

Ultrafast Sunlight-Induced Polymerization: Unveiling 2-Phenylnaphtho[2,3-*d*]Thiazole-4,9-dione as a Unique Scaffold for High-Speed and Precision 3D Printing

Ji Feng, Yijun Zhang, Fabrice Morlet-Savary, Michael Schmitt, Jing Zhang, Pu Xiao,*
Frédéric Dumur,* and Jacques Lalevée*

A series of 15 dyes based on the 2-phenylnaphtho[2,3-*d*]thiazole-4,9-dione scaffold and 1 compound based on the 2,3-diphenyl-1,2,3,4-tetrahydrobenzo[*g*]quinoxaline-5,10-dione scaffold are studied as photoinitiators. These compounds are used in two- and three-component high-performance photoinitiating systems for the free radical polymerization of trimethylolpropane triacrylate (TMPTA) and polyethylene glycol diacrylate (PEGDA) under sunlight. Remarkably, the conversion of TMPTA can reach $\approx 60\%$ within 20 s, while PEGDA attains a 96% conversion within 90 s. To delve into the intricate chemical mechanisms governing the polymerization, an array of analytical techniques is employed. Specifically, UV-vis absorption and fluorescence spectroscopy, steady-state photolysis, stability experiments, fluorescence quenching experiments, cyclic voltammetry, and electron spin resonance spin trapping (ESR-ST) experiments, collectively contribute to a comprehensive understanding of the photochemical mechanisms. Photoinitiation capacities of these systems are determined using real-time Fourier transformed infrared spectroscopy (RT-FTIR). Of particular interest is the revelation that, owing to the superior initiation ability of these dyes, high-resolution 3D patterns can be manufactured by direct laser write (DLW) technology and 3D printing. This underscores the efficient initiation of free radical polymerization processes by the newly developed dyes under both artificial and natural light sources, presenting an avenue for energy-saving, and environmentally friendly polymerization conditions.

1. Introduction

In recent years, the application of photopolymerization has witnessed a significant expansion, both in industrial production and academic research. This surge can be attributed to the myriad advantages of photopolymerization, encompassing its environmentally friendly nature, absence of organic solvents, and safe operational conditions when employing visible light.^[1,2] With the evolution of LED technology, energy-efficient conditions have further become applicable to photopolymerization processes. The versatility of photopolymerization technology is exemplified in its applications, spanning 3D printing, biomedical materials development, coatings, dentistry, and various other applications.^[3–10]

Among the diverse photopolymerization techniques, free radical polymerization (FRP) stands out as one of the most prevalent and important technologies,^[11,12] offering mild reaction conditions, high monomer conversions, and rapid polymerization rates. The efficacy of FRP processes is closely tied to the properties of the employed photoinitiators (PIs). Over the years, various photoinitiators have been explored

J. Feng, Y. Zhang, F. Morlet-Savary, M. Schmitt, J. Lalevée
Université de Haute-Alsace
CNRS
IS2M UMR7361, Mulhouse F-68100, France
E-mail: jacques.lalevee@uha.fr

J. Feng, Y. Zhang, F. Morlet-Savary, M. Schmitt, J. Lalevée
Université de Strasbourg
Strasbourg F-67081, France



The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smll.202400230>

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DOI: 10.1002/smll.202400230

J. Zhang
Future Industries Institute
University of South Australia
Mawson Lakes, South Australia 5095, Australia

P. Xiao
State Key Laboratory of High Performance Ceramics and Superfine Microstructure
Shanghai Institute of Ceramics
Chinese Academy of Sciences
Shanghai 200050, P. R. China
E-mail: p.xiao@mail.sic.ac.cn

F. Dumur
Aix Marseille Univ
CNRS
ICR, UMR 7273, Marseille F-13397, France
E-mail: frederic.dumur@univ-amu.fr

to enhance their performance across visible range. The pivotal factor in photopolymerization revolves around the ability of the photoinitiator/photosensitizer to efficiently interact with the light source.^[13,14] The initiation process hinges on the light absorption capacity of the photoinitiating systems that is governed by the molar extinction coefficients of the PIs. Additionally, the absorption maximum plays a crucial role in determining the excitation wavelength of a chromophore, influencing the efficacy of the electron or energy transfer from the photosensitizer to the different additives within the photocurable resin.^[15] Up to now, common irradiation wavelengths have resided in the UV (<400 nm) and UV–vis (405 nm, 415 nm, etc.) range.^[16,17] However, the most optimal light source remains sunlight, presenting a renewable, and free energy option for photopolymerization. Similar to photosynthesis in plants,^[15] direct photopolymerization under natural sunlight is now a focal point of intense research efforts.

Sunlight, as a rich and sustainable energy source, remains inexhaustible as long as the sun shines. Consequently, the development of sunlight-induced reactions holds a prominent position in contemporary,^[18] encompassing areas such as CO₂ conversion and decomposition.^[19,20] Another critical consideration in photopolymerization is the photoinitiator itself, posing challenges in the development of efficient photoinitiators suitable for sunlight-induced reactions.^[21] Unlike artificial light sources, sunlight exhibits lower intensity than LEDs, accompanied by a much wider emission spectrum.^[22] This distinction renders many photoinitiating systems, easily activated with LEDs, and ineffective in initiating polymerization under sunlight.^[23] Even in instances where polymerization can be initiated under sunlight, the process often extends over several hours, with reduced monomer conversions compared to LED-initiated polymerization.^[3] Our previous research has identified many dyes with excellent photoinitiation performance when used in multicomponent systems^[24,25]; however, most of these were limited to LED activation. Thus, the development of dyes capable of efficiently initiating polymerization processes under sunlight assumes paramount significance.

This study introduced 15 dyes based on the 2-phenylnaphtho[2,3-*d*]thiazole-4,9-dione scaffold and 1 dye based on 2,3-diphenyl-1,2,3,4-tetrahydrobenzo[*g*]quinoxaline-5,10-dione, hitherto unreported in the literature. These dyes exhibited outstanding photoinitiation abilities under UV–vis light (e.g., LED@405 nm and LED@450 nm). Notably, five of the dyes exhibited exceptional photoinitiating ability under sunlight, enabling rapid resin curing within 1 min of exposure. The achieved monomer conversions, obtained at low photoinitiator/additive content, and short exposure time (RT-FTIR profiles), represented an unprecedented advancement in the field. The elucidation of the photochemical mechanisms governing the polymerization process involved a comprehensive analysis of light absorption and fluorescence characteristics, cyclic voltammetry, and ESR-ST experiments. The findings culminated in the successful application of several formulations exhibiting excellent photoinitiation abilities in DLW and 3D printing, yielding clear, and precise 3D patterns. Leveraging the remarkable performance in outdoor sunlight polymerization and applications in 3D printing, the dyes based on 2-phenylnaphtho[2,3-*d*]thiazole-4,9-dione scaffold have emerged as promising candidates for green polymer synthesis and large-scale outdoor applications.

2. Experimental Process

2.1. Dyes and Other Materials

A collection of 16 dyes used for photopolymerization (under UV–vis light and under sunlight in the air) was successfully synthesized. Chemical structures are shown in **Figure 1**, and the synthetic routes used to prepare these compounds are detailed in the following Section 3.1 and in supporting information. The different monomers, i.e., TMPTA and PEGDA (average Mn 575 g mol^{−1}) were all purchased from Sartomer (France). The benchmark commercial photoinitiator 2-isopropylthioxanthone (ITX) used for comparison was obtained from Sartomer–Lambson (United Kingdom). Ethyl 4-dimethylaminobenzoate (EDB) was used as the electron donor and *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod) as the electron acceptor was purchased from Sartomer–Lambson (United Kingdom) (See **Figure S1**, Supporting Information).

2.2. UV–Vis Absorption and Fluorescence Properties of Dyes

The UV–vis absorption properties and UV steady-state photolysis of the sixteen dyes, dissolved in dichloromethane at a concentration of 5×10^{-5} M, were studied using a JASCO V730 spectrophotometer. Steady-state photolysis of the different systems (dye, dye/EDB, dye/Iod, dye/EDB/Iod) was investigated upon irradiation (e.g., under LED@405 nm). Maintaining the consistent dye concentration in dichloromethane, fluorescence spectra of the different dyes were measured using the JASCO FP-6200 fluorescence spectrophotometer, and the fluorescence excited state lifetimes were determined using the HORIBA PPD-850 fluorimeter. The singlet excited state energy level (E_{S1}) of the dyes was determined from the intersection of the normalized UV–vis absorption and fluorescence spectra.

Fluorescence quenching experiments were performed using the JASCO FP-6200 spectrofluorometer, allowing for the extraction of pertinent of parameters such as the electron transfer quantum yields (ϕ_{et}) using Equation (1). The Stern–Volmer coefficients (K_{sv}) correspond to the slopes of the Stern–Volmer treatment in the fluorescence quenching experiments.

$$\phi_{et} = \frac{K_{sv} [\text{additive}]}{1 + K_{sv} [\text{additive}]} \quad (1)$$

2.3. Free Radical Photopolymerization (FRP) under Near UV/Visible-Light Irradiation and Sunlight-Induced Polymerization under Air

The different formulations used for photopolymerization were prepared as follows: dye/EDB (two-component) and dye/EDB/Iod (three-component) were mixed and dissolved into TMPTA, and then stirred overnight in the dark. The weight content of dye, EDB, and Iod was calculated based on the weight of the monomer, and the influence of the different weight content ratio of each component on the photopolymerization efficiency was investigated. After that, the prepared formulations were subjected to photopolymerization experiments of thick and thin

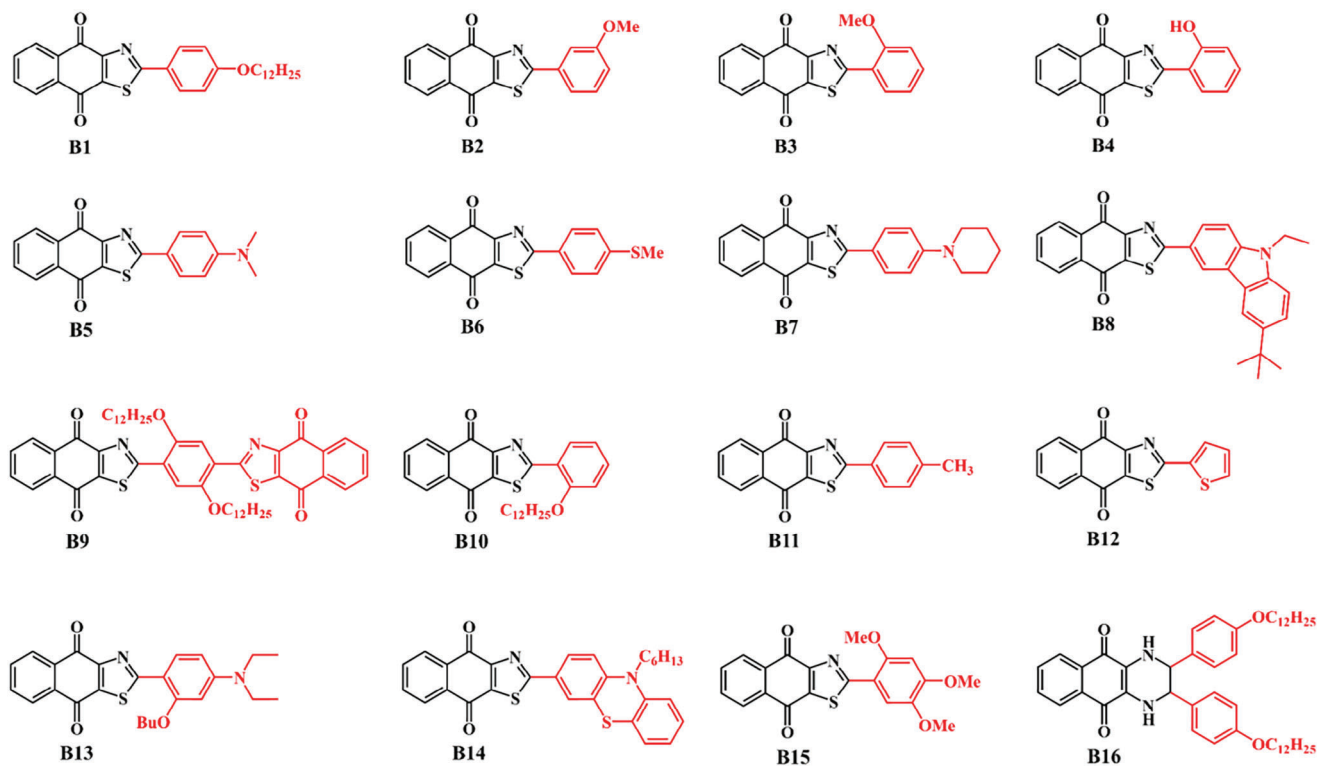


Figure 1. Chemical structures of dyes B1–B16.

samples, and the specific operations were as follows: one drop of the prepared resin was dropped between two polypropylene films (for thickness from 10 to 100 microns) for thin samples, and five drops of the prepared resins were dropped into a plastic mold (2 mm) for thick samples. Then, the characteristic peaks of acrylate functional groups were continuously detected at $\approx 6150\text{ cm}^{-1}$ (2 mm thick sample) and 1650 cm^{-1} (thin sample 10 to 100 microns) by RT-FTIR (JASCO FTIR-4700). The acrylate conversions were obtained by the following equation:

$$\text{Conversion (\%)} = \left(1 - \frac{A_t}{A_0}\right) \times 100\% \quad (2)$$

where A_0 is the initial peak area before light irradiation and A_t is the peak area after being irradiated with light for t s.

In addition to the polymerization experiments conducted under artificial light sources, we explored sunlight-induced photopolymerization using the same formulations as described earlier. The sunlight-induced polymerization experiment was carried out on August 22, 2023, from 1 to 3 pm, aligning with French time. The experiment site was in Mulhouse (+77 43' E, 47 75' N), France, where the weather conditions were sunny. The conversions of the acrylate functional groups were monitored by RT-FTIR spectroscopy.

2.4. Redox Potentials of Dyes obtained by Cyclic Voltammetry

Redox potentials of the dyes were measured using cyclic voltammetry. The specific operation was that the dyes and the supporting electrolyte (tetrabutylammonium hexafluorophosphate) were

dissolved in dichloromethane, and the redox potentials of the dyes were measured under nitrogen atmosphere, and the values are listed in Table 4. Finally, the oxidation potential of EDB is 1.0 V and the reduction potential of the iodonium salt (Iod) is -0.7 V , as reported in the literature.^[26,27]

2.5. Electron Spin Resonance – Spin Trapping (ESR-ST) Experiments

ESR-ST experiments were carried out with the ESR X-band spectrometer (Bruker EMX-plus) to study the free radicals generated under the LED@405 nm irradiation. Under nitrogen atmosphere, free radicals were captured by phenyl-*N*-tert-butyl nitron (PBN). The concentration of PBN was $\approx 5 \times 10^{-4}\text{ M}$. All operations were carried out at room temperature. In addition, ESR-ST spectra were simulated by PEST WINSIM program.

2.6. Application of 3D Printing Experiments

The formulations with good photopolymerization performance were selected for 3D printing experiments. First of all, a two-component system (0.1 wt.% dye/1 wt.% EDB, TMPTA as the monomer) was used to conduct the direct laser write (DLW) experiments with a computer-programmed x,y desk with a mounted laser diode at 405 nm, in which the glass tank (3 cm in length, 2 cm in width, and 0.3 cm in height) for printing was made by ourselves. Furthermore, a three-component system (0.1 wt.% dye/1 wt.% EDB/1 wt.% Iod, TMPTA as the monomer)

Table 1. Reaction total yields obtained during the synthesis of B1–B16.

Compounds	Reaction yields [%]	Compounds	Reaction yields [%]
B1	81	B9	58
B2	77	B10	92
B3	89	B11	81
B4	80	B12	88
B5	67	B13	65
B6	88	B14	85
B7	88	B15	85
B8	91	B16	84

was used to print 3D objects with a Digital Light Processing (DLP) 3D Printer (Anycubic Photon D2, China), and the thickness of the layer was controlled at 0.02 mm. The printed patterns were observed by Scanning Electron Microscope (SEM) and Numerical Optical Microscope (DSX-HRSU from Olympus Corporation).

3. Results and Discussion

3.1. Synthesis of the Dyes

B1–B15 were prepared in one step starting from 2-aminonaphthalene-1,4-dione A1 and the appropriate aldehyde ALD1–ALD15 using the synthetic route as reported previously^[28] (See Scheme 1). With this method, all dyes could be obtained with the reaction yields ranging between 58% yield for B9 and 92% yield for B10 after purification/isolation (See Table 1). It has to be noticed that all dyes exhibited a D- π -A structure (with D and A standing for donor and acceptor respectively) except for B9 that A- π -D- π -A was found. To access to this structure, 2,5-bis(dodecyloxy)terephthalaldehyde ALD9 was used as the dialdehyde (See Scheme 2). Among the series of dyes, the lowest reaction yield (58%) was obtained during the synthesis of this dye, 4-(4,9-dioxo-4,9-dihydronaphtho[2,3-*d*]thiazol-2-yl)-2,5-bis(dodecyloxy)benzaldehyde B9' being isolated as the side product of this reaction in 19% yield. A different synthesis was used for B16. Starting from 2,3-diaminonaphthalene-1,4-dione A2 and two equivalents of 4-(dodecyloxy)benzaldehyde, B16 could be identified as the main product of the reaction, and isolated in 84% yield. As a side product of this second reaction, 2-(4-(dodecyloxy)phenyl)-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione B16' could be obtained in 9% yield (See Scheme 2). It has to be noticed that the synthetic route used to produce B16 was first reported in 1987 and the synthesis of such compounds has never been revisited since this pioneering work.^[29]

3.2. Light Absorption Properties of the Different Dyes

UV–vis absorption spectra of the 16 dyes and the commercial photoinitiator 2-isopropylthioxanthone (ITX) dissolved in dichloromethane were recorded and the results are shown in Figure 2. Light absorption characteristics of the different dyes are summarized in Table 2. Figure 2 vividly illustrates robust absorption peaks in the UV–vis region for all dyes, assigned to $\pi \rightarrow \pi^*$ transitions.^[30] Notably, the maximum absorption wavelengths ($\lambda_{\max}$) of B1, B2, B3, B10, and B11 were 420, 400, 410, 410,

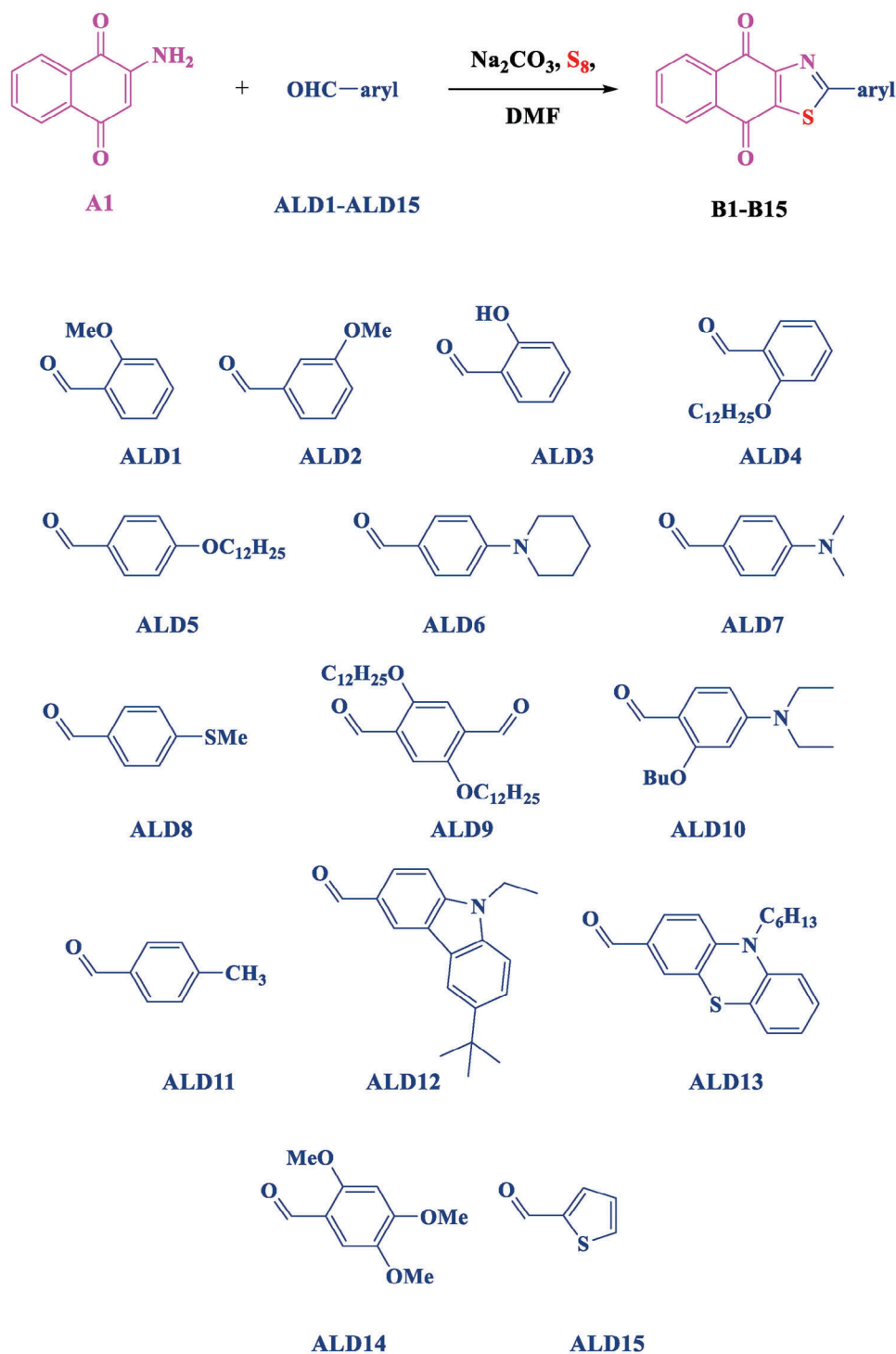
Table 2. Light absorption characteristics of the dyes ($\lambda_{\max}$ for the red-shifted transitions).

Pls	$\lambda_{\max}$ [nm]	$\epsilon_{\max}$ [M ⁻¹ cm ⁻¹]	ϵ_{405} [M ⁻¹ cm ⁻¹]	Moiety
B1	420	2610	2310	4-dodecyloxyphenyl
B2	400	4170	3870	3-methoxyphenyl
B3	410	1320	1320	2-methoxyphenyl
B4	410	5600	5410	2-hydroxyphenyl
B5	510	7990	4110	4-dimethylaminophenyl
B6	430	6340	5630	4-methylthiophenyl
B7	510	4810	4570	4-piperidinylphenyl
B8	480	7830	2400	<i>tert</i> -butyl-(<i>N</i> -ethyl)carbazolyl
B9	450	11690	8760	naphthothiazolodione-bis(dodecyloxy)phenylene
B10	410	4690	4690	2-dodecyloxyphenyl
B11	400	4920	4730	<i>p</i> -tolyl
B12	410	4660	4570	thiophenyl
B13	530	8630	12120	2-butoxy-4-(diethylamino)phenyl
B14	500	6130	11240	<i>N</i> -hexyl-phenothiazinyl
B15	460	9460	4530	2,4,5-trimethoxyphenyl
B16	590	1220	420	bis(<i>p</i> -dodecyloxy)phenyl
ITX	390	5890	1000	

and 400 nm, respectively. Correspondingly, their molar extinction coefficients ($\epsilon_{\max}$) at $\lambda_{\max}$ were 2610, 4170, 1320, 4690, and 4920 M⁻¹ cm⁻¹, respectively. In addition, the molar extinction coefficients ($\epsilon_{405\text{nm}}$) at $\lambda_{405\text{nm}}$ were 2310, 3870, 1320, 4690, and 4730 M⁻¹ cm⁻¹, respectively. These five dyes demonstrated excellent photoinitiation abilities, and the results presented in Section 3.3 also confirmed their high photoinitiation performance as photoinitiators in free radical polymerization when 2 mm thick resin samples in open molds (no protection against oxygen inhibition) were exposed to sunlight outdoors (clear sky conditions). Contrastingly, B5, B7–B9, and B13–B16 showed strong absorption peaks in the 450–600 nm range, which may be due to a redshift of the $\pi \rightarrow \pi^*$ transition with an increase of the electronic density, resulting from the presence of strong electron-donating groups, which is consistent with the literature results.^[30] However, these dyes exhibited poor photoinitiation abilities, as elaborated in Section 3.3.

3.3. Photopolymerization Kinetics with the Dyes in Two or Three-Component Photoinitiating Systems under LED@405 nm, 450 nm, and Sunlight

To investigate the photoinitiation ability of the fifteen dyes based on the 2-phenylnaphtho[2,3-*d*]thiazole-4,9-dione scaffold and the one dye based on the 2,3-diphenyl-1,2,3,4-tetrahydrobenzo[*g*]quinoxaline-5,10-dione scaffold, photopolymerization were carried out under LED@405 nm, LED@450 nm, and sunlight exposure. The photoinitiation ability of two different two-component (dye/EDB and dye/Iod) systems and one three-component (dye/EDB/Iod) system were studied to clarify the influence of co-initiators (EDB as the

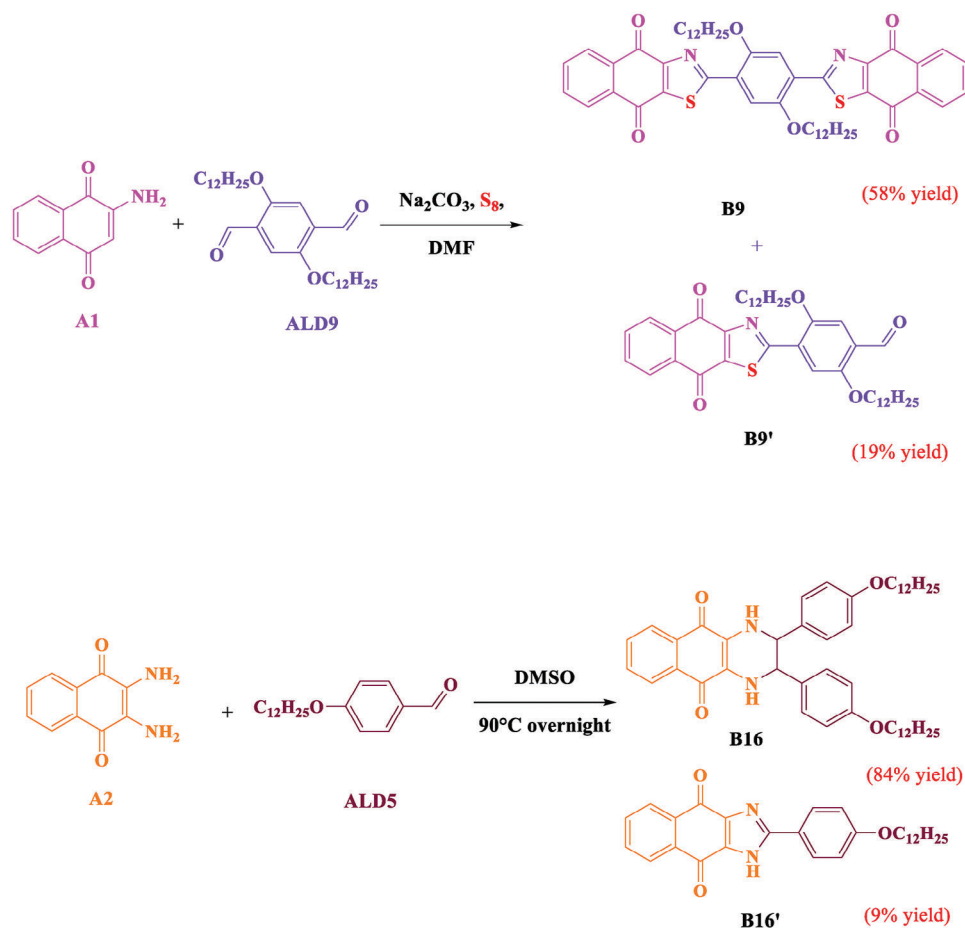


Scheme 1. Synthetic routes to B1-B15.

electron/hydrogen donor and Iod as the electron acceptor) on the polymerization kinetics of TMPTA. The conversions of acrylate functional groups were determined using the RT-FTIR at room temperature. Specifically, for the blank groups shown in Figure S2 (Supporting Information) (i.e., dye alone, EDB alone, and Iod alone), no polymerization or poor photoinitiation

abilities were determined, evidencing that the two co-initiators EDB, and Iod may only play a crucial role in the initiation step once combined with the dyes.

Polymerization profiles obtained with the two-component dye/EDB systems are shown in Figure S3 (Supporting Information) (thick sample) and Figure S4 (Supporting Information)



Scheme 2. Synthetic routes to B9 and B16.

(thin sample), while the final acrylate function conversions (FCs) are listed in Table S1 (Supporting Information) (thick sample) and Table S2 (Supporting Information) (thin sample). The influence of the dye concentrations on the polymerization performance of TMPTA was also investigated. Specifically, for the two-component dye/EDB system, EDB concentration was fixed to 1 wt.%. When the dye concentration was set to 0.1 wt.%, the

conversions of thick samples (See Figure S3c, Supporting Information) and thin samples (See Figure S4c, Supporting Information) were optimal, especially for thick samples containing B1 and B10 and thin sample containing B16. The conversions of thick samples were close to 80%, while it can reach 90% for the thin samples. It implied that when the dye concentrations were 1 wt.%, the solubility of the dyes in TMPTA was low and the

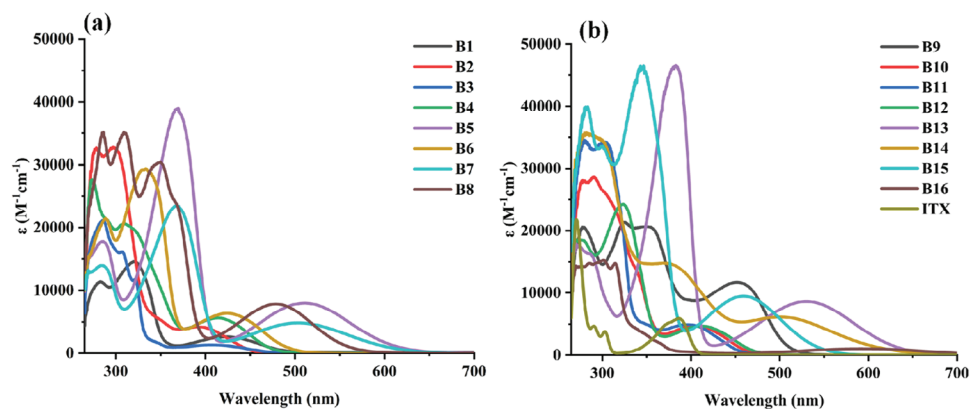


Figure 2. UV-vis absorption spectra of dyes in dichloromethane. a) B1–B8, b) B9–B16, and ITX.

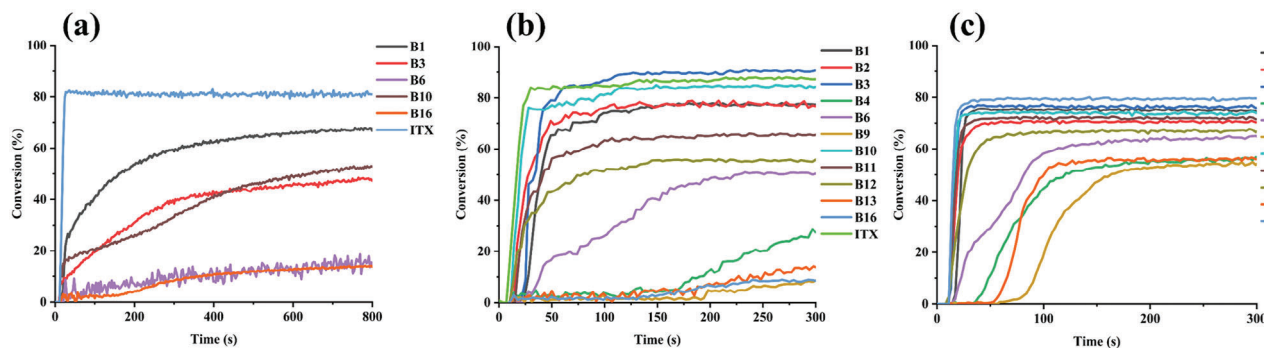


Figure 3. Photopolymerization profiles of TMPTA for thick sample (2 mm) upon exposure to LED@405 nm irradiation. Initiated by a) dye/EDB/Iod 1%/1%/1% w/w/w; b) dye/EDB/Iod 0.1%/1%/1% w/w/w; c) dye/EDB/Iod 0.1%/0.1%/0.1% w/w/w. The irradiation starts at $t = 10$ s.

precipitation can be clearly seen in the different formulations, which led to a poor light penetration, i.e., inner filter effect due to the high light absorption properties of the dyes. By decreasing the dye concentrations, the different formulations became clearer and more transparent, which can be beneficial to photopolymerization.

In the case of the two-component dye/Iod (1 wt.%) system (See Figure S5, Supporting Information) (thin sample) and Figure S6 (Supporting Information) (thick sample)), the results were basically consistent with that obtained with the two-component dye/EDB system. Considering that numerous dyes exhibited good light absorption properties in the 450–550 nm range, polymerization experiments were also carried out under the LED@450 nm, using the two-component dye/EDB (0.1%/1% w/w) system in TMPTA, both in thick and thin samples. Excellent polymerization performance could be determined, as shown in Figure S7 (Supporting Information).

Considering that the different dyes can form photoinitiating systems with Iod and EDB, their combination in three-component dye/Iod/EDB systems was also investigated. As shown in Figures 3 a,b), in thick samples, when the concentration of EDB and Iod in TMPTA was kept constant at 1 wt.%, the dye concentration of 0.1 wt.% furnished excellent polymerization profiles (See Figure 3b). The FC with B3 even reached 91%, and the conversions with B10 and B1 were $\approx 80\%$. However, when the concentration of dyes was set to 1 wt.%, the dyes were not completely dissolved in TMPTA, resulting in low polymerization efficiency (again ascribed by an inner filter effect due to the high light absorption properties of the dyes). When the amount of EDB and Iod was reduced to 0.1 wt.% (See Figure 3c), the different three-component photoinitiating systems could maintain a high conversion level and all thick samples could be deeply cured (See Figures S8 and S9, Supporting Information). In the case of thin samples (See Figure S10, Supporting Information), the higher conversions could be determined. Specifically, polymerization of TMPTA initiated with the photoinitiating systems based on B1, B2, B3, B10, and B11 was very fast, and the maximum monomer conversion could be obtained within only 20 s of irradiation with LED@405 nm and LED@450 nm. On the contrary, other photoinitiating systems only showed poor photoinitiation abilities, which were characterized by low conversions obtained after a long induction period. As a result, B1, B2, B3, B10, and B11 were selected as the photoinitiators/photosensitizers for

photopolymerization experiments done under sunlight and under air.

The sunlight-induced photopolymerization was carried out at 1–4 pm on August 22, 2023, in Mulhouse, France. As shown in Figure 4, three kinds of two-component and three-component systems with excellent photoinitiation abilities under artificial irradiation were selected for the photopolymerization under sunlight (thick sample, 2 mm). Interestingly, the three systems showed high performance under sunlight. Photopolymerization profiles obtained with the two-component (dye/EDB 0.1%/1% w/w) system are shown in Figure 4a, while those of the three-component systems are presented in Figure 4b,c. All FCs are listed in Table 3. It can be seen from the three-component systems that B10 reached over 50% functional conversion (green curve) within 10 s and compared to the other four dyes, even for the system with the low concentrations of additives (i.e., dye/EDB/Iod 0.1%/0.1%/0.1% w/w/w; Figure 4c. Change of the formulations before and after polymerization is also given at the bottom of Figure 4 and according to the experimental results, there was still a little liquid at the surface of the resins containing B1 and B2 after polymerization, but for resins containing B3, B10, B11, and ITX, they were completely polymerized as solids (tack-free surfaces). It can be seen that all thick samples could be deeply cured with sunlight. Based on the excellent polymerization performance of these dyes under sunlight, polymerization experiments were also carried out with the

Table 3. Final acrylate function conversions (FCs) of TMPTA in the presence of dyes with co-initiators under sunlight-induced polymerization.

Two-component		Three-component		Three-component	
Dye/EDB (0.1%/1% w/w)		Dye/EDB/Iod (0.1%/1%/1%)		Dye/EDB/Iod (0.1%/0.1%/1%)	
Monomer: TMPTA		Monomer: TMPTA		Monomer: TMPTA	
Dye	FCs (%)	Dye	FCs (%)	Dye	FCs (%)
B1	52	B1	53	B1	45
B2	52	B2	48	B2	50
B3	37	B3	56	B3	46
B10	58	B10	58	B10	58
B11	50	B11	61	B11	50

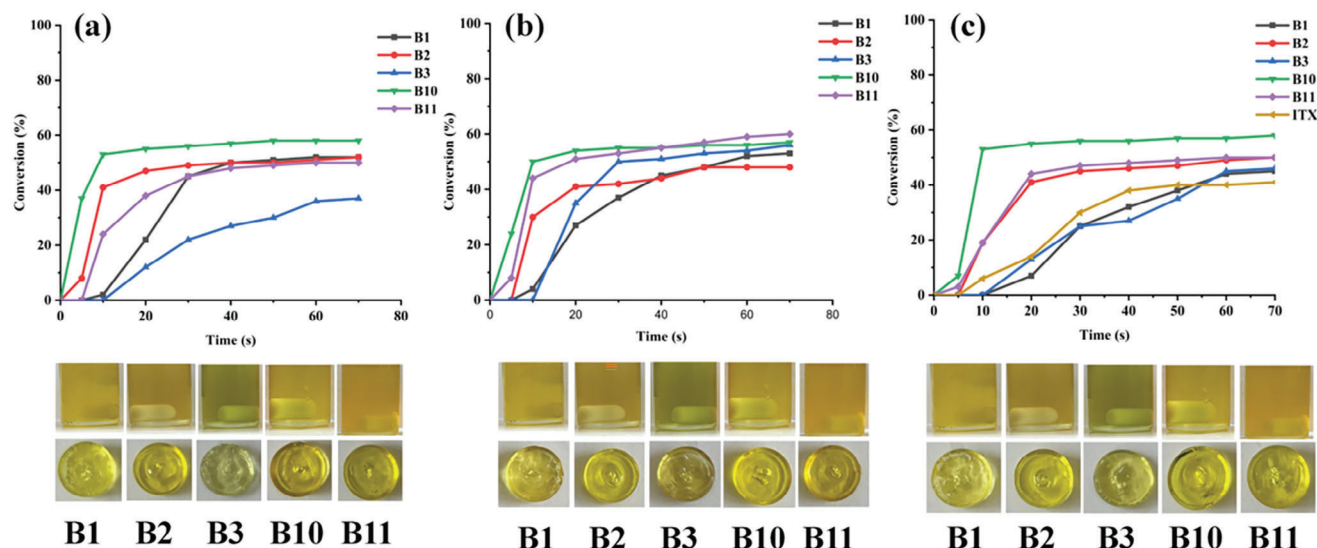


Figure 4. Photopolymerization profiles of TMPTA for thick sample (2 mm) under sunlight in the air. Initiated by a) dye/EDB 0.1%/1% w/w; b) dye/EDB/Iod 0.1%/1%/1% w/w/w; c) dye/EDB/Iod 0.1%/0.1%/0.1% w/w/w. (Black curve for B1, red curve for B2, blue curve for B3, green curve for B10, purple curve for B11, and yellow curve for ITX)

three-component (dye/EDB/Iod 0.1%/1%/1% w/w/w) system in another monomer PEGDA. As shown in Figure S11 (Supporting Information), the acrylate functional group conversion of PEGDA initiated by B10 reached 96%, which was similar to that of the commercial initiator ITX. According to the above experimental results, B10 synthesized in this study has a great application prospect in inducing photopolymerization under sunlight.

3.4. Steady State Photolysis Experiments of Dye, Dye/EDB, and Dye/Iod Photoinitiation Systems

To understand the interaction between the different dyes, EDB, and Iod, and to clarify the chemical mechanism involved in the photopolymerization process, steady-state photolysis experiments were carried out under the irradiation of LED@405 nm. As shown in Figure 5, the UV-vis absorption profiles of dye, dye/EDB, and dye/Iod dissolved in dichloromethane were studied respectively. The concentration was set as 5×10^{-5} M for dye, 1×10^{-4} M for EDB, and 1×10^{-4} M for Iod. All the steady-state photolysis profiles are shown in Figures S12–S14 (Supporting Information).

As shown in Figure 5a–c, the steady-state photolysis profiles of B1, B10, and B11 are presented after 18 min of irradiation with the LED@405 nm. The absorbance of the three dyes decreased slightly by elongating the irradiation time, indicating that the dyes alone were relatively stable upon the irradiation with the LED@405 nm, which was in line with the photopolymerization results presented in Section 3.3. Notably, the dyes alone cannot initiate any polymerization, or the monomer conversion was low. However, in the case of the two-component dye/EDB systems, as shown in Figure 5d, it can be seen that the absorbance of the B1/EDB system obviously decreased within 4 min compared with the single dye system. In the case of the B10/EDB system in Figure 5e and the B11/EDB system in Figure 5f, these

photolysis of two two-component systems were significant within only 30 s. Interestingly, for the three two-component dye/Iod systems presented in Figure 5g–i, after a long period of irradiation, the absorbance was almost the same as that of the single dye system. Obviously, the efficiency of dye/EDB combination was higher than that of dye/Iod in the photopolymerization process.

In addition, to test the stability of dyes under sunlight, steady-state photolysis experiments of B1, B2, B3, B10, and B11 were also carried out under sunlight and under air. As shown in Figure S15 (Supporting Information), after a long-term sunlight irradiation, the absorbance hardly changed, which proved that the dyes had good stability under sunlight. This also provides a basis for the practical application of these dyes.

3.5. Fluorescence Properties, Fluorescence Quenching Experiments, and Chemical Mechanisms in Electron Transfer Reaction for Dyes

The fluorescence spectra of the different dyes are shown in Figure S16 (Supporting Information), and the fluorescence lifetime spectra are shown in Figure 6 and Figure S17 (Supporting Information). The fluorescence characteristics of some dyes were not detected in the 200–1000 nm range due to their chemical structures. Various parameters in electron transfer reaction, such as E_{S1} (See Figure 6; Figure S18, Supporting Information) and Table 4), were obtained from the intersection of the normalized UV-vis absorption and fluorescence spectra ($E_{S1} = 1240/\text{wavelength of intersection}$). In addition, the oxidation (E_{ox}) and reduction (E_{red}) potentials of B1, B3, B10, B12, and B16 were measured by cyclic voltammetry (See Figure S19, Supporting Information), and the values of E_{ox} and E_{red} are summarized in Table 4. From Figure S19 (Supporting Information), the reduction peaks were clearly observed for the five investigated dyes, and the oxidation peaks were only observed for B3 and B16 during the sweep cycle.

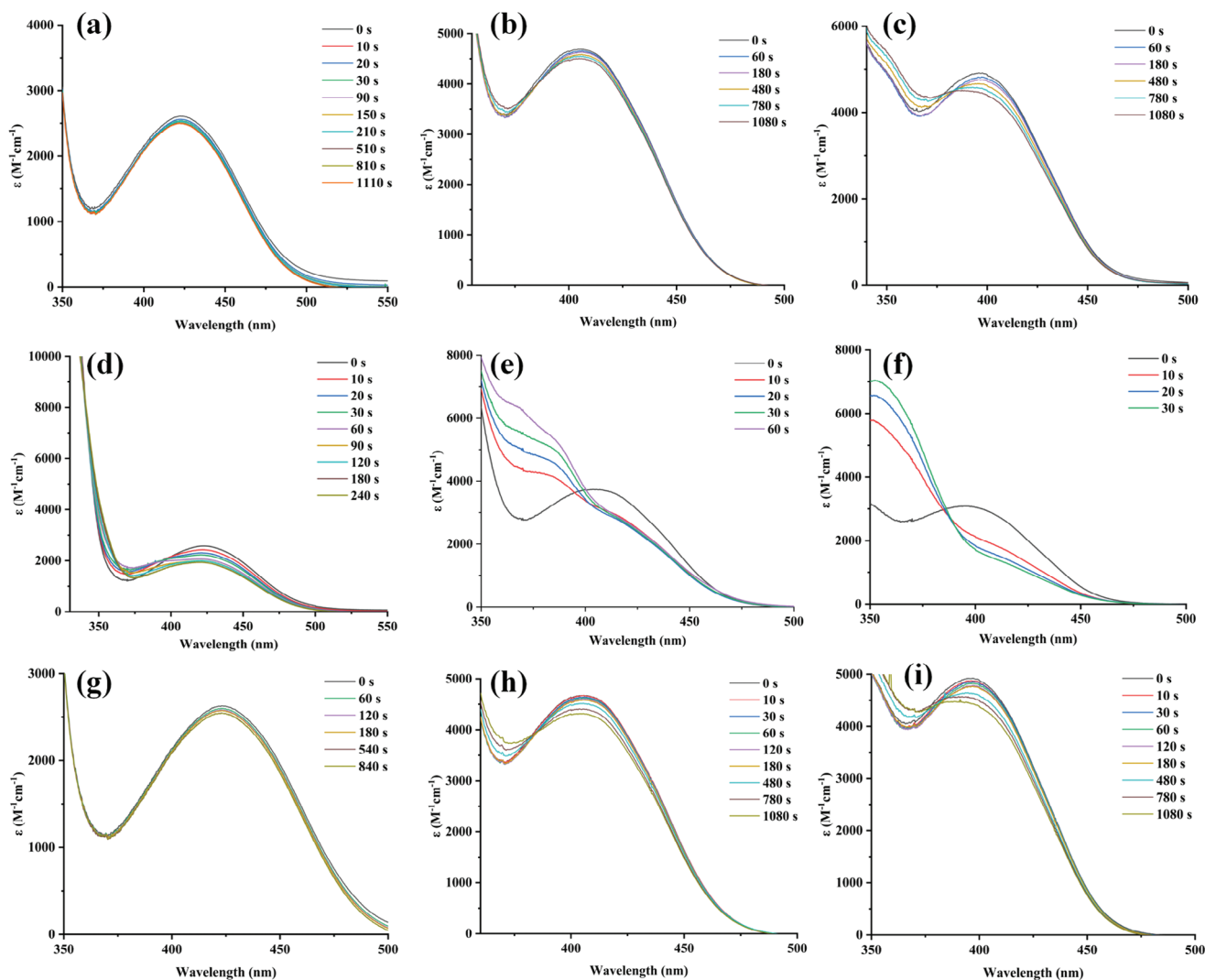


Figure 5. Steady-state photolysis of dye (5×10^{-5} M), EDB (1×10^{-4} M), and Iod (1×10^{-4} M) in dichloromethane under LED@405 nm. a) dye-B1 (alone), b) dye-B10 (alone), c) dye-B11 (alone), d) dye-B1 and EDB, e) dye-B10 and EDB, f) dye-B11 and EDB, g) dye-B1 and Iod, h) dye-B10 and Iod, i) dye-B11 and Iod.

Fluorescence quenching experiments of the dye/EDB systems and the dye/Iod systems were also carried out in

Table 4. Parameters of the chemical mechanisms associated with B1, B3, B10, B12, and B16 in dichloromethane.

	Dye-B1	Dye-B3	Dye-B10	Dye-B12	Dye-B16
E_{ox} (eV)	-	0.83	-	-	1.02
E_{red} (eV)	-0.85	-1.09	-1.12	-1.04	-1.23
E_{S1} (eV)	2.49	2.64	2.63	2.59	2.29
K_{sv} (EDB) s^{-1}	43.9	19.1	58.4	91.3	-
K_{sv} (Iod) s^{-1}	24.7	23.5	17.2	34.6	18.9
ϕ_{et} (EDB) ^{a)}	0.69	0.49	0.74	0.82	-
ϕ_{et} (Iod) ^{a)}	0.33	0.32	0.26	0.41	0.27

^{a)} the electron transfer quantum yield is calculated from: $\phi_{et} = K_{sv} [additive] / (1 + K_{sv} [additive])$; with [additive] the EDB (0.05 M) and Iod (0.02 M) concentration.

dichloromethane, as shown in **Figure 7** and Figures **S20** and **S21** (Supporting Information) For B1, B10, and B11, the addition of additives (EDB and Iod) significantly decreased their fluorescence intensity. Conversely, the fluorescence intensity of B11/EDB increased at 400–450 nm, which may be due to the fact that dye-B11 reacted with EDB upon irradiation to generate new chromogenic substances, which indicated that there was an efficient interaction between the dyes and EDB or Iod. The results were consistent with the above free energy changes and steady-state photolysis experiments. According to our previous research, this may be due to the reaction between dyes and the additives to produce active free radicals (see quenching experiments above).

The Stern–Volmer coefficients (K_{sv}) of dye/EDB or dye/Iod were determined by the slope of the Stern–Volmer treatment of fluorescence quenching (See **Figure S22**, Supporting Information), and the electron transfer quantum yields (ϕ_{et}) (See **Table 4**) can be calculated by Equation 1, which was helpful for a deep

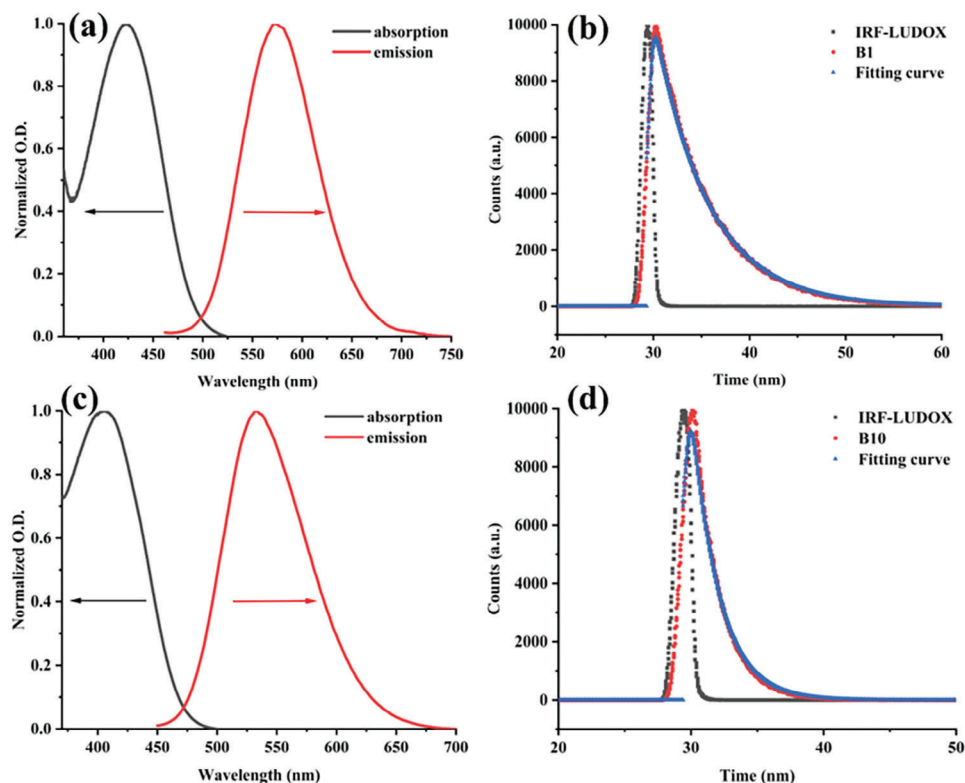


Figure 6. a) Singlet state energy of B1, b) fluorescence decay curve of B1, c) singlet state energy of B10, d) fluorescence decay curve of B10.

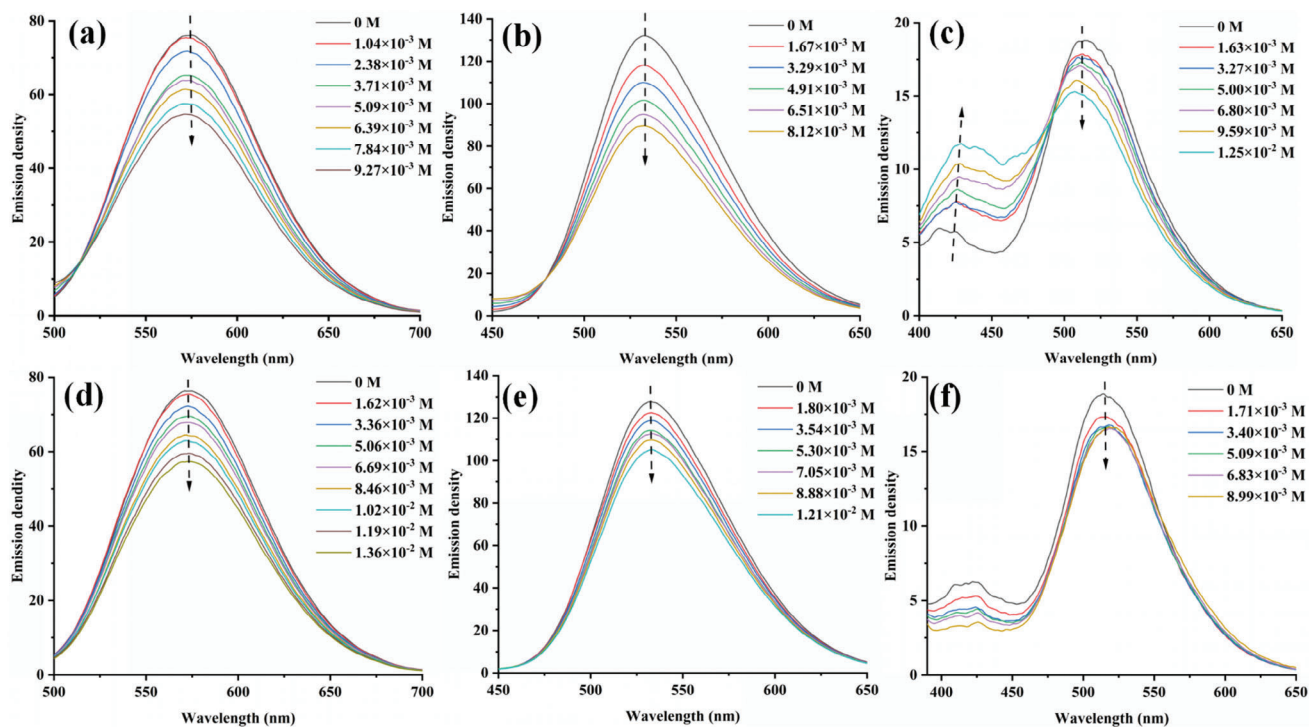


Figure 7. Fluorescence quenching of a) dye-B1 and EDB, b) dye-B10 and EDB, c) dye-B11 and EDB, d) dye-B1 and Iod, e) dye-B10 and Iod, f) dye-B11 and Iod in dichloromethane.

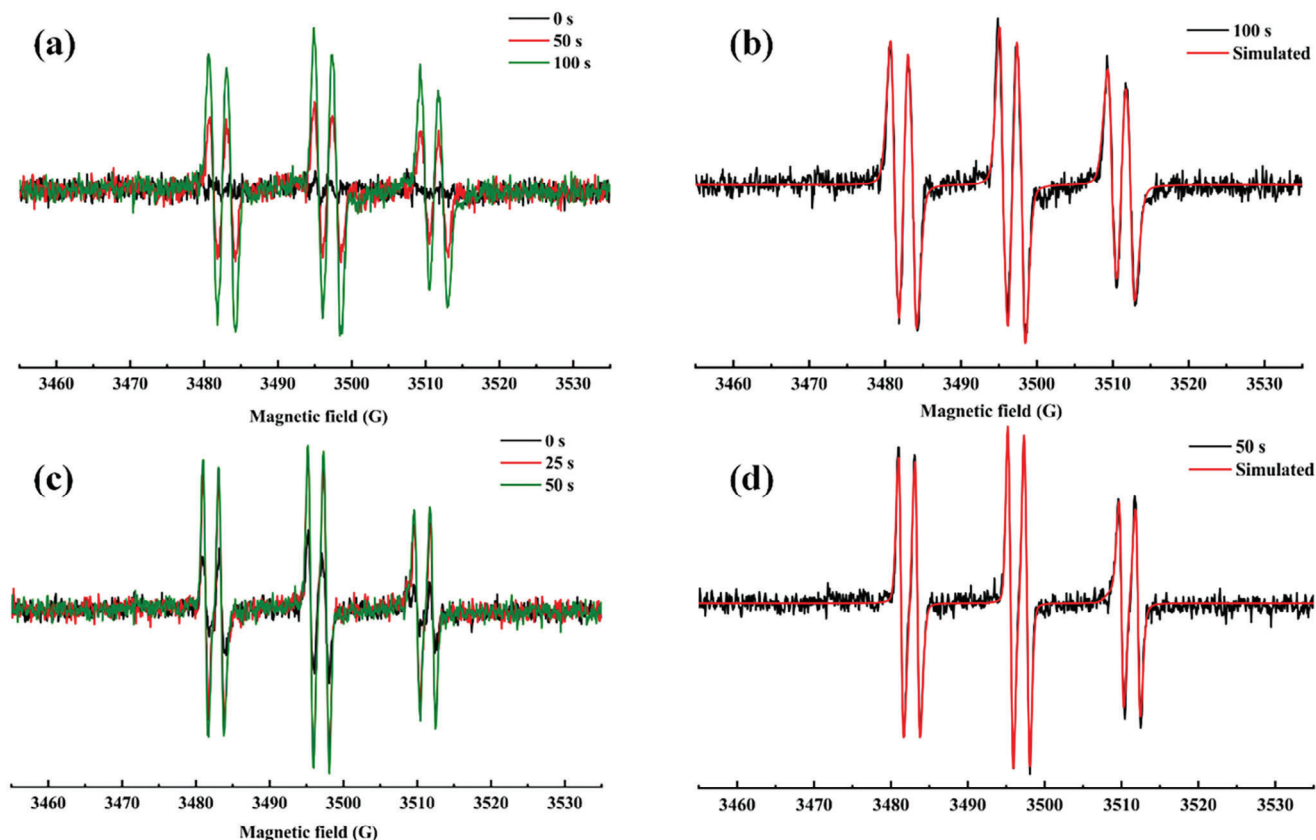


Figure 8. ESR-ST spectra of the PBN radical adducts (in *tert*-butylbenzene under nitrogen atmosphere). a) and b) B1/EDB, c) and d) B1/Iod under LED@405 nm irradiation.

understanding of the chemical mechanism in photopolymerization.

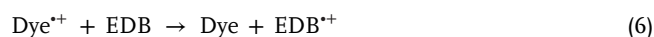
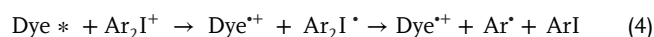
3.6. ESR-ST Experiments

To determine the nature of the free radicals produced by the interaction between dye/EDB and dye/Iod, B1 was used as an example to successfully carry out ESR-ST experiments under the LED@405 nm (See Figure 8). As shown in Figure 8a,b, for the dye/EDB system, a free radical was successfully captured by PBN, and its hyperfine coupling constants were $\alpha_N = 14.3$ G and $\alpha_H = 2.6$ G, which may be aminoalkyl radical $\text{EDB}_{(-H)}\cdot$. In Figure 8c,d, a radical in the dye/Iod system was captured by PBN, and its hyperfine coupling constants were $\alpha_N = 14.3$ G and $\alpha_H = 2.2$ G, which may be aryl radical. The results are in accordance with the experimental data reported in the literature.^[31]

3.7. Summary of Photoinitiation Mechanisms of Dye

Based on the above results, the chemical mechanisms induced by the three-component photoinitiating dye/EDB/Iod system were proposed, which can be divided into three steps. The first step consisted of the excitation of the chromophore with light, enabling to promote the dye from its initial ground state to the

excited state (See Equation 3). In the second step, the excited dye* reacted with Iod and EDB respectively to generate free radicals, as shown in Equations 4 and 5. Specifically, the dye* reacted with Iod to generate $\text{Ar}\cdot$ free radicals and dye^{*+} . In addition, dye* reacted with EDB to produce $\text{EDB}_{(-H)}\cdot$ free radicals and $\text{dye-H}\cdot$. In fact, the excited dye (dye*) can react with EDB and Iod separately according to a reductive and an oxidative pathway so that free radicals capable of initiating polymerization processes are produced. In the third step, Dye^{*+} produced by an oxidation reaction and $\text{Dye-H}\cdot$ produced by a reduction reaction can be regenerated into Dye by the interaction with EDB and Iod respectively (See Equations 6 and 7), and finally, the catalytic cycle of the three-component system was completed. Notably, the free radicals $\text{EDB}_{(-H)}\cdot$ and $\text{Ar}\cdot$ produced during the catalytic cycle were successfully detected by ESR, which provided clear evidence for the proposed chemical mechanisms.



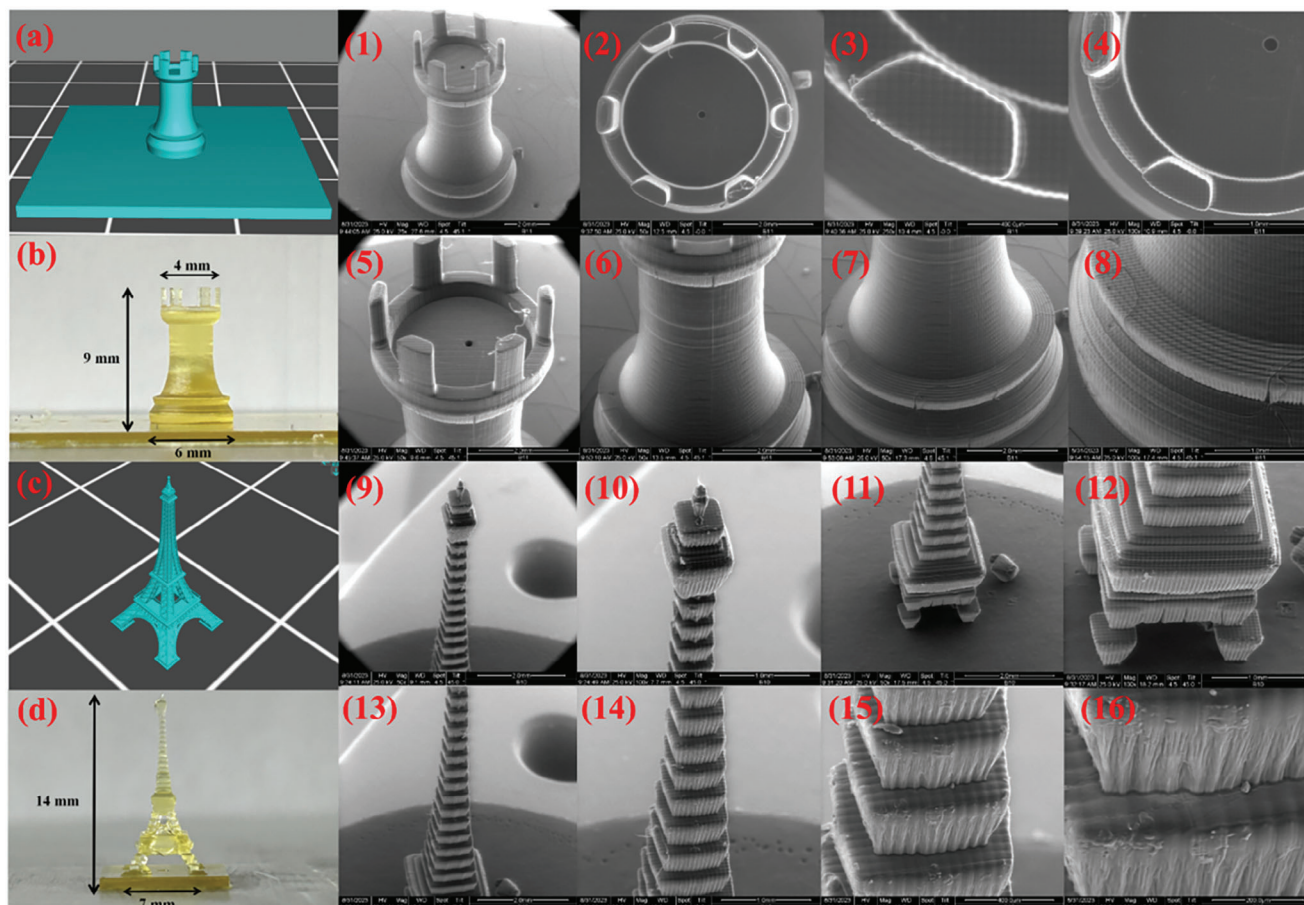


Figure 9. Digital photos of 3D printed objects. a) and b) dye-B11(0.1 wt.)/EDB(1 wt.)/Iod(1 wt.)/TMPTA system; c) and d) dye-B10(0.1 wt.)/EDB(1 wt.)/Iod(1 wt.)/TMPTA system; 1–8 SEM images of surface of the 3D printed objects using dye-B11/EDB/Iod/TMPTA system; 9–16 SEM images of surface of the 3D printed objects using dye-B10/EDB/Iod/TMPTA system.

3.8. Application in 3D Printing

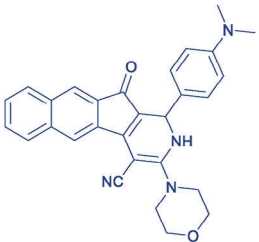
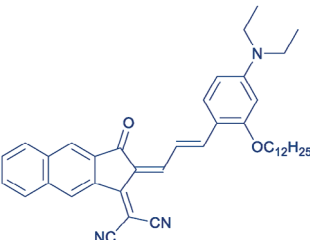
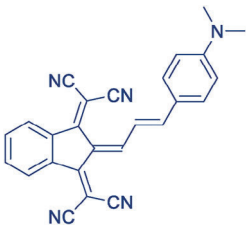
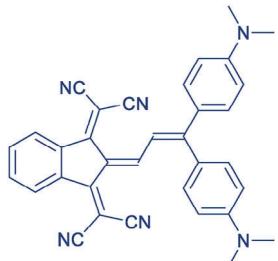
Exploiting the impressive photoinitiation capabilities demonstrated by several dyes in this study (efficiently initiate the FRP of TMPTA under both LED@405 nm irradiation and exposure to sunlight) we selected the two-component systems B3/EDB, B10/EDB, and B12/EDB, along with the three-component systems B10/EDB/Iod and B11/EDB/Iod for 3D printing. For the DLW experiments, the two-component systems were employed, resulting in the rapid production of 3D letters within 2 min of irradiation at 405 nm, as depicted in Figure S23 (Supporting Information). These outcomes were verified through digital camera and numerical optical microscopy, highlighting the distinct, and well-defined outlines of printed letters. Moving to the 3D printing experiment involving the three-component system, Figure 9 illustrates the successful printing of an exquisite chess piece and an Eiffel Tower model using a 3D printer. Figures 9a,b depict the chess piece model printed by B11/EDB/Iod/TMPTA system, and Figure 9c,d showcase the Eiffel tower model printed by B10/EDB/Iod/TMPTA system. The clear outline of the model is readily discernible through digital camera observation, and SEM photos (See Figure 9 1–16) further confirm the smooth surfaces and excellent spatial resolution achieved in the production of

these 3D objects. These results underscore the potential of the selected photoinitiating systems for high-quality and precise 3D printing applications.

3.9. Comparisons with Solar Photoinitiators from Previous Studies

In Figure 4, photopolymerization profiles obtained with B1, B2, B3, B10, and B11 upon sunlight irradiation in two- and three-component photoinitiating systems are presented. A thorough comparison with dyes previously reported in the literature accentuates the remarkable performance of the dyes investigated in this study. Table 5 outlines the superior attributes of the identified top candidates for the FRP of TMPTA in the literature, where all polymerization experiments utilized a three-component dye/EDB/Iod system with concentrations set at 0.1%/2%/2% w/w/w. In contrast to prior experiments, our approach exhibited a substantial 20 fold reduction in the concentration of additives while maintaining a high monomer conversion. Simultaneously, the exposure time to sunlight was significantly curtailed, achieving remarkable monomer conversions within just 70 s of sunlight irradiation, as opposed to the to

Table 5. Acrylate function conversions obtained during the FRP of TMPTA at 405 nm and sunlight (30 min) using three-component photoinitiating dye/Iod/EDB (0.1%/2%/2% w/w/w) systems.

	Push-pull dyes	Absorption properties	Final Acrylate function conversion
Dye8 [34]		$\lambda_{\max} = 491 \text{ nm}$ $\epsilon_{\max} = 5330 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon_{405\text{nm}} = 3340 \text{ M}^{-1} \text{ cm}^{-1}$	$\approx 91\%$ (LED@405 nm, $I = 110 \text{ mW cm}^{-2}$, 400 s); $\approx 88\%$ (sunlight, 30 min)
CP7 [35]		$\lambda_{\max} = 689 \text{ nm}$ $\epsilon_{\max} = 113870 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon_{405\text{nm}} = 13640 \text{ M}^{-1} \text{ cm}^{-1}$	$\approx 97\%$ (LED@405 nm, $I = 30 \text{ mW cm}^{-2}$, 400 s); $\approx 93\%$ (sunlight, 30 min)
CP9 [35]		$\lambda_{\max} = 627 \text{ nm}$ $\epsilon_{\max} = 51700 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon_{405\text{nm}} = 4610 \text{ M}^{-1} \text{ cm}^{-1}$	$\approx 98\%$ (LED@405 nm, $I = 30 \text{ mW cm}^{-2}$, 400 s); $\approx 91\%$ (sunlight, 30 min)
CP11 [35]		$\lambda_{\max} = 671 \text{ nm}$ $\epsilon_{\max} = 47770 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon_{405\text{nm}} = 6560 \text{ M}^{-1} \text{ cm}^{-1}$	$\approx 99\%$ (LED@405 nm, $I = 30 \text{ mW cm}^{-2}$, 400 s); $\approx 92\%$ (sunlight, 30 min)

30 min required in earlier studies. In light of these findings and to the best of our knowledge,^[32,33] B1, B2, B3, B10, and B11 represent the inaugural sunlight photoinitiators capable of utilizing additives at such minimal concentrations, concurrently achieving high monomer conversions within ≈ 1 min of sunlight exposure. This advancement positions these dyes at the forefront of solar photoinitiators in terms of efficiency and expeditious polymerization under sunlight.

4. Conclusion

In this study, we synthesized and explored the potential of 15 new dyes based on the 2-phenylnaphtho[2,3-*d*]thiazole-4,9-dione scaffold and 1 dye based on the 2,3-diphenyl-1,2,3,4-tetrahydrobenzo[*g*]quinoxaline-5,10-dione scaffold as photoinitiators. All dyes examined in this work have never previously been studied as photosensitizers for photopolymerization pro-

cesses. Particularly noteworthy is the fact that, despite the synthesis of 2,3-diphenyl-1,2,3,4-tetrahydrobenzo[*g*]quinoxaline-5,10-diones being reported in 1987, subsequent investigations into this family of dyes have been notably sparse. Diverse photoinitiating systems were prepared by combining these dyes with additives such as EDB and Iod. The strong absorption of these dyes exhibited in the UV-vis region ($>400 \text{ nm}$) facilitated photopolymerization under the irradiation of LED@405 nm and LED@450 nm. The proposed chemical mechanism was corroborated using complementary techniques including steady-state photolysis, fluorescence quenching experiments, cyclic voltammetry, and ESR-ST experiments. Remarkably, B1, B2, B3, B10, and B11 emerged as successful photoinitiators for the FRP of TMPTA under sunlight due to their excellent photoinitiation ability. Among these, B10 exhibited the highest reactivity, achieving unprecedented monomer conversions under sunlight, with FCs of 58% for TMPTA and 96% for PEGDA, all at significantly low

concentrations of photosensitizers and additives. These findings position these dyes as promising candidates for the future development of efficient sunlight photoinitiators. Finally, the three-component systems, B10/EDB/Iod and B11/EDB/Iod, were successfully applied to 3D printing. In summary, the demonstrated ability of these dyes to initiate polymerization under sunlight, coupled with their ease of synthesis, rapid polymerization under both sunlight, and artificial light sources, aligns with the principles of green chemistry. These chromophores present a viable option for large-scale industrial applications, such as exterior wall coatings, offering energy efficiency, and environmental sustainability in outdoor polymerization processes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research project was supported by the China Scholarship Council (CSC) (No.202208220049).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2-phenylnaphtho[2,3-*d*]thiazole-4,9-dione, 3D printing, naphthoquinone, photoinitiators, sunlight-induced polymerization

Received: January 10, 2024
Revised: March 6, 2024
Published online:

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