the design of push-pull dyes by one of the simplest reactions, namely the Knoevenagel reaction. This group is also a good electron acceptor as the two ketone groups can be advantageously used in the electronic delocalization by mesomerism. If this electron acceptor has been extensively studied for the design of push-pull dyes, its scope of application was not only limited to the design of push-pull dyes and products issued from cyclization reactions, the design of compounds with extended aromaticities, improvement of the electron-withdrawing ability by substitution of the ketone groups by appropriate groups were examined as possible chemical modifications enabling to improve the photoinitiating ability of photoinitiators based on indane-1,3-dione and its related derivatives. In this review, an overview of the different visible light photoinitiators based on indane-1,3-dione and derivatives is provided. To evidence the performance of the different photoinitiators, comparisons with reference compounds will be provided.

Keywords

Photoinitiator; push-pull dyes; photopolymerization; LED; visible light; low light intensity; indanedione; cyclization reaction; azafluorenone

1. Introduction

In recent years, visible light photoinitiators have been the focus of numerous research efforts due to the numerous advantages these last generations of photoinitiators exhibit.[1-12] Contrarily to the traditional UV photoinitiators that are the subject of numerous controversies (possibility of eye and skin damages due to the use of UV light, use of irradiation setups involving high energy consumptions and inefficient energy-to-light conversions, heat release by the irradiation setups, low light penetration of the UV light within the photocurable resins), visible light photoinitiators clearly constitute a breakthrough in photopolymerization. Even if visible light photoinitiators exhibit several appealing features, visible light photoinitiators also exhibit limitations that can't be denied, namely the fact that these compounds and the formulations containing them must be handled with exclusion of visible light which also constitutes a hurdle for their uses with conventional working setups. Notably, visible photoinitiators such as titanocenes or borate dyestuff did not find widespread use in technical application except in niche applications.[13-15] Therefore, a great deal of effort has still to be done in order to render these photoinitiators appealing candidates for industrial applications. Compared to the classical thermal initiators, a perfect spatial and temporal control can be obtained during the photopolymerization process. The kinetic of photopolymerization can also be fast and the possibility to polymerize without any solvents enabling a drastic reduction of the release of volatile organic compounds (VOCs) constitute the most attractive features of photopolymerization.[16-20] Compared to UV photoinitiators, a better light penetration can also be obtained with visible light, as shown in the graph presented in the Figure 1 and established for a polystyrene latex.[21] Indeed, if the light penetration is limited to 600 μm at 320 nm, this latter can reach 4 mm at 450 nm and 5 cm at 800 nm. As a result of this, the access to thick samples by photopolymerization is now possible.[22] In fact, scope of applications of photopolymerization has been totally revolutionized during the last decade, shifting from the elaboration of thin coatings to thick samples containing fillers. Parallel to this, emerging applications such as 3D and 4D printing have clearly provided a revival of interest for this polymerization technique.[23-29]

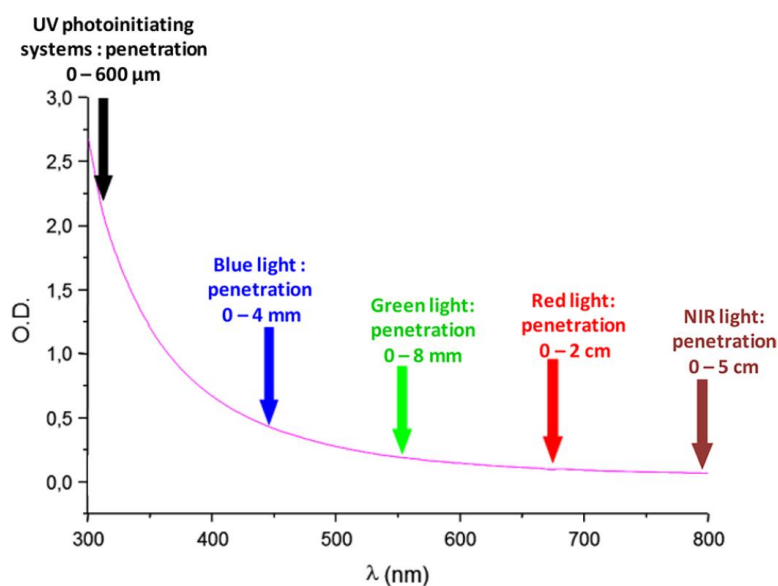


Figure 1. Light penetration within a photurable resin composed of a polystyrene latex with an average diameter of 112 nm. Reproduced with permission from Bonardi et al. [21].

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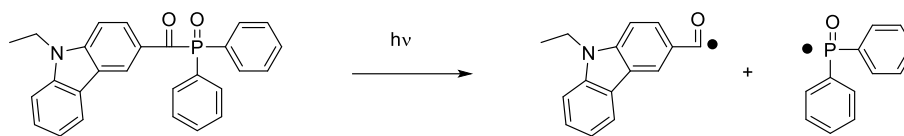
Over the years, several scaffolds have been identified as being promising structures for the design of efficient visible light photoinitiators, especially of Type II photoinitiators. Among these structures, phenothiazines **1**, [30] porphyrins **2**, [31-33] pyrenes **3**, [34-39] squaraines **4**, [31] thioxanthenes **5**, [40-43] iodonium salts **6**, [44-46] iridium complexes **7**, [47-52] iron complexes **8**, [53-57] naphthalimides **9**, [58-69] perylenes **10**, [70-72] 2,3-diphenylquinoxaline derivatives **11**, [73] diketopyrrolopyrrole **12**, [74-76] flavones **13**, [77-78] ferrocenes **14**, [79-83] helicenes **15**, [84-85] chromones **16**, [86-88] coumarins **17**, [89-94] copper complexes **18**, [95-105] cyclohexanones **19**, [106-109] dihydroanthraquinone **20**, [110] acridones **21**, [111-112] acridine-1,8-dione **22**, [113-114] benzophenones **23**, [115-117] camphorquinones **24**, [119-120] carbazoles **25**, [121-126] chalcones **26**, [126-131] push-pull dyes **27**, [132-140] cyanines **28** [141-143] and zinc complexes **29** [144] can be cited as the most explored structures. However, the polymerization efficiency of these compounds is still insufficient to be used in industry so that a great deal of efforts has still to be done. Several issues of visible light photoinitiators have still to be addressed such as the stability of the resins upon storage and the photobleaching of the resins during photopolymerization. Indeed, contrarily to the traditional UV photoinitiators that are colorless compounds and that can furnish colorless coatings after polymerization, conversely, visible light photoinitiators are strongly colored compounds that can impose the color of the final coatings, except if photobleaching is obtained. Concerning photopolymerization, two distinct photoinitiation mechanisms have to be distinguished, differing by the way how the initiating radicals are formed.

The first approach relies in the homolytic photocleavage of photoinitiators (Type I photoinitiators) so that two radicals are simultaneously formed. As the main drawback of this

approach, an irreversible consumption of photoinitiators is observed during polymerization so that the polymerization kinetic is highly dependent of the initial amount of photoinitiators introduced within the photocurable resins. Among Type I photoinitiators, 2,2-dimethoxy-2-phenylacetophenone (DMPA),[145] acyl phosphine oxides (phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (TPO)) [140-154] are among the most widely studied. Parallel to these cleavable photoinitiators, a second category of photoinitiators exists where the light-absorbing compounds can be consumed or not during the polymerization process, depending on the conditions. Notably, when an amine is introduced in the reaction media, the sacrificing agent can re-oxidize the reduced photosensitizer to its initial state, enabling to use it in catalytic amount. Conversely, in the absence of sacrificial amine, an irreversible consumption of the photosensitizer is also detected, as observed for Type I photoinitiators. These compounds are named Type II photoinitiators and these compounds can be combined with a co-initiator to undergo an intermolecular hydrogen abstraction or an electron/proton transfer reaction.[155-161] Multicomponent systems comprising three and even more components can also be used.[162-164]

As interesting feature, when incorporated in three-component systems, the dye acts as a photosensitizer and can thus be regenerated during polymerization so that a catalytic amount of dye can be used, as shown in the Figure 2. In fact, visible dyes are commonly used to sensitize UV photoinitiators such as iodonium salts. Upon photoexcitation, an electron transfer from the photosensitizer towards the iodonium salt can occur in the excited state, inducing the decomposition of the iodonium salt and the formation of initiating radicals Ph•. Therefore, in these systems, the iodonium salt is the photoinitiator and this compound is also consumed during the polymerization process, as in the case of Type I photoinitiators. As a result of this, the photosensitizer is oxidized, irreversibly consumed and cannot contribute anymore to the sensitization of the iodonium salt. To address this issue, addition of a sacrificial amine (*N*-vinylcarbazole (NVK) for example) as a third component in the resin enables the oxidized photosensitizer to be reduced and thus regenerated (See Figure 2).[165] Therefore, the main difference between Type I and Type II photoinitiators relies in the use of a photosensitizer in the case of Type II photoinitiators that can be or not consumed, depending of the presence of a sacrificing agent. As shown in the Figure 2, two different types of polymerization can be induced by the use of three-component systems. Notably, by reaction of the phenyl radical Ph• with NVK, a highly reactive radical Ph-NVK• capable to initiate a free radical polymerization (FRP) is produced. Parallel to this, Ph• can also react with the iodonium salt Ph₂I⁺, producing the cation Ph-NVK⁺ capable to initiate a free radical-promoted cationic polymerization (FRPCP) of epoxides. Therefore, the concomitant polymerizations of acrylates and epoxides is thus possible, enabling to access to interpenetrated polymer networks (IPNs).[167-169]

Type I photoinitiators



Type II photoinitiators

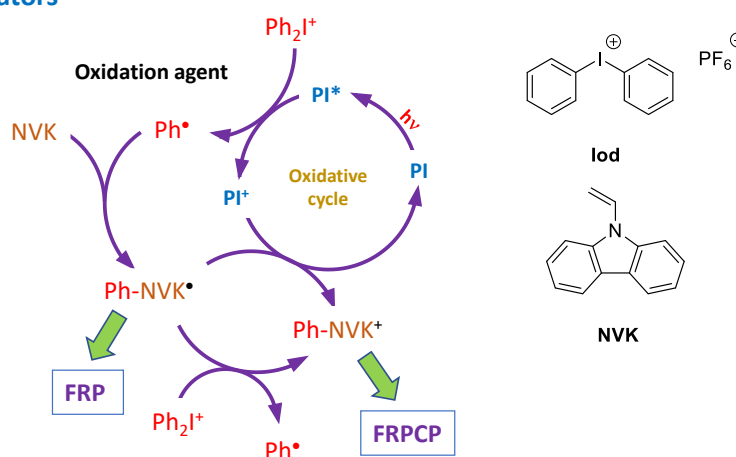


Figure 2. Photoinitiating mechanisms involved by the Type I and the Type II photoinitiators.

Among dyes strongly absorbing in the visible range, push-pull dyes composed of an electron-donating group connected to an electron-accepting group by mean of a π -conjugated spacer have been examined in numerous research fields such as non-linear optics,[170-174] organic photovoltaics[175-180] and organic field effect transistors.[181] If several electron acceptors have been examined for this purpose over the years such as pyrazines **A1**,[182] dicyanoimidazoles **A2**,[183] benzo[*d*]thiazoliums **A3**,[184] benzo[*d*]imidazoliums **A4**,[185] dicyanovinyl-thiophen-5-ylidenes **A5**[186] and 9-methylene-2,4,5,7-tetranitro-9*H*-fluorene **A6**[187], malononitrile **A7**,[188] (thio)barbituric derivatives **A8**,[189] Meldrum derivatives **A9**, [190] pyridinium **A10**,[191] methyl-containing tricyanofurans **A11**,[192] substituted tricyanopropenes **A12**,[193] pyran derivatives **A13** and **A14**,[194-195] 1,1,3-tricyano-2-substituted propenes **A15**,[196] isoxazolones **A16**,[197] hydantions and rhodanines **A17**,[198] indane-1,3-dione derivatives **A18** remains the most efficient one (See Figure 3).[199-210]

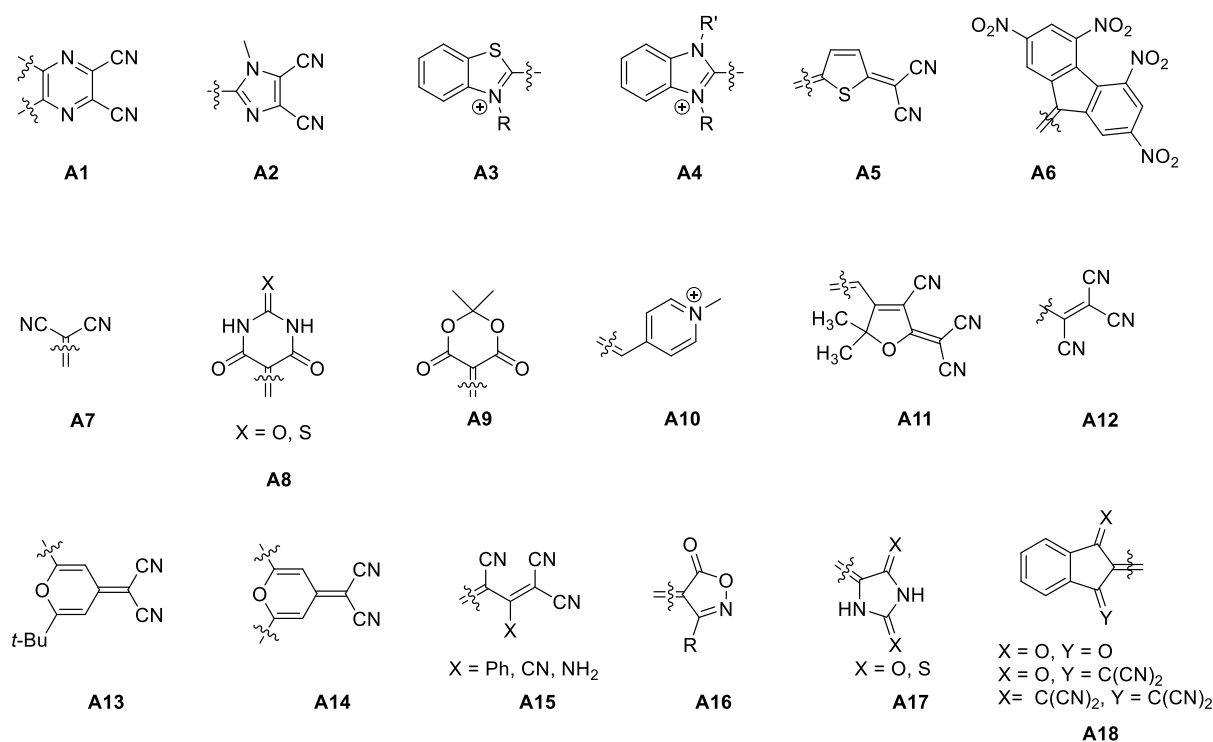


Figure 3. Chemical structures of electron acceptors **A1-A18** commonly used for the design of push-pull dyes.

Indeed, contrarily to numerous electron acceptors that cannot be modified subsequent to their syntheses such as **A1-A17**, on the opposite, numerous chemical modifications can be done on the indane-1,3-dione scaffold **A18**, subsequent to its synthesis, as shown in the Figure 4.[201]

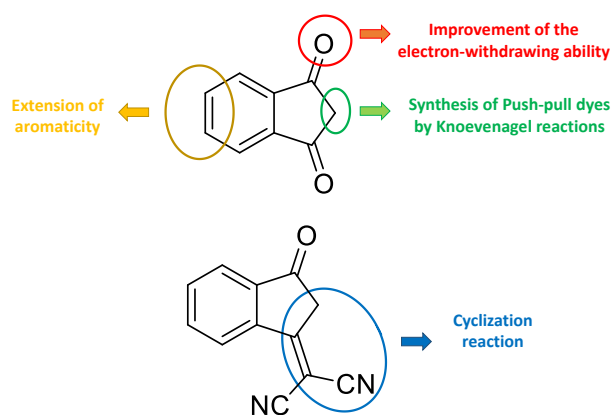


Figure 4. The possible chemical modification of the indane-1,3-dione scaffold.

Notably, electron-withdrawing ability of indane-1,3-dione can be reinforced by performing Knoevenagel reactions with malononitrile on the ketone groups.[202-206] Presence of the activated methylene group make this molecule an excellent candidate for

elaborating push-pull dyes by Knoevenagel reactions while reacting the appropriate aldehyde.[207-211] Electron-withdrawing ability of indane-1,3-dione can also be reinforced by using indane-1,3-dione-inspired acceptors of extended aromaticity compared to the parent structure. However, such compounds cannot be obtained from indane-1,3-dione. Finally, when nucleophilic bases are used during the synthesis of push-pull dyes, intramolecular cyclization reactions can occur by nucleophilic attack of a secondary amine onto the cyano groups, providing azafluorenones.[212] When compared to the other photoinitiating systems, push-pull dye-based photoinitiating systems and especially indane-1,3-dione-based photoinitiating systems exhibit several advantages that are summarized in the Table 1.

Table 1. Comparisons between indane-1,3-dione-based dyes and the other synthetic dyes used as photoinitiators/photosensitizers.

Parameters	Push-pull dyes	Other dyes
Cost/synthesis	Compounds can be prepared in one step by Knoevenagel reactions	Other photoinitiators are often prepared by multi-step synthesis, rendering these compounds more expensive than push-pull dyes.
Environmental impact	Push-pull dyes are mostly prepared by refluxing in ethanol and often precipitate after reaction. Isolation of products in pure form can be obtained by filtration.	Most of synthetic dyes are often prepared in organic solvent. A purification by column chromatography is also required.
Photochemical stability	Push-pull dyes are stable compounds often used in solar cells. Therefore, their photochemical stability is often good.	Dyes can be highly stable, especially with the development of polyaromatic structures.
Absorption range	Push-pull dyes exhibit a broad absorption and their absorption spectra can be finely tuned.	Other synthetic dyes can also exhibit a broad absorption.
Photoinitiating ability	Push-pull dyes are ideal candidates for photoinitiation. Ability of dyes to release or acceptor electrons is the basis of their use in Organic Electronics (OFET, OLED, OPVs).	Photoinitiating systems based on dyes can compete or being on par with that of push-pull dyes-based systems
Availability	Electron donors and acceptors used to design push-pull dyes can be both commercially available. Especially, this is the case when indane-1,3-dione is used as electron acceptor. Compounds are generally obtained in high yield.	Availability can be restricted, especially when multistep syntheses are used.

In this review, an overview of the different indane-1,3-dione derivatives used as photoinitiators of polymerization activable in the visible range and under low light intensity are reported. At present, several challenges remain concerning the use of indane-1,3-dione-based photoinitiating systems : design of dyes with high molar extinction coefficients enabling

to reduce the photosensitizer content, control of the absorption maxima to perfectly fit the emission of the different irradiation sources, if possible designing panchromatic photoinitiators absorbing over the whole visible range, ability of the photoinitiating systems to bleach in order to provide colorless coatings. With regards to these different challenges, and to evidence the photoinitiating ability of the different indane-1,3-dione-based photoinitiating systems, comparisons with benchmark photoinitiators is also provided.

2. Push-pull dyes based on indane-1,3-dione

Push-pull dyes have been the focus of numerous research efforts for the design of chromophoric dyes due to their easiness of synthesis and the facile tunability of both the absorption maxima and the molar extinction coefficients. However, several studies also evidenced that all push-pull dyes could not be used as photosensitizers. Indeed, as demonstrated in 2013, only the dyes for which a linear and positive solvatochromism could be determined could also act as photoinitiators.[213] This point was notably demonstrated with **D1** and **D2** (See Figure 5) for which a positive solvatochromism could be evidenced with several solvent polarity scales such as the Kawski–Chamma–Viallet’s,[214] McRae’s,[215] Bakhshiev’s,[216] Lippert–Mataga’s,[217] Dimroth–Reichardt’s,[218] Kamlet–Taft’s,[219] Catalan’s,[220] McRae’s,[221] and Suppan’s scales (See Figure 6).[222] Interestingly, if this relation existing between solvatochromism and polymerization efficiency was confirmed with several studies done by different research groups, origin of this relationship has not been clearly identified at present.[223-224]

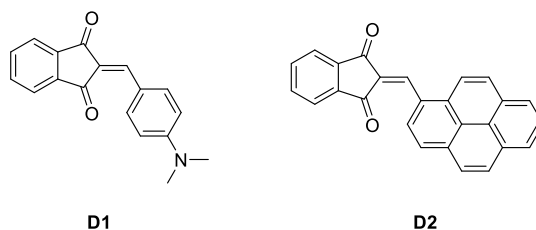


Figure 5. Chemical structures of **D1** and **D2**.

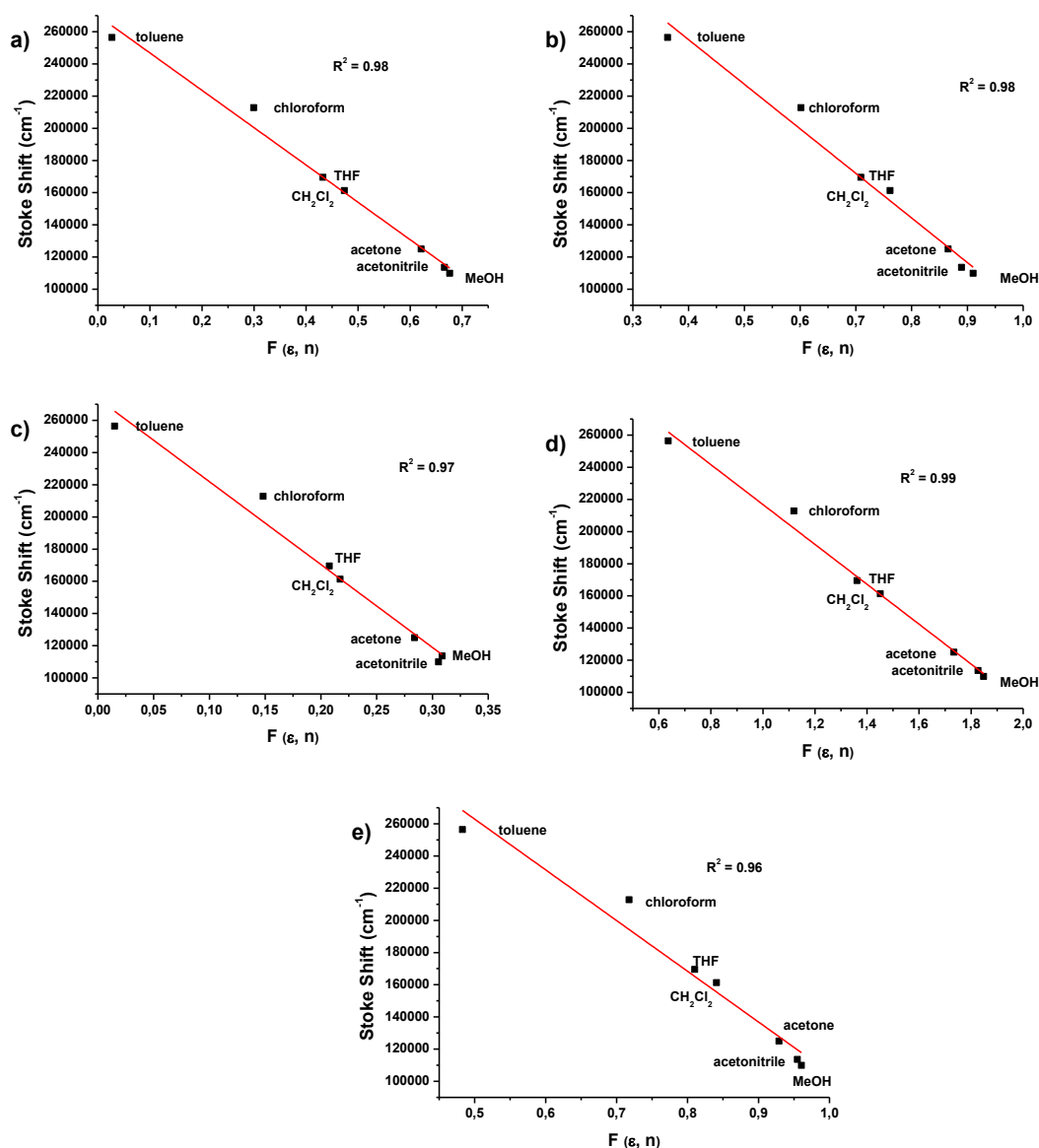


Figure 6. Linear plots obtained with different solvent polarity scales for **D1**. Bakhshiev's (a), Kawski-Chamma-Viallet's (b), Lippert–Mataga (c), McRae's (d) and Suppan's (e) scales. Reproduced with permission from Tefhe et al. [213]. Copyright 2013 American Chemical Society.

From the absorption viewpoint, an absorption extending between 350 and 750 nm for **D1**, 350 and 550 nm for **D2** could be measured in acetonitrile solutions. As anticipated, pyrene being a weaker electron donor than dimethylaminobenzene, a blue-shift of the intramolecular charge transfer band could be determined for **D2** ($\lambda_{\text{max}} = 464 \text{ nm}$, $\epsilon = 21\,000 \text{ M}^{-1}$) compared to that of **D1** ($\lambda_{\text{max}} = 478 \text{ nm}$, $\epsilon = 38\,000 \text{ M}^{-1}$). Based on their absorption spectra, the two dyes proved to be suitable candidates for photopolymerization done with laser diodes emitting at 457, 473, 532, and 635 nm ($100 \text{ mW}\cdot\text{cm}^{-2}$) or with a halogen lamp (370–800 nm range, $12 \text{ mW}\cdot\text{cm}^{-2}$). While examining the cationic polymerization (CP) of a difunctional epoxide i.e. 3,4-

epoxycyclohexane)methyl 3,4-epoxy-cyclohexylcarboxylate (EPOX) with the two-component **D_x** (**x = 1 or 2**)/Iod system (0.3%/2% w/w) where Iod stands for diphenyliodonium hexafluorophosphate, a final monomer conversion of 35% was determined with **D1** whereas no polymerization was detected with **D2** (halogen lamp (370-800 nm range, 12 mW.cm⁻²)). This trend was confirmed with the three-component **D_x** (**x = 1 or 2**)/NVK/Iod (0.3%/3%/2% w/w) system of higher reactivity for which no polymerization could be still detected with **D2** upon irradiation with a laser diode at 473 nm (100 mW/cm²). Depending of the irradiation wavelengths, monomer conversions of 40% at 405 and 532 nm, 80% at 473 nm could be determined with the three-component **D1**/NVK/Iod (0.3%/3%/2% w/w) system. Differences of monomer conversions are directly related to the difference of absorption maxima of **D1** at the irradiation wavelengths. Similarly, with a second monomer (triethylene glycol divinyl ether (DVE-3)), a final monomer as high as 95% could be determined for the three-component **D1**/NVK/Iod (0.3%/3%/2% w/w) system. A similar behavior was observed during the free radical polymerization (FRP) of trimethylolpropane triacrylate (TMPTA) (See Figure 7).

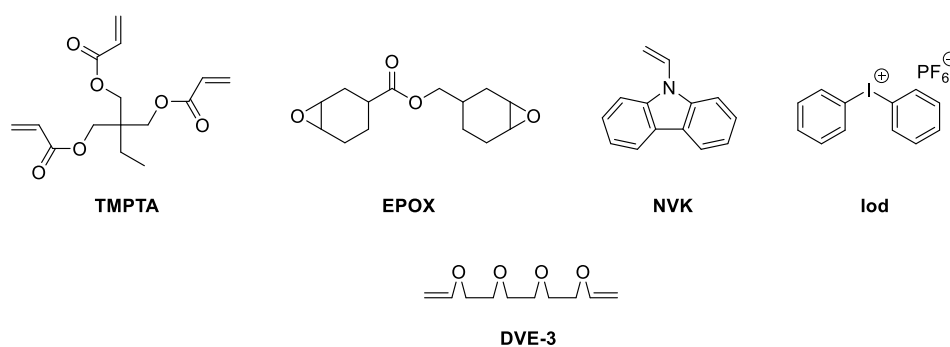


Figure 7. Chemical structures of the different monomers and additives used with **D1** and **D2** as photoinitiators.

Thus, a monomer conversion of 50% could be determined with the three-component system **D1**/NVK/Iod (0.3%/3%/2% w/w) upon irradiation at 473 nm (laser diode, 100 mW cm⁻²) in laminate for 200 s whereas no polymerization could be initiated with **D2**. Photolysis experiments done upon irradiation at 473 nm revealed for the two-component **D_x** (**x = 1 or 2**)/Iod systems, the decrease of the absorbance to be extremely fast with **D1** whereas no modification of the absorption spectrum was detected for **D2**. It was thus concluded that the photoassisted electron transfer from **D2** towards Iod was thus unfavorable, explaining the inability of **D2** to initiate a polymerization. From a mechanistic viewpoint, the mechanism supporting the FRP and the CP was consistent with that depicted in the Figure 3.

Mismatch of the redox potentials between Iod and the excited dye is not the only reason supporting the inability of a dye to initiate a polymerization. Several other reasons can be mentioned. Thus, **D3** proved to be a poor candidate for photoinitiation due to the lack of solubility in resins whereas presence of the weak electron donor in **D4** could not provide a

sufficient absorption in the visible range to this dye ($\lambda_{\max} = 351 \text{ nm}$) in order to be usable (See Figure 8).[225] Conversely, use of strong electron donors such as carbazole in **D5** ($\lambda_{\max} = 448 \text{ nm}$) or anthracene ($\lambda_{\max} = 467 \text{ nm}$) in **D6** could furnish dyes strongly absorbing in the visible range. With the most reactive dye i.e. **D5**, a final monomer conversion of 59% was obtained with EPOX, upon irradiation at 457 nm with a laser diode (100 mW/cm^2) and while using the three-component **D5/Iod/NVK** (0.5%/2%/3%, w/w/w) system. This value could be increased up to 64% while using a halogen lamp of broader emission spectrum (370-800 nm range, 12 mW.cm^{-2}) than the laser diodes while nonetheless emitting a lower light intensity than the laser diodes. Conversely, EPOX conversion was reduced to 33% with **D3** in the same conditions, due to its low solubility in resins.

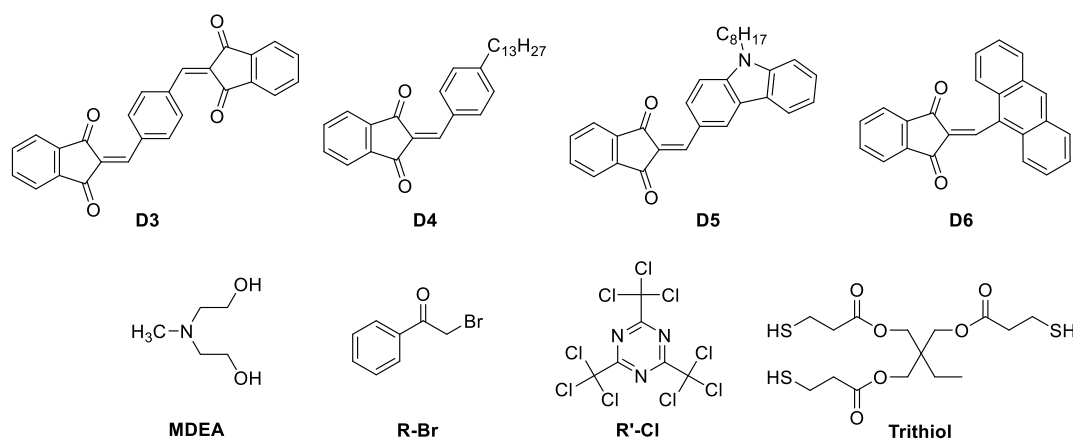
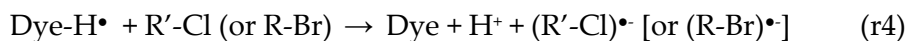
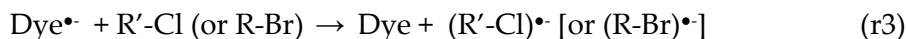
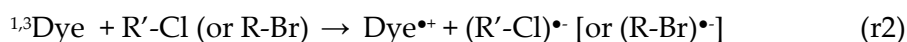
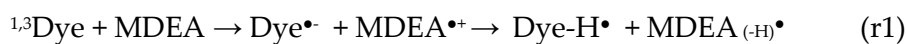


Figure 8. Chemical structure of **D3-D6**, the different monomers and additives

D5 proved also to be a versatile photosensitizer, especially during the FRP of TMPTA. Indeed, at least four efficient three-component photoinitiating systems could be prepared with this dye, consisting in the **D5/Iod/NVK** (0.5%/2%/3%, w/w/w), **D5/MDEA/R-Br** (0.5%/2%/1%, w/w/w) (with R-Br which stands for phenacyl bromide), **D5/MDEA/R'-Cl** (0.5%/2%/1%, w/w/w) (with R'-Cl which stands for 2,4,6-tris(trichloromethyl)-1,3,5-triazine) and **D5/MDEA/R'-Cl** (0.5%/2%/3%, w/w/w) systems. Using these different photoinitiating systems, TMPTA conversions of 58, 42, 52 and 60% were respectively determined upon irradiation with a laser diode at 457 nm for 400 s. From a mechanistic viewpoint, a mechanism differing from that of observed with an iodonium salt could be established. Notably, upon photoexcitation, the amine (MDEA) can interact in the excited state with the dye, inducing the formation of the anion radical $\text{Dye}^{\bullet-}$ which can subsequently react with the cation radical of MDEA i.e. $\text{MDEA}^{\bullet+}$, giving rise to a hydrogen abstraction and the formation of Dye-H^{\bullet} (See equation r1 in Scheme 1). This radical can then react with R'-Cl (or R-Br) according to reaction (r4). Parallel to this, the dye can also react with R'-Cl (or R-Br), furnishing $(\text{R}'\text{-Cl})^{\bullet}$ [or $(\text{R-Br})^{\bullet}$] (See r3) which can decompose, producing the initiating species R'^{\bullet} (or R^{\bullet}) (See equation r5).



Scheme 1. Reactions involved during the polymerization process with the three-component **Dye/MDEA/R-X** systems

While coming back to the polymerization efficiency, comparison with the reference systems i.e. camphorquinone (CQ)/Iod (0.5%/2%, w/w) (35% monomer conversion) or CQ/MDEA (0.5%/2%, w/w) (46% monomer conversion) revealed the new photoinitiating systems to outperform these benchmarked photoinitiators. This is directly related to the low absorbance of camphorquinone at this specific wavelength. Therefore, the advantage for **D5** to exhibit a redshifted absorption compared to that of camphorquinone was clearly evidenced with the polymerization results. Interestingly, the possibility to perform a thiol-ene polymerization was also demonstrated with **D5**. As shown in the Figure 9, polymerization of a DVE-3/trithiol blend at 457 nm with a laser diode and at 462 nm with a LED furnished different monomer conversions. Indeed, if a similar conversion of 99% was found for DVE-3 at the two wavelengths, different trithiol conversions were determined at 457 nm (46%) and 462 nm (49%), resulting from a competitive cationic polymerization of DVE-3 initiated by the iodonium salt, improving the conversion of this monomer (see reaction mechanism detailed below in equations r6-r9c).

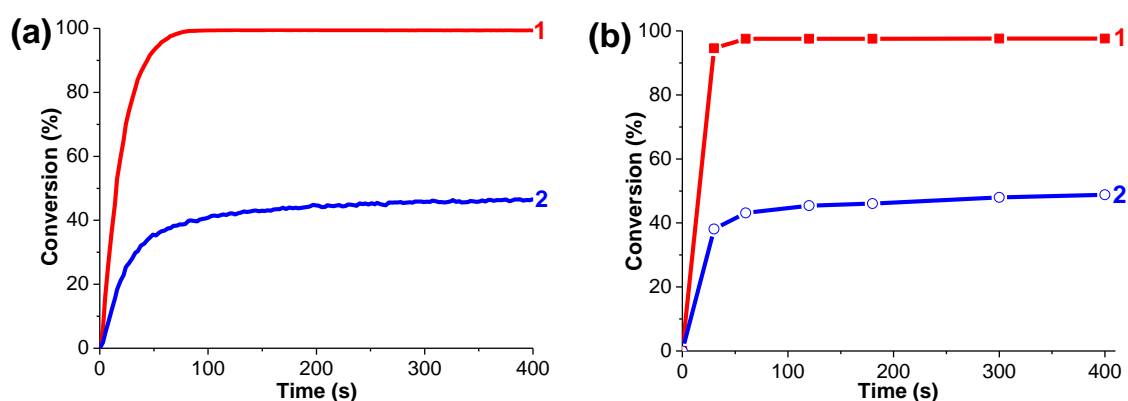
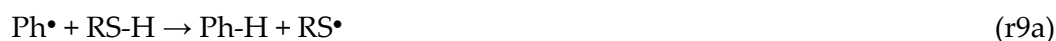
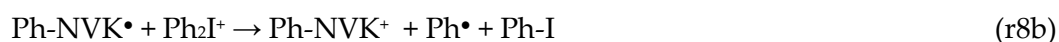


Figure 9. Photopolymerization profiles of a Trithiol/DVE-3 blend in laminate with **D5/Iod** (0.5%/2%, w/w) upon irradiation (a) with a laser diode at 457 nm and (b) a LED at 462 nm. (1) DVE-3 conversion (2) trithiol conversion. Reproduced with permission from Xiao et al. [225]. Copyright 2014 American Chemical Society.

By combining several techniques such as cyclic voltammetry, laser flash photolysis experiments and electron spin resonance (ESR) spin trapping (ESR-ST), the following initiating mechanism could be deduced. Upon photoexcitation, an electron transfer can occur in the excited state between **D5** and Ph₂I⁺, enabling to reduce the iodonium salt and generate the reactive phenyl radicals Ph• (see r7a and r7b in Scheme 2). Upon reaction of Ph• with *N*-vinylcarbazole (NVK), the more reactive radicals Ph-NVK• can be formed (see r8a), reacting with Ph₂I⁺ and providing Ph-NVK⁺ capable to initiate the CP of DVE-3 (see r8b). Parallel to this, Ph• can also react with the thiol derivative, producing the initiating thyl radicals (see r9a and r9b) and enabling the thiol-ene reaction to proceed.



Scheme 2. Mechanism involved during the polymerization process of the thiol-ene reaction

Interest for **D5** also relies in the fact that this dye was of equivalent efficiency in oxidative cycle (when combined with an iodonium salt) but also in reductive cycle (when combined with MDEA). Such a behavior is rarely observed and is directly related to its oxidation and reduction potentials perfectly fitting with those two additives. This dual photoinitiating ability of the carbazole-based photoinitiator **D5** could not be evidenced with another strong electron donor of similar structure, namely phenothiazine.[226] Indeed, in this last case, photolysis of the **D7**/Iod system revealed the absorption spectrum to remain unchanged upon irradiation. Conversely, a fast photolysis was observed for the **D7**/*N*-phenylglycine (NPG) system, revealing that **D7** was easier to reduce than to oxidize (See Figure 10).

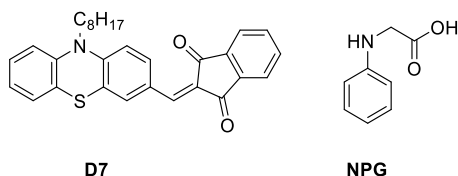


Figure 10. Chemical structure of **D7** and NPG.

With aim at red-shifting the ICT band of the push-pull dyes, introduction of electron donors with extended π -conjugated spacers was examined. A relevant example of this strategy was developed with **D8**, comprising Michler's aldehyde as the donor (See Figure 11).[134]

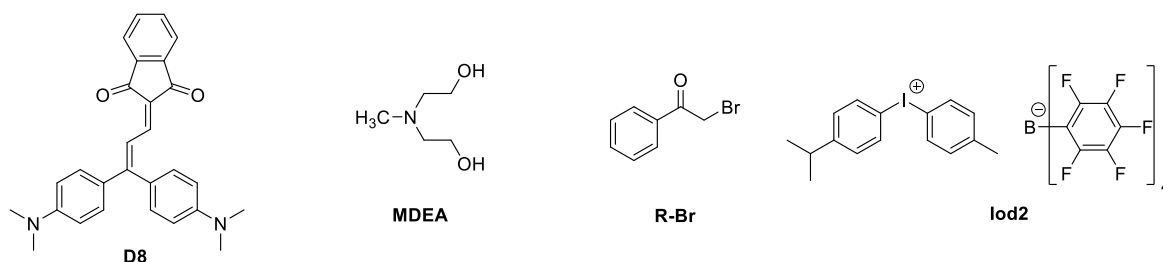


Figure 11. Chemical structure of **D8** and additives.

Benefiting from the extended π -conjugated spacer, a red-shift of the ICT band from 478 nm for **D1** to 532 nm for **D8** was found. However, once again, **D8** proved to be a poor photosensitizer. Especially, **D8** could only work in oxidative conditions. Indeed, a final monomer conversion of 35% could be determined during the CP of EPOX with the three-component system **D8**/NVK/Iod2 (0.3%/3%/2% w/w) after 800 s of irradiation at 532 nm whereas no polymerization could even be initiated with the three-component **D8**/MDEA/R-Br (0.3%/4%/3% w/w) system (where MDEA stands for *N*-methyldiethanolamine and R-Br for phenacyl bromide (See Figure 11)). Here again, photolysis experiments in solution revealed the lack of reactivity for the **D3**/Iod2 combination. However, as interesting findings, presence of radicals could be still detected within the EPOX films even after several weeks of storage, evidencing their remarkable stabilities. Even if origin of this unexpected behavior could not be rationalized, such long-living radicals could be of crucial interest for applications in electronics such as data storage.

With aim at developing a structure-performance relationship, a series of ten indane-1,3-dione-based dyes **D1**, **D8**-**D16** were examined in similar conditions (See Figure 12).[227] First, a clear change of the absorption spectra of the dyes with the donor strength could be evidenced. Thus, absorption maxima ranging from 383 nm for **D9** possessing the weakest electron donor to 567 nm for **D8** exhibiting the strongest electron donor could be determined in dichloromethane (See Figure 13). Even if major differences in terms of absorption can be found between **D8** and **D9**, choice was done by the authors to examine their photoinitiating

abilities only at 405 nm, this wavelength being a reference for 3D printing applications.[228-230]

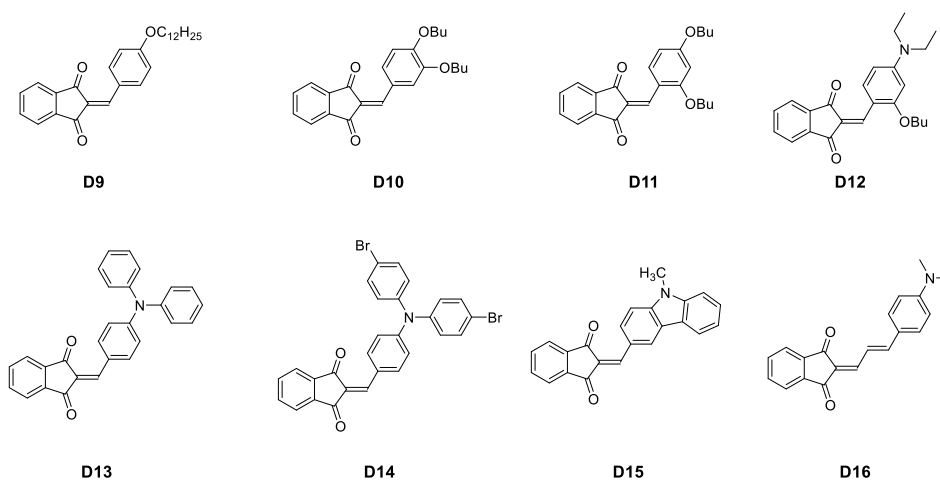


Figure 12. Chemical structures of **D9-D16**.

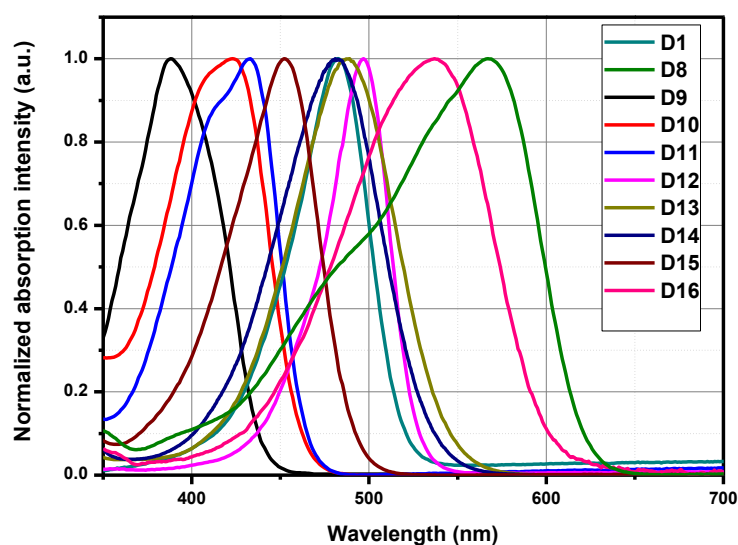


Figure 13. Normalized UV-visible absorption spectra of **D1, D8-D16** in dichloromethane. Reproduced with permission from Ref [227].

While examining their photoinitiating abilities during the FRP of the tetrafunctional acrylate Ebecryl 40, the final monomer conversions obtained with the two-component **Dx** (**x = 1,8-16**)/Iod (0.1%/2% w/w) systems remained low, below 40%. While using a three-component **Dx** (**x = 1,8-16**)/Iod3/EDB (0.1%/2%/2% w/w) system enabling the dye to be regenerated during the polymerization process, all photoinitiating systems could outperform that of the reference system Iod3/ethyl dimethylaminobenzoate (EDB) except **D13** for which a lower monomer conversion could be determined (60% conversion for ebecryl 40 after 400 s of irradiation at 405 nm). The best monomer conversion was determined for **D12**, reaching 93% after only 25 s.

Interestingly, an efficient photobleaching could be observed during the polymerization process with the three-component **D12**/Iod3/EDB (0.1%/2%/2% w/w) system so that a colorless coating could be obtained after polymerization. Such a property is highly researched in industries as it allows to produce colorless coatings.[231-246] Photolysis experiments realized with the **D12**/EDB and **D12**/Iod systems proved the photobleaching to be extremely fast compared to that observed for the other dyes. It can be thus concluded that the superiority of **D12** over the other dyes relies in its fast interaction with the two co-initiators, speeding up the polymerization process so that the oxidative and the reductive cycles could concomitantly contribute to the formation of initiating radicals (See Figure 14).

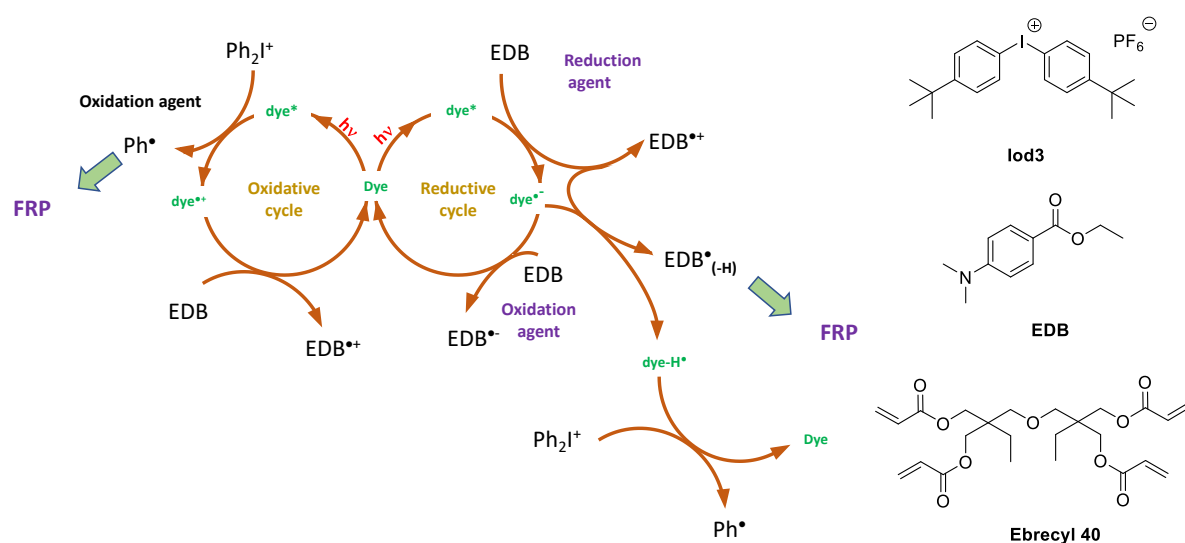


Figure 14. The concomitant mechanistic pathways enabling the polymerization of ebecryl 40.

Considering that **D12** was the most efficient photoinitiator of the series, laser write experiments were carried out. As shown in the Figure 15, precise 3D patterns could be prepared using the three-component system **D12**/Iod/amine (0.1%/2%/2% w/w/w) in ebecryl 40.

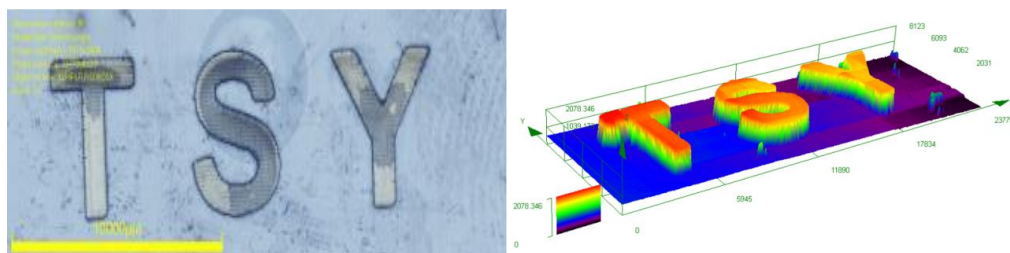


Figure 15. 3D patterns obtained by laser write experiments using the three-component system **D12**/Iod/amine (0.1%/2%/2% w/w/w) in Ebecryl 40. Reproduced with permission from Ref [227].

3. Push-pull dyes based on 1*H*-cyclopentanaphthalene-1,3-dione and related derivatives

As mentioned in the introduction section, one efficient strategy to red-shift the absorption of push-pull dyes consists either to improve the electron-donating ability of the donor or to improve the electron-withdrawing ability of the acceptor. From a synthetic viewpoint, improvement of the electron-withdrawing ability of the electron-acceptor requires additional synthetic steps. Indeed, indane-1,3-dione is commercially available, facilitating the synthesis of numerous dyes. Conversely, when the electron acceptor is not commercially available, its synthetic access can constitute a major impediment for the development of a wide range of dyes. This approach was nevertheless examined by the group of Lalevée et al. who developed a series of dyes **D17-D26** bearing 1*H*-cyclopentanaphthalene-1,3-dione as the electron acceptor (See Figure 16).[227] To evidence the pertinence of the approach, a comparison with their indane-1,3-dione analogues **D1**, **D8-D16** was established. Compared to the **D1**, **D8-D16** series, a red-shift by ca. 20 nm was found for **D17-D26** at identical electron donors.

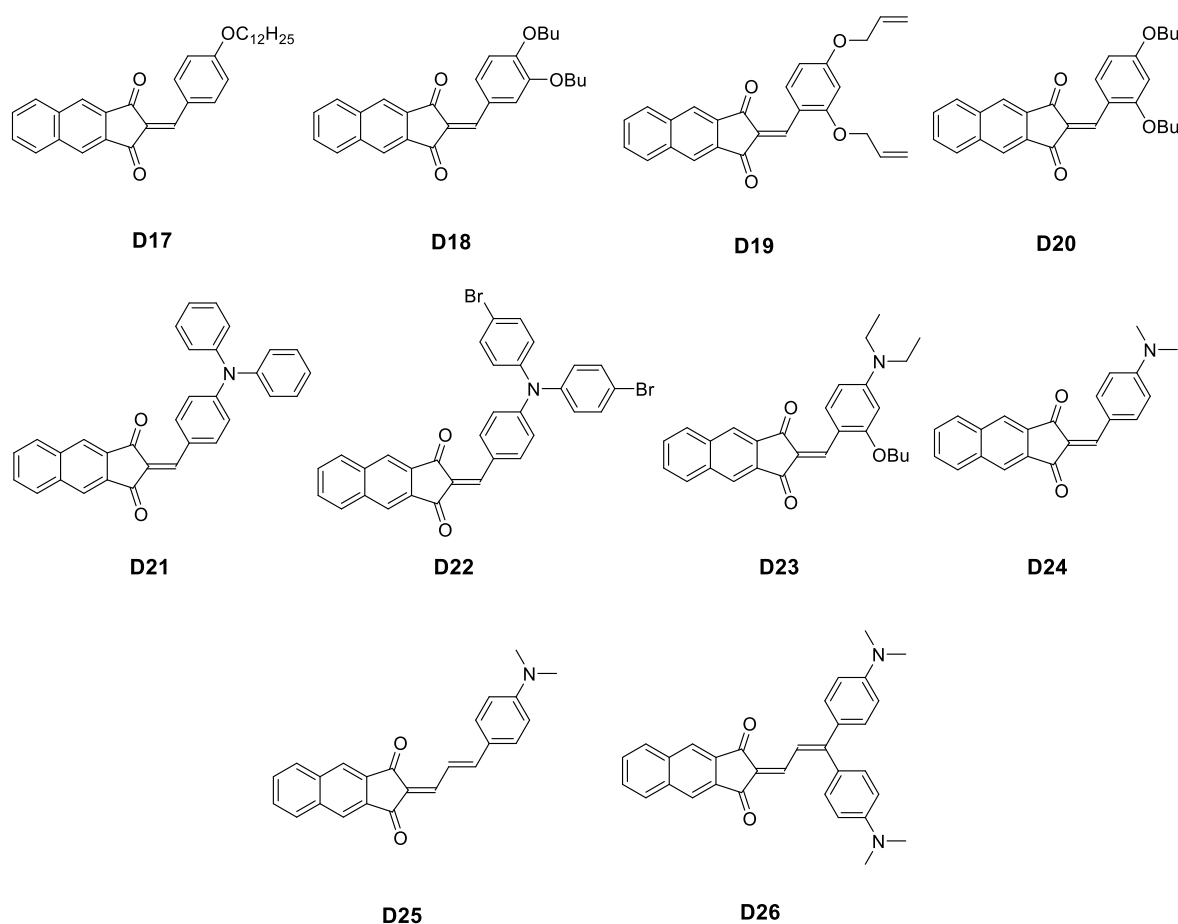
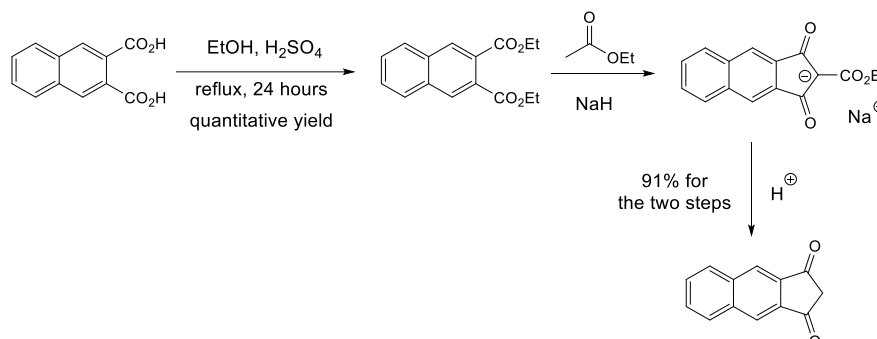


Figure 16. Chemical structures of **D17-D26**.

From a synthetic viewpoint, 1*H*-cyclopentanaphthalene-1,3-dione can be prepared in three steps starting from naphthalene-2,3-dicarboxylic acid according to the synthetic route depicted in the scheme 3.[237-238]



Scheme 3. Synthetic route to 1*H*-cyclopentanaphthalene-1,3-dione.

Here again, the best monomer conversion obtained during the FRP of Ebecryl 40 at 405 nm was obtained for **D23** exhibiting the same electron donor than **D12**. Besides, contrarily to that obtained for **D12**, no photobleaching of the coating was observed with **D23**. Therefore, it can be concluded that such studies combining within a unique work the investigation of numerous dyes is essential to establish a structure-performance relationship. In 2020, two new dyes **D27** and **D28** were examined in a new study devoted to the FRP of TMPTA (See Figure 17).[239] As a typical feature nonetheless observed for push-pull dyes but also for chalcones, a severe reduction of the monomer conversion was observed for the ferrocene derivative compared to that of the carbazole analogue. Thus, upon irradiation at 405 nm under air, final monomer conversions of 76 and 51% were respectively determined after 400 s of irradiation using the three-component **Dx** (**x = 27 or 28**)/Iod3/EDB (0.1%/2%/2% w/w/w) systems (See Table 2). Reduction of the monomer conversion with the ferrocene derivative **D28** is directly related to an inefficient electron transfer from the dye to the iodonium salt, what was demonstrated during the photolysis experiments.

Table 2. Final monomer conversions obtained upon irradiation at 405 nm of an Ebecryl 40 resin using the three-component **Dx** (**x = 17-26**)/iodonium salt/amine (0.1%/2%/2%, w/w)

Dye	0 (Blank) ^a	D9	D10	D11	D1	D12	D13
FCs	60%	80%	86%	78%	66%	93%	60%
Dye	D14	D15	D16	D8	D17	D18	D19
FCs	80%	83%	83%	84%	50%	70%	78%
Dye	D20	D21	D22	D23	D24	D25	D26
FCs	92%	90%	92%	94%	56%	85%	92%

a: iodonium salt / amine (2%/2%, w/w) without dye.

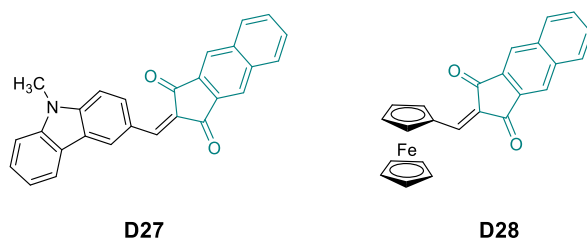


Figure 17. Chemical structures of **D27** and **D28**.

Recently, a series of dyes **D29-D35** exhibiting redshifted absorptions compared to that of 1*H*-cyclopentanaphthalene-1,3-dione-based push-pull dyes **D17-D26** were obtained by improving the electron-withdrawing ability of the electron acceptor (See Figure 18).[239] To achieve this goal, a procedure similar to that used for improving the electron-withdrawing ability of indane-1,3-dione was used. By substituting 1*H*-cyclopentanaphthalene-1,3-dione **EA1** with one or two equivalents of malononitrile, two new electron-acceptors 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile **EA2** and 2,2'-(1*H*-cyclopenta[*b*]naphthalene -1,3(2*H*)-diylidene)dimalononitrile **EA3** could be respectively obtained in 67 and 41% yields (See Scheme 4).

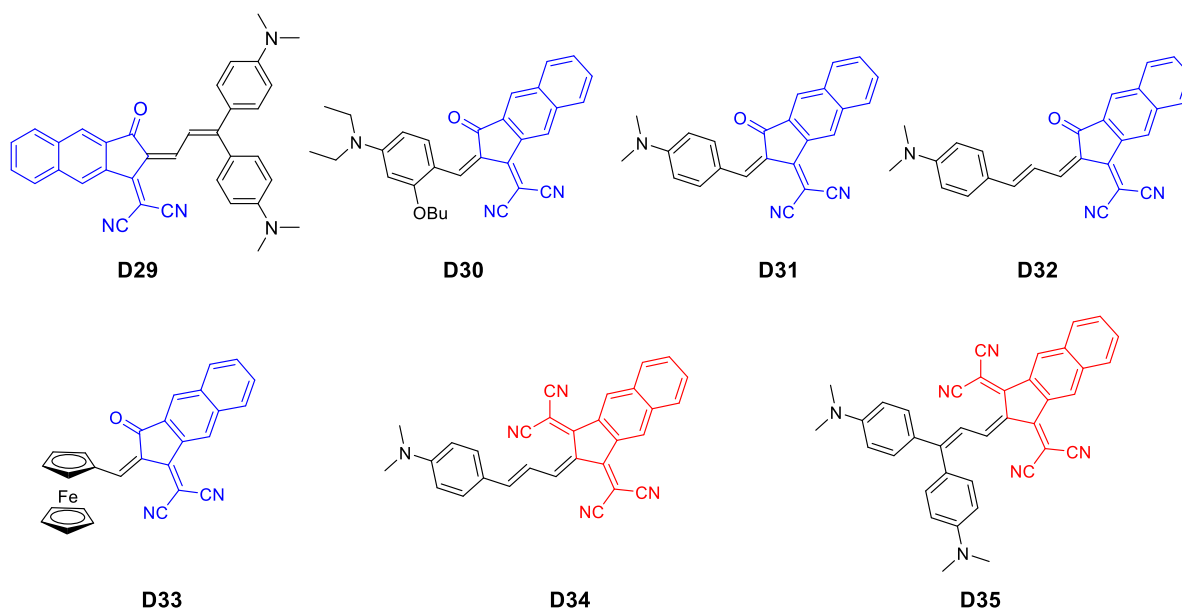
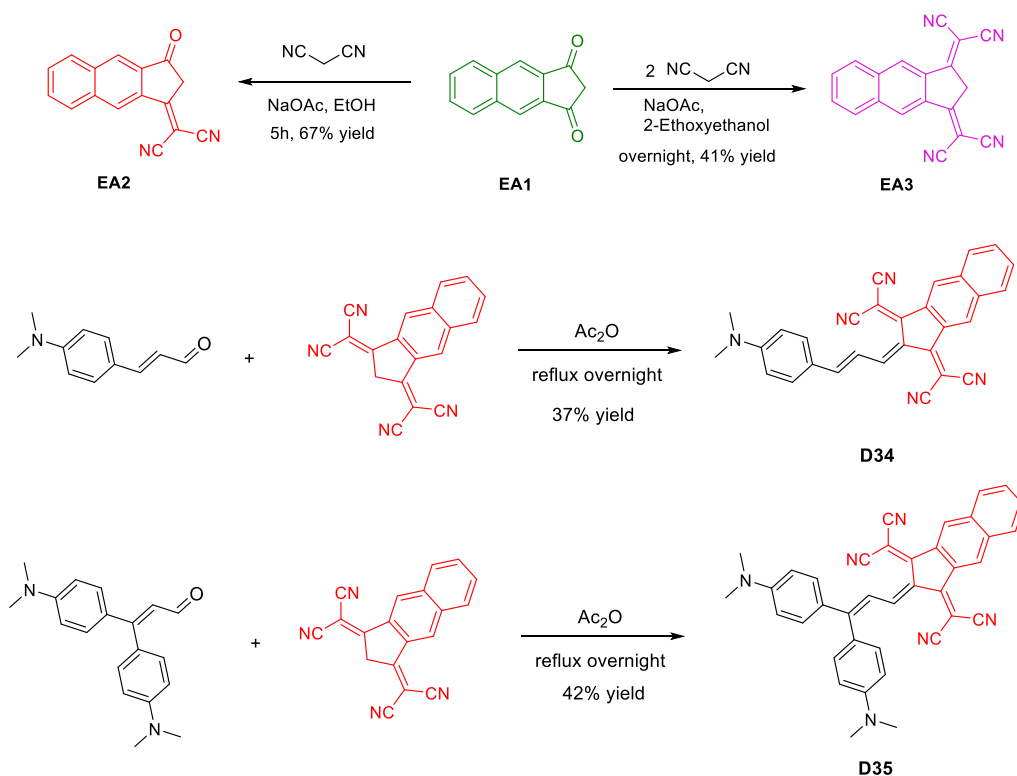


Figure 18. Chemical structures of **D29-D35**.

However, it has to be noticed that if the Knoevenagel reactions done to introduce the cyano group onto indane-1,3-dione are classically done in ethanol as the solvent, due to the remarkable stability of the **EA1** anion in basic conditions resulting from the electronic delocalization, condensation of malononitrile on **EA1** could only be realized in more drastic conditions than classically used and an elevation of the reaction temperature could be obtained by using 2-ethoxyethanol as the solvent.



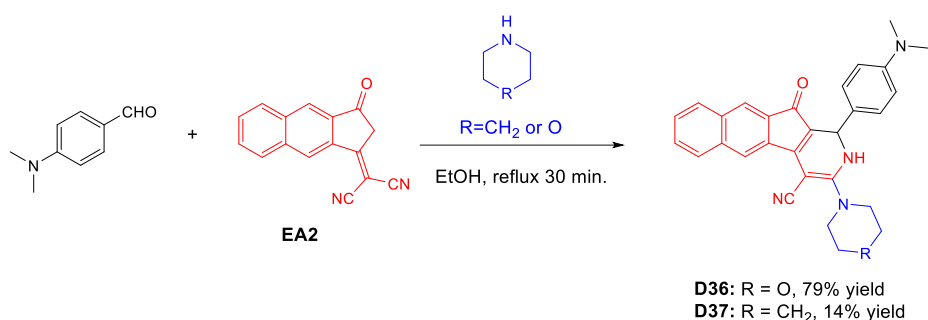
Scheme 4. Synthetic routes to building blocks EA1-EA3 and push-pull dyes D34 and D35.

Due to the strong electron-withdrawing ability of EA3, D34 and D35 should be prepared by refluxing EA3 in acetic anhydride with the appropriate aldehyde, providing D34 and D35 in 37 and 42% yields respectively. Conversely, D29-D33 could be prepared in standard conditions for a Knoevenagel reaction, namely in ethanol as the solvent and with diisopropylethylamine (DIPEA) as the base. Thus, the different dyes could be obtained with reaction yields ranging from 37% for D32 to 87% for D30 and 90% for D19. When tested as photoinitiators for the FRP of acrylates in three-component D_x ($x = 29-35$)/Iod3/EDB (0.1%, 2%/2%, w/w) systems, D34 and D33 proved to be less efficient than the reference two-component Iod/EdB system (2%/2%, w/w) (43 and 56% conversions vs 60% for Iod/EDB respectively). Conversely, for the other dyes, the three-component D_x ($x = 29-35$)/iodonium salt/amine (0.1%, 2%/2%, w/w) system could outperform the reference system (78% monomer conversion for D30, 80% for D31). Here again, the lower reactivity of the ferrocene-based dye D33 compared to that of the purely organic analogues was confirmed, the monomer conversion only reaching 56%.

4. Azafluorenones

Azafluorenones are polycyclic compounds whose synthesis has recently been identified as a side-reaction occurring during the synthesis of push-pull dyes when a nucleophilic base was used.[212] Indeed, the first report mentioning the condensation of an activated methylene group to an aldehyde was reported as soon as 1896 by Knoevenagel and in this pioneering work, benzaldehyde was condensed to ethyl acetoacetate in the presence of piperidine.[240] However, when nucleophilic bases are used, an adverse nucleophilic attack

onto the cyano groups of the electron acceptor can occur, as depicted in the Scheme 5. Using piperidine or morpholine as the nucleophilic base, compounds **D36** and **D37** could be prepared in 79 and 14% yields respectively.[238]



Scheme 5. Synthetic route to compounds **8** and **9**.

In 2020, azafluorenones that are compounds rarely prepared were examined as potential photoinitiators for the FRP of TMPTA and a comparison with **D30-D35** was established.[239] Surprisingly, dyes **D36** and **D37** could greatly outperform all the other dyes, the monomer conversion reaching 91 and 88% respectively (See Figure 19 and Table 3). In fact, a two-fold enhancement of the monomer conversion could be determined for dye **D36** compared to dye **D34**. In light of the remarkable performance of dye **D36**, photopolymerization experiments using sunlight were carried out. As shown in the Figure 20 and despite the severe decrease of the light intensity ($I_0 < 5 \text{ mW/cm}^2$ in the 350–500 nm range for sunlight vs. 110 mW/cm^2 for the LED@405nm), the polymerization of TMPTA was determined as being ended after only 10 min. under sunlight exposure while using the three-component **D36**/Iod3/EDB (0.1%, 2%/2%, w/w) system. Finally, still to evidence the remarkable reactivity of dye **D36**, laser write experiments were carried out using the same resins. Here again, the high reactivity could be demonstrated by the precision of the letters written with the laser emitting at 405 nm (See Figure 21).

Table 3. Final monomer conversions obtained upon irradiation at 405 nm of a TMPTA resin using the three-component **Dx** ($x = 27,28,30-38$)/iodonium salt/amine (0.1%,2%/2%, w/w)

Dye	0 (Blank) ^a	D27	D28	D30	D31	D32
FCs	60%	76%	51%	92%	80%	78%
Dye	D33	D34	D35	D36	D37	D38
FCs	56%	43%	84%	91%	88%	85%

a: iodonium salt / amine (2%/2%, w/w) without dye.

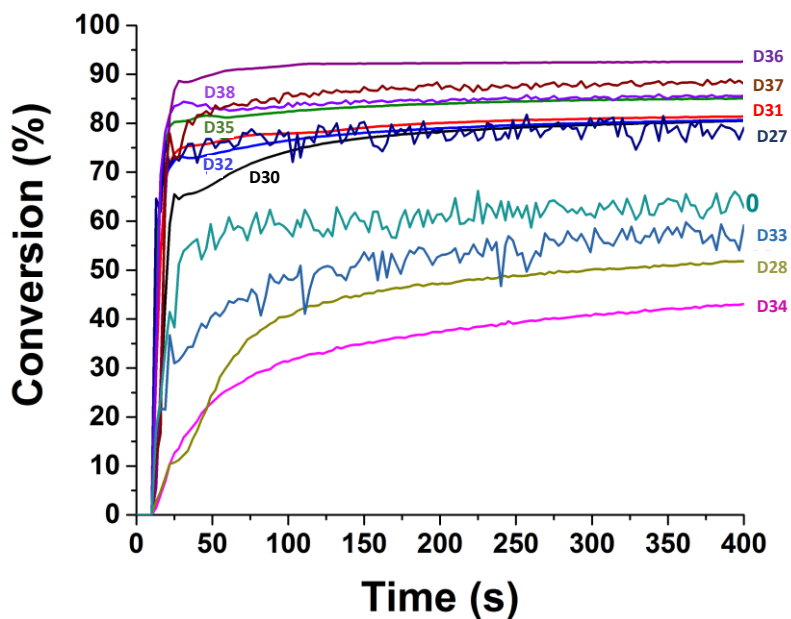


Figure 19. Photopolymerization profiles of TMPTA using the three-component dyes/iodonium salt/amine (0.1%, 2%/2%, w/w) system. Irradiation with a LED@405 nm under air with dyes **D27, D28, D30-D38**. The curve 0 corresponds to the photoinitiating system (iodonium/amine) without dye. Reproduced with permission from Ref [239].

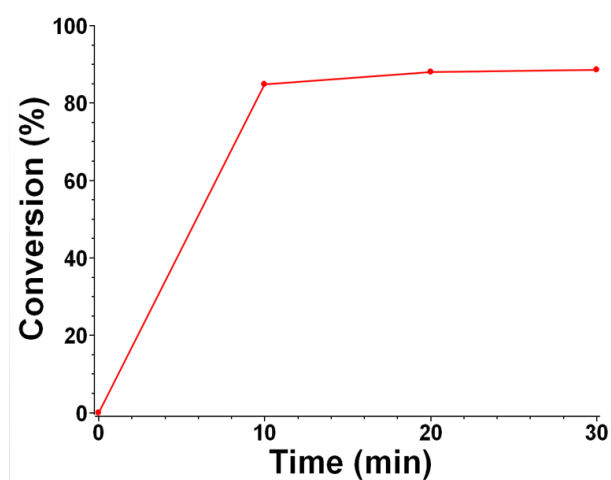
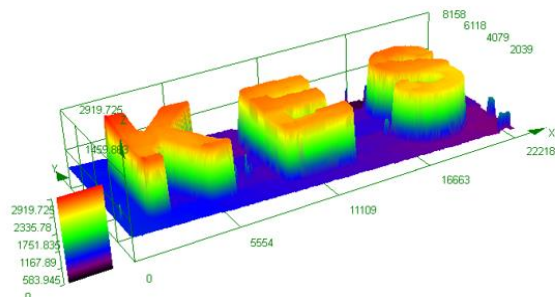


Figure 20. TMPTA conversion vs. Time obtained upon irradiation with sunlight using the three-component **D36/Iod3/EDB** (0.1%, 2%/2%, w/w) system. Reproduced with permission from Ref [239].



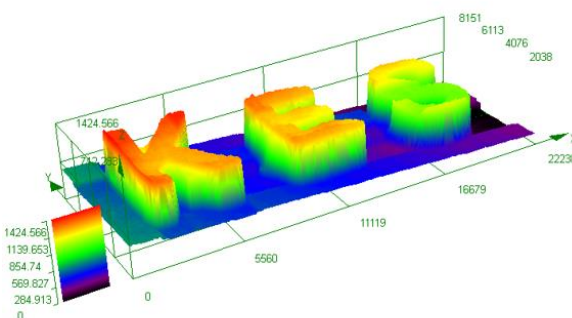
(a)



(b)



(c)

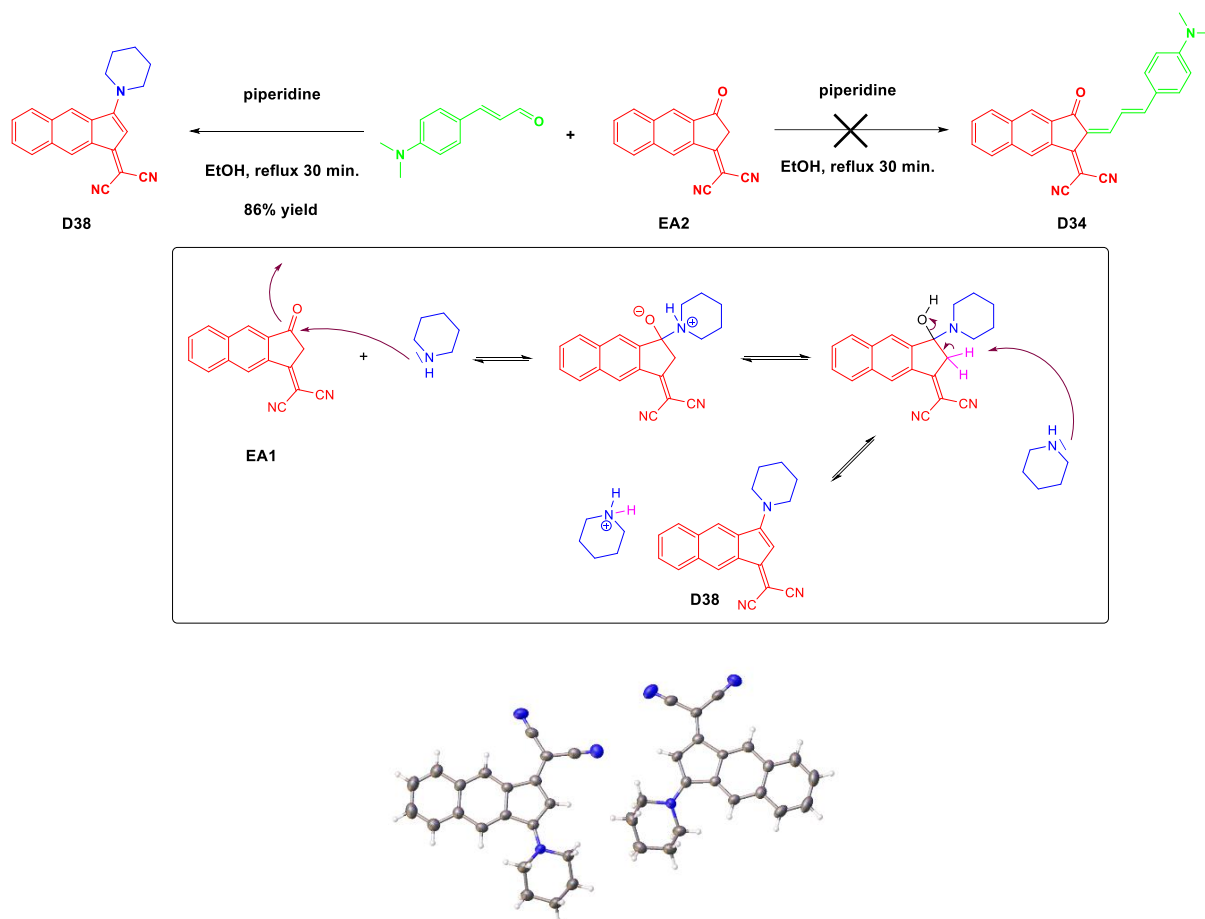


(d)

Figure 21. Different letters written by laser write experiments using a laser@405 nm and the three-component **D36**/Iod3/EDB (0.1%, 2%/2%, w/w) system. Reproduced with permission from Ref [239].

5. Nucleophilic adducts of indane-1,3-dione derivatives.

In 2020, the nucleophilic addition of piperidine onto 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile **EA2** was reported for the first time.[238] Surprisingly, this unexpected reaction could only occur while using 3-(4-(dimethylamino)phenyl)acrylaldehyde as the aldehyde. If the corresponding push-pull dye **D34** could not be obtained in these conditions, compound **D38** could be prepared in 86% yield (See Scheme 6). To confirm its structure, crystals could be obtained, and the crystal structure solved.



Scheme 6. Synthetic route to dye **D38**, the mechanism of formation and the crystal structure of dye **D38**. Reproduced with permission from Ref [238].

Examination of its photoinitiating ability during the FRP of TMPTA using the three-component **D38**/Iod3/EDB (0.1%, 2%/2%, w/w) system revealed **D38** to be on par with dye **D35** and to furnish only a slightly lower monomer conversion than dyes **D36** and **D37** (85% vs. 91 and 88% monomer conversion respectively). This new family of compound, even if difficult to prepare deserves to be more extensively studied in the future.

6. 1,3-Bis(dicyanomethylidene)indane

As mentioned in the paragraph 3, anions of tetracyano derivatives of indane-1,3-dione are highly stable in solution so that the Knoevenagel reaction with these electron acceptors can only be carried in acidic conditions (i.e. acetic anhydride). Indeed, when the Knoevenagel reaction are performed in classical conditions, i.e. ethanol in the presence of piperidine, no reaction occurs. Considering that the deprotonation of these species is easy in solutions and that the anions are strongly colored, in 2013, 1,3-bis(dicyanomethylidene)indane **D39** and 1-(dicyanomethylene)-3-indanone **D40** were examined as strong acids capable to initiate the CP of various epoxides, namely (3,4-epoxycyclohexane)methyl-3,4-epoxycyclohexylcarboxylate

(EPOX), (epoxycyclohexylethyl)methylsiloxane-dimethylsiloxane copolymer (EPOX-Si) and an epoxidized soybean oil (ESO) (See Figure 22).[241] In fact, advantages of these molecules are threefold. First, remarkable stability of the anions enables **D39** and **D40** to act as acid generators. Second, due to the strong color of the anions, these latter can be used as photosensitizers for the decomposition of an iodonium salt (Iod). Indeed, as shown in the Figure 24, an absorption spectrum extending from 400 to 650 nm could be found for **D39** in a protic acetonitrile/water solution.

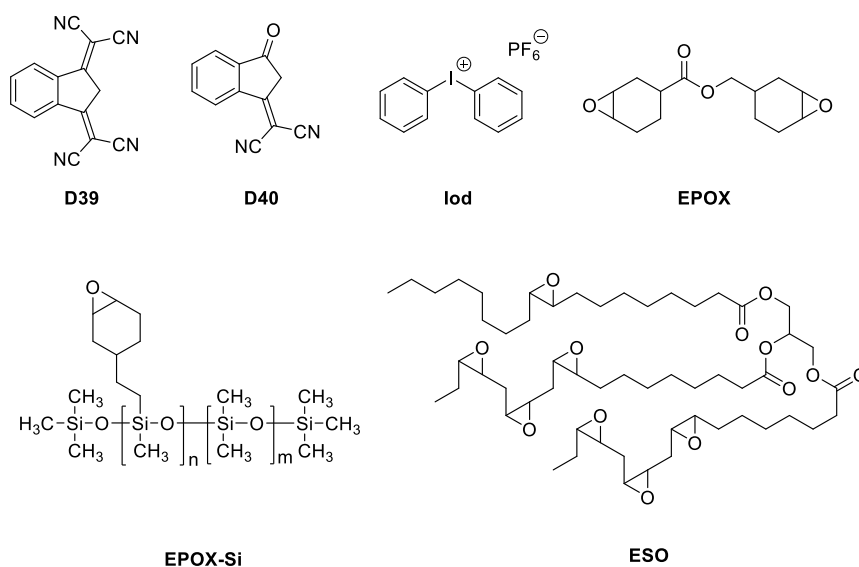


Figure 22. Chemical structures of **D39** and **D40** and the different epoxide monomers.

It has to be noticed that, in-situ generation of strong acids in resins is already reported in the literature, except that these strong acids have only been obtained by mean of redox reactions involving the use of transition metals. Thus, the generation of strong acids by reaction of a copper-catalyzed reduction of iodonium salts with benzoines,[242,243] or the platinum-catalyzed reduction of iodonium salts with boranes or silanes[244-247] have previously been reported in the literature. Besides, traces of residual metals can constitute a major impediment for further use of polymers.

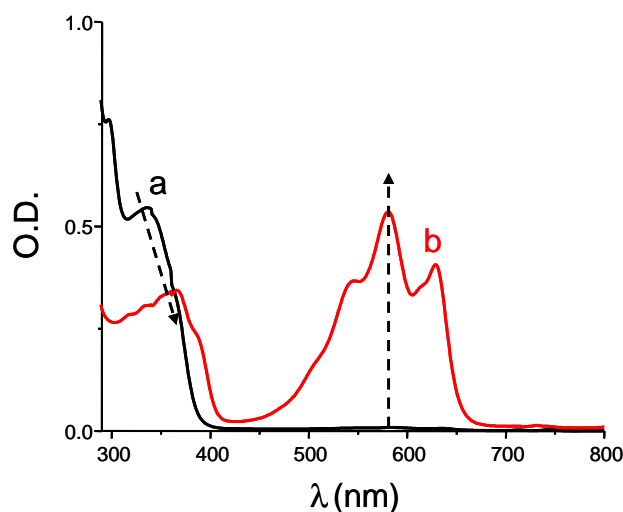


Figure 23. UV-visible absorption spectra of **D39** in *tert*-butylbenzene (a), in acetonitrile–water (b). Adapted from ref. [241] with permission from The Royal Society of Chemistry

In the present work, by simply dissolving **D39** in EPOX (2% w/w), a conversion of 45% could be determined at room temperature after 1200 s of monitoring (See Figure 24). Conversely, **D40** could not initiate any polymerization in the same conditions. In fact, these results were corroborated by NMR analyses experiments in deuterated DMSO. Indeed, if a complete deprotonation of **D39** in DMSO was detected by NMR, coexistence of the protonated and the deprotonated form for **D40** was also evidenced, supporting the lack of reactivity of **D40** in resins.

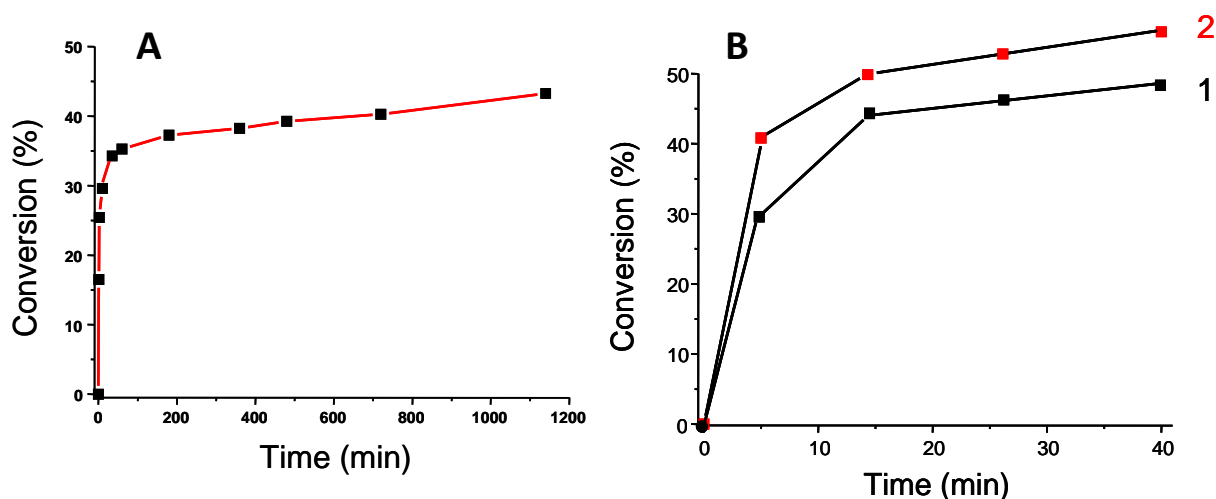
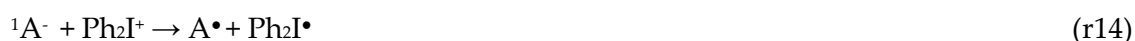


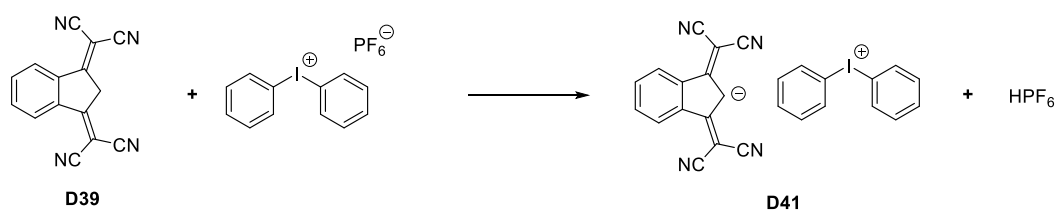
Figure 24. Monitoring of the EPOX conversion A) using **D39** ((2% w/w) in EPOX; B) with (curve 1) and without (curve 2) irradiation with a laser diode at 532 nm. Adapted from ref. [241] with permission from The Royal Society of Chemistry.

Possibility to photoactivate the CP of EPOX was also examined. By using the two-component **D39**/Iod (2%/2% w/w) system, as anticipated, an improvement of the monomer conversion was obtained, as shown in the Figure 25. Upon irradiation at 532 nm, the monomer conversion could be improved from 45% without light to 55% in the presence of light, indicative of a photoactivation of the polymerization process. To support the polymerization reaction, the following mechanisms were proposed in the absence (r10-r12) and in the presence of light (r13-r17).



Scheme 7. Mechanism of the cationic polymerization of epoxides.

Finally, considering that the iodonium salts are still accompanied by an inorganic counter-anion, the design of a soft salt with **D39** and the iodonium salt was proposed (See Scheme 8). By use of a polar solvent and by using procedure previously reported in the literature for the design of soft salts, **D39** could spontaneously deprotonate, enabling the formation of the soft salt **D41**. [248-250] By water treatment, HPF_6 could be easily removed from the organic phase, enabling to get the organic salt in pure form.



Scheme 8. Synthetic route to dye **D41**.

By electron-spin resonance (ESR) spectroscopy, formation of radicals upon light irradiation was clearly evidenced (See Figure 25). Finally, examination of the photoinitiating ability of the soft salt **D41** used as a single component for the photopolymerization of a methacrylate resin composed of a mixture of bisphenol-A epoxy diacrylate oligomer and tripropyleneglycol diacrylate showed the soft salt to furnish similar monomer conversions

than 2,2-dimethoxy-2-phenylacetophenone (DMPA) (58% monomer conversions after 200 s of irradiation with a Xe–Hg lamp (>330 nm) (See Figure 26). Therefore, by preparing the soft salt **D41** with the iodonium salt, a simplification of the formulation could be obtained without adversely affecting the photoinitiating ability. Besides, interest for such salt remains limited, due to the similarity of monomer conversion with the benchmark and cheap DMPA.

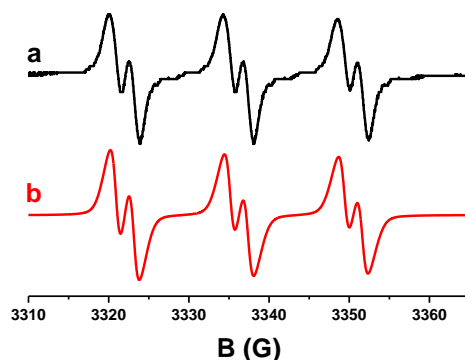


Figure 25. Experimental (a) and theoretical (b) ESR spectra obtained upon irradiation of the soft salt **D41** in *tert*-butylbenzene under nitrogen using phenyl-*N-tert*-butylnitron as the spin trap agent. Adapted from ref. [241] with permission from The Royal Society of Chemistry

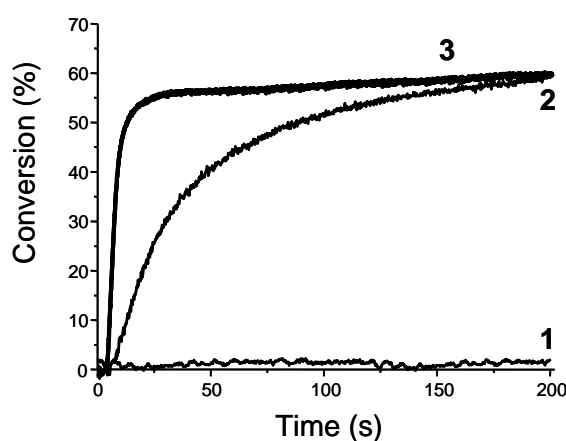


Figure 26. Monomer conversions obtained during the FRP of a methacrylate resin using the soft salt **D41** (2) and DMPA (3). (0) : control experiments without photosensitizer. Adapted from ref. [241] with permission from The Royal Society of Chemistry

Conclusion

To conclude, a series of 41 dyes based on indane-1,3-dione and related derivatives have been synthesized and tested as photoinitiators of polymerization under low light intensity and in the visible range. By finely tuning the substitution pattern, dyes absorbing between 300 and 850 nm were prepared (See Figure 27 and Table 4).

Table 4. Summary of the photopolymerization characteristics of the different photoinitiating systems based on dyes **D1-D41**.

dye	Absorption range (nm)	Molar extinction coefficient	Irradiation conditions	Additives	Monomers	Polymerization type	Reference
D1	400-750	40 000	laser diodes at 405, 457, 473, 532, and 635 nm	Iod, NVK	TMPTA, EPOX, DVE-3	FRPCP FRP	[213]
D2	350-550	22 000	laser diodes at 405, 457, 473, 532, and 635 nm	Iod, NVK	TMPTA, EPOX, DVE-3	FRPCP FRP	[213]
D3	insoluble	-	halogen lamp, laser diode 457 nm	Iod, NVK, MDEA, R-Br, R'-Cl	EPOX, TMPTA, DVE-3, trithiol	FRPCP, FRP, Thiol-ene reaction	[225]
D4	300-450	29 900	halogen lamp, laser diode at 457 nm	Iod, NVK, MDEA, R-Br, R'-Cl	EPOX, TMPTA, DVE-3, trithiol	FRPCP, FRP, Thiol-ene reaction	[225]
D5	350-525	42 200	halogen lamp, laser diode at 457 nm	Iod, NVK, MDEA, R-Br, R'-Cl	EPOX, TMPTA, DVE-3, trithiol	FRPCP, FRP, Thiol-ene reaction	[225]
D6	350-550	7 700	halogen lamp, laser diode at 457 nm	Iod, NVK, MDEA, R-Br, R'-Cl	EPOX, TMPTA, DVE-3, trithiol	FRPCP, FRP, Thiol-ene reaction	[225]
D7	400-650	16 400	LED at 405 nm	Iod, NPG,	TMPTA, EPOX, TEGDMA	FRPCP, FRP	[226]
D8	350-650	14 400	halogen lamp, laser diodes at 457, 473, and 532 nm	Iod, NVK, MDEA, R-Br, (TMS) ₃ Si-H	TMPTA, EPOX	FRPCP FRP	[134]
D9	350-450	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D10	350-475	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D11	350-475	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D12	400-550	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D13	400-575	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D14	350-575	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D15	350-525	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D16	350-650	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]

D17	350-475	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D18	375-550	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D19	375-550	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D20	375-550	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D21	400-600	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D22	400-600	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D23	450-575	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D24	400-575	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D25	450-675	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D26	400-680	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D27	350-525	49 650	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D28	350-750	4 550	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[227]
D29	400-780	56 330	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D30	500-700	38 580	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D31	450-700	24 872	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D32	500-750	16 330	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D33	350-800	5 950	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D34	350-750	11 600	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D35	350-800	23 000	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D36	350-600	5 330	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D37	350-600	9 800	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D38	350-580	14 300	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[239]
D39	400-700	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[241]
D40	-	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[241]
D41	400-650	-	LED at 405 nm	Iod, EDB	Ebecryl 40	FRP	[241]

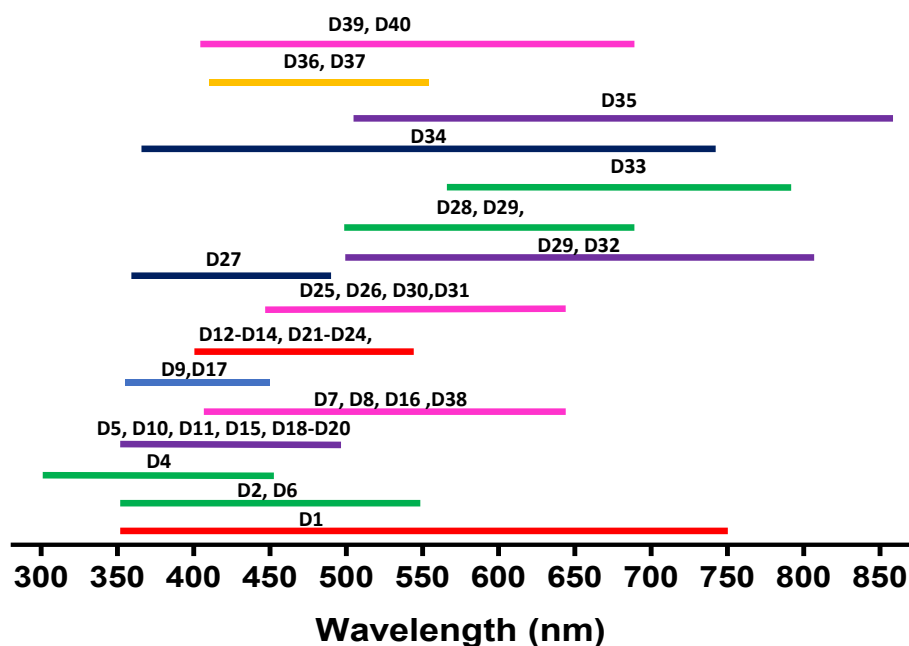


Figure 27. Summary of the absorption properties of all dyes discussed in this review.

By examining these different structures, several interesting features have been identified. Thus, elongation of the electron-acceptor greatly contributed to red-shift the absorption while maintaining a similar reactivity. In this series, a dye i.e. **D12** was identified as being capable to bleach, even in three-component systems and this property is highly researched by industry. The most promising results in terms of photoinitiating abilities have been obtained with the less common dyes namely the azafluorenones (**D36**, **D37**) that clearly outperform the rest of the dyes. Parallel to this, **D38** whose synthesis is unprecedented in the literature could furnish monomer conversions on par with that of **D36** and **D37**. With aim of developing high-performance photoinitiators, future works will typically consist in developing new derivatives of these two families (azafluorenones and nucleophilic adducts). It will also consist in developing crosslinkable dyes, with aim at addressing the extractability issue. Indeed, at present almost no crosslinkable push-pull dyes have been examined as photosensitizers, what deserves to be more systematically studied in the Future.

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