Sunlight-driven photoinitiating systems for photopolymerization and application in direct laser writing†

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Currently, there are only a few industrial and academic works focused on photopolymerization conducted under natural light. To address this challenge, six new dyes are synthesized as photosensitizers and combined with additives (an amine and an iodonium salt) to create three-component photoinitiation systems. These systems can efficiently initiate both the free radical polymerization (FRP) of an acrylate monomer and the cationic polymerization (CP) of an epoxy monomer. Remarkably, the FRP process, facilitated by these systems under natural sunlight, required only a low loading of dyes (0.1 wt% relative to the monomer), and the conversion obtained with dye-B1 as the photosensitizer can reach 90% within 5 minutes. It highlights the viability of natural sunlight as an efficient light source for polymerization processes. More interestingly, dye-B1 can effectively initiate metal-free CP of an epoxy monomer. The chemical mechanism underlying photopolymerization is comprehensively investigated through a combination of theoretical calculations, photolysis experiments, fluorescence quenching experiments, cyclic voltammetry (CV), and electron spin resonance spin trapping (ESR-ST) experiments. Leveraging the exceptional photoinitiation ability of dye-B1, the corresponding three-component photoinitiating system is applied to 3D printing, achieving high-precision 3D patterns via direct laser writing (DLW).

1. Introduction

In the field of polymer synthesis, researchers are actively searching mild reaction conditions for performing photopolymerization. Inspired by natural processes like photosynthesis, which efficiently converts solar energy into chemical energy,1 early innovators like Ciamician proposed the use of photocatalysts to mediate chemical reactions with light as early as 1912.2 Since then, photochemistry has continued to evolve with photopolymerization emerging as a promising method due to its lower synthetic costs and reduced environmental impact. This shift has sparked considerable interest, particularly because photopolymerization techniques leverage clean energy sources such as solar radiation and offer potential applications including solar cell power generation7 and wastewater treatment.7 Various energy-efficient light sources can initiate catalytic free radical polymerizations or cationic polymerizations,8,9 including metal photocatalysts (fac-Ir(ppy)3, Ru(bpy)3Cl2, and ZnTPP),10 semiconductor nano-quantum dot photocatalysts11 and organic photocatalysts.12 Considering that metal-free photocatalytic systems have the advantages of environmental friendliness, low cost, and prevention of metal pollution in polymer products,13 they have attracted significant attention in the polymer and composite materials fields.7 Despite these advancements, many metal-free photocatalytic polymerization processes still rely on UV and UV-visible light sources.14,15 Thus, there is a pressing need to harness solar energy for photocatalysis and enable large-scale industrialization.

Sunlight, as an abundant and sustainable energy source, holds immense potential for driving photopolymerization reactions.1,2,16–19 However, the limited availability of efficient photocatalysts or photoinitiators and the challenges posed by UV light sources have hindered widespread industrial adop-

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tion. This has spurred intensified research into photopolymerization using sunlight, particularly considering the broad emission spectrum of sunlight compared to the narrow emission spectra of LEDs.20–22 At present, there are very few initiators used to initiate polymerization under sunlight, including our previous research on push–pull dyes (e.g., 1,3-dione, 1H-cyclopenta[b]naphthalene-1,3(2H)-dione and 4-dimethylhydroxyphenyl-1-allylidene) used for polymerization under sunlight. However, the reactivity of these reported photoinitiators is still low and the photoinitiation takes a long time.23 The pursuit of environmentally friendly and efficient photocatalytic polymerization induced by sunlight presents challenges, notably in achieving stability and usability under natural light conditions.24 Despite recent research efforts, stability issues persist, with most studies focusing on LED-based systems rather than sunlight-induced reactions.25–27 Based on these statements, photocatalysts with excellent storage stability under sunlight and under air are actively researched. It is of great significance to develop such photoinitiating systems applicable for sunlight irradiation.

To address these challenges, we designed and synthesized a series of six new dyes for FRP and CP experiments. Remarkably, these metal-free dyes alone exhibit good stability under sunlight, becoming reactive only when combined with co-initiators to form three-component photoinitiating systems. The six dyes could effectively induce the FRP of acrylates under sunlight, achieving excellent curing of resins within 5 minutes of exposure. Notably, dye-B1 also successfully induced the CP of epoxides upon exposure to LED@405 nm, offering intriguing possibilities for sunlight-induced reactions. The functional group transformation occurring during the polymerization reaction process was monitored using Real-Time Fourier Transform Infrared Spectroscopy (RT-FTIR), and then the chemical mechanisms involved in the polymerization process were elucidated in detail through photolysis experiments, fluorescence quenching, and ESR-ST experiments. Finally, the accurate 3D patterns obtained via direct laser writing (DLW) technology underscores the practical application of our findings. This study represents a significant advancement in photopolymerization, offering an unprecedented reactivity under sunlight, the potential for using a low photoinitiator content, and high conversion rates, paving the way for practical applications in various fields.

2. Experimental

2.1 Dyes and other materials

Six novel dyes were successfully synthesized and used for photopolymerization. The synthetic routes used to prepare these compounds are detailed in the following section 3.1 and in the ESI† The chemical structures of the six dyes investigated in this work are shown in Fig. 1. Other materials and structures of the monomers and co-initiators/additives (amine (EDB) or iodonium salt (Iod)) are shown in Fig. S1 and the ESI†

2.2 UV-vis absorption and fluorescence properties

The UV-Vis absorption spectra were recorded and steady-state photolysis (dye-alone, dye/EDB, and dye/Iod) was carried out in acetonitrile under the irradiation of LED@405 nm (JASCO V730 spectrometer). The fluorescence spectra of dyes in acetonitrile were recorded and the quenching experiments of dyes by EDB or Iod were performed with a JASCO FP-6200 fluorescence spectrometer. The electron transfer quantum yields (\(\phi_{et}\)) were obtained using eqn (1). The fluorescence excited state lifetime was measured with a HORIBA PPD-850 fluorometer.

\[
\phi = \frac{K_{SV}^*[\text{additive}]}{1 + K_{SV}^*[\text{additive}]}
\]

where the \(K_{SV}\) in the equation corresponds to the slope of the Stern–Volmer plot in the fluorescence quenching experiment.

Fig. 1 Chemical structures of dyes B1–B6.
2.3 Redox potentials of dyes obtained by cyclic voltammetry (CV)

The redox potentials (oxidation is $E_{ox}$ and reduction is $E_{red}$) of dyes were measured by CV. The different dyes and tetrabutylammonium hexafluorophosphate used as the support electrolyte were dissolved in acetonitrile under a nitrogen atmosphere. The singlet excited state energy level ($E_{S1}$) of the dyes was determined from the intersection of the normalized UV-visible absorption and fluorescence spectra. Similarly, the triplet energy level ($E_{T1}$) was determined by molecular modeling (Gaussian 03). According to the Rehm–Weller equation,28,29 the change of free energy from the singlet excited state ($\Delta G_{S1}^{\text{EB}}$ or $\Delta G_{S1}^{\text{Iod}}$) and the triplet free energy ($\Delta G_{T1}^{\text{EB}}$ or $\Delta G_{T1}^{\text{Iod}}$) in the electron transfer reaction between dyes and additives can be calculated. In particular, the $E_{ox}$ of the amine (EDB) is 1.0 V and the $E_{red}$ of the iodonium salt (Iod) is $-0.7$ V.

2.4 FRP and metal-free CP under UV/visible-light irradiation and high-performance sunlight-induced polymerization under air

FRP and CP conducted under mild and low-cost conditions are the focus of this study. Five drops (~250 μL) of the investigated formulation dripped into a round gripper with a thickness of 2 mm under air and one drop (~50 μL) of the formulation deposited between two layers of polypropylene films in laminate (100 microns; see the text and figure captions) were prepared for thick and thin samples, respectively (among them, the thin sample is uniformly deposited between two layers of polypropylene films by pressing and standing). The polypropylene films were purchased from Lyreco France (Product Code: 317.868). The round gripper was purchased from VWR Germany (Product Code: 216-1759). Among them, the FRP of TMPTA and the CP of EPOX were carried out under LED@405 nm ($I_0 = 110$ mW cm$^{-2}$) and under sunlight. Then, RT-FTIR (JASCO FTIR-4700) was adopted to monitor the polymerization of TMPTA ($\sim 6150$ cm$^{-1}$ in the thick sample and $\sim 1650$ cm$^{-1}$ in the thin sample) and EPOX ($\sim 3770$ cm$^{-1}$ in the thick sample and $\sim 791$ cm$^{-1}$ in the thin sample$^{30}$) in real time. The specific preparation of the formulation is as follows: the two-component systems (dye/EDB and dye/Iod) and the three-component systems (dye/EDB/Iod) were fully mixed and dispersed into the monomers and then stirred in the dark for 12 hours. And the effect of different dye contents on the photopolymerization efficiency was investigated. For the FRP of TMPTA with two-component photoinitiating systems, the formulations were dye/EDB or dye/Iod 1%/1%, 0.5%/1%, and 0.5%/0.5%, w/w. For the FRP of TMPTA with three-component systems, the formulations were dye/EDB/Iod 1%/1%/1%, 0.5%/1%/1%, 0.1%/1%/1%, 0.05%/1%/1%, 0.5%/0.5%/0.5%, and 0.05%/0.5%/0.5%, w/w/w. For the CP of EPOX with three-component systems, the formulation was dye/EDB/Iod 0.1%/1%/1% w/w/w. The final functional acrylate or epoxy conversions (FCs) were obtained using the following equation:

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

where $A_0$ and $A_t$ are the initial peak area before irradiation and the peak area after irradiation for $t$ seconds, respectively.

In addition, the polymerization of TMPTA with the three-component dye/EDB/Iod system under sunlight was also studied. The sunlight-induced polymerization experiments were carried out on December 15, 2023, from 10 am to 2 pm, aligning with French time. The experiment site was in Mulhouse (+77 43'E, 47 75'N), France, where the weather conditions were cloudy and the temperature varied between 1 °C and 8 °C.

2.5 ESR-ST experiments

To detect the radicals formed by the reaction between the dye and additives (EDB or Iod), ESR-ST was carried out using an X-band spectrometer (Brook EMX-plus). Precisely, the solutions were prepared with the dye/EDB and dye/Iod systems with concentrations of $2 \times 10^{-4}$ M, and the spin trap agent phenyl-$N$-tert-butynitrone (PBN) was added to them, and the concentration of PBN was about $5 \times 10^{-4}$ M. Then, upon irradiation at 405 nm and under nitrogen, the generation of free radicals could be observed.

2.6 Application of 3D printing

The 3D printing experiments were carried out using DLW. The photosensitive formulations containing dye-B1 and B6 were dripped into a self-made square tank and irradiated with a computer-controlled laser diode at 405 nm. The spot size was about 50 microns. The 3D pattern was observed and analyzed with a digital microscope.

2.7 Computational procedure

Gaussian 03 was used to optimize the geometry at the B3LYP/6-31G* level, but also used to determine the triplet energy levels.$^{31}$

3. Results and discussion

3.1 Synthesis of the dyes

The various dyes investigated in this work were synthesized through a multistep synthesis approach. Notably, 7-hydroxy-4-methyl-2H-chromen-2-one R3 was prepared under acidic conditions, by means of the Pechmann condensation between resorcinol R1 and a β-ketoester (i.e., ethyl acetoacetate R2 in our case) in sulfuric acid.$^{32,33}$ Coumarin could be isolated in 61% yield. Parallel to this, R8, B5 and R9 were prepared starting from R4–R6, by condensation of different anilines with bromoacetyl bromide R7 in the presence of triethylamine as the base. R8, B5 and R9 were respectively obtained with reaction yields of 91, 88 and 84%. In the case of 4-aminobenzophenone R6, by replacing triethylamine with pyridine as the base, a different product was obtained, resulting from the formation of a pyridinium salt, followed by the alkylation of the aniline moiety. B4 could be isolated in pure form in 44% yield. Finally, R10, B2 and B3 were prepared by alkylation of R3 with R8, R9 and B2, enabling the preparation of substituted cou-
marins with reaction yields ranging from 52% for B2 to 72% for B3. The N-substituted 7-aminocoumarin R11 could be readily synthesized from R10 by a tandem O → N Smiles rearrangement-hydrolysis reaction using cesium carbonate as the base.34 R11 was obtained in 41% yield (see Scheme 1). Finally, B1 was obtained by alkylation of the secondary amine of R11 with iodohexane, using sodium hydride as the base. B1 was isolated after purification in 89% yield. In the case of the meta-aminophenol B6, the treatment of cyclohexane-1,3-dione R12 with diphenylamine R13 in acetic acid for 14 days enabled the preparation of the N,N-diphenyl enaminone B6 in 58% yield.

Scheme 1  Synthetic routes to B1–B6.
3.2 Light absorption properties

The light absorption properties of the six dyes were determined in acetonitrile. The concentration of dyes was 2.5 × 10⁻⁵ M; their UV-visible absorption spectra are shown in Fig. 2 and the molar extinction coefficient spectra are shown in Fig. 2. Obviously, the absorption wavelengths (λ) of the six dyes and isopropylthioxanthone (ITX, used as the benchmark photoinitiator) were between 300 and 400 nm, and the molar extinction coefficients (ε) of the six dyes and their ε₄₀₅ nm at 405 nm are summarized in Table 1. Dye-B1 and dye-B6 exhibited the largest ε values, which were 15 940 M⁻¹ cm⁻¹ and 19 420 M⁻¹ cm⁻¹, respectively. These molar extinction coefficients were higher than that of the commercial photoinitiator ITX, and the ε₄₀₅ nm of dye-B1 was the largest in this series of dyes. This result is consistent with their high initiation performance in photopolymerization, and the ε₄₀₅ nm of dye-B1 was also selected as the appropriate photosensitizer for sunlight-induced polymerization. In addition, the ε and ε₄₀₅ nm of dye-B2, B3, B4, and B5 were low, and their photoinitiation abilities in photopolymerization were correspondingly poor, as shown below.

![Fig. 2](image-url)  
Fig. 2 UV-visible absorption spectra of the dyes in acetonitrile (B1–B6 and ITX).

<table>
<thead>
<tr>
<th>Pls</th>
<th>ε (M⁻¹ cm⁻¹)</th>
<th>ε₄₀₅ (M⁻¹ cm⁻¹)</th>
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<tr>
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<td>15 940</td>
<td>1450</td>
</tr>
<tr>
<td>B2</td>
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3.3 Fluorescence properties (i.e., fluorescence spectra, fluorescence excited state lifetimes, and fluorescence quenching experiments) and chemical mechanisms of electron transfer reactions

Parallel to the absorption properties, the fluorescence spectra of the six dyes in acetonitrile were determined, as shown in Fig. S2(b).† Dye-B5 demonstrated no or only weak fluorescence. In contrast, dye-B1 and B6 exhibited strong fluorescence in the range of 400–700 nm and these two dyes showed a long fluorescence excited state lifetime (see Fig. S3†), which may be an important reason for their good photoinitiation abilities. The interaction between the dyes and co-initiators and various parameters in the electron transfer reaction are summarized in Table 2. Among them, the Φₛₛ was calculated from the intersection between the normalized fluorescence spectrum and the UV-visible absorption spectrum of the dye (see Fig. 3). The Φₛₛ and Φₛₑ potentials of the six dyes were determined by CV (see Fig. S4†). From Fig. S4, the oxidation and reduction peaks of the six dyes studied can be clearly observed. According to Rehm–Weller29,35 equations, the ΔGстро values of electron transfer between dyes and additives were calculated, and the values are listed in Table 2. From the values, the ΔGстроен values of all dyes were negative, indicating that the reactions of dye/EDB and dye/Iod are feasible.

In addition, the interaction between the dyes and EDB/Iod was further characterized by fluorescence quenching experiments. The fluorescence quenching spectra obtained with the dye/EDB and dye/Iod systems in acetonitrile are shown in Fig. 4 and S5.† Fig. 4(a and b) show the change in fluorescence emission caused by the interaction between dye-B1, dye-B2 and Iod. After the addition of a certain amount of Iod to the dye, the intensity of dye fluorescence decreased obviously (see Fig. 4(a)), which indicated that Iod had an efficient fluorescence quenching effect on dye-B1. Therefore, the Φₑ of dye/Iod could be determined by fluorescence quenching (see Table 2). Parameters of the chemical mechanisms associated with dyes in acetonitrile

<table>
<thead>
<tr>
<th>Pls</th>
<th>Φₑ (EDB)</th>
<th>Φₑ (Iod)</th>
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<tr>
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<td>3.13</td>
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<td>3.13</td>
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<tr>
<td>B6</td>
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<td>0.98</td>
<td>3.13</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Table 2 Parameters of the chemical mechanisms associated with dyes in acetonitrile

- HOMO and LUMO energies are computed at an MPW1PW91/6-31G* level of theory on structures optimized at a UB3LYP/6-31G* level of theory. a Triplet energies are computed at a UB3LYP/6-31G* level of theory.
Fig. 4(c), (d) and S6†. Similarly, dye-B2, B3 and B6 all showed a downward trend in strength after the addition of co-initiators (see Fig. S5†), and the corresponding $K_{SV}$ values are summarized in Table 2. After the addition of a certain amount of EDB to the dye, the fluorescence intensity slightly increased (see Fig. S5(a)†). The possible reason can be that dye-B1 reacted with EDB to generate a new fluorescent product, which increased the fluorescence intensity.

3.4 FRP kinetics under near UV/visible-light irradiation in TMPTA

To investigate the photoinitiation abilities of the six dyes, the photopolymerization profiles of two and three-component systems were determined upon irradiation at 405 nm with a LED, and the conversions of acrylate double bond functional groups were monitored using RT-FTIR at room temperature. The results showed that the FCs obtained with the three-component systems were higher than those obtained with the two-component systems (see Table S1 and Fig. S7† for the conversions of thick samples (about 2 mm), and Table S2 and Fig. S8† for the conversions of thin samples (about 100 microns)) which could be deeply cured (see Fig. S9†). It was particularly noted that the dye-free two-component system EDB/Iod (1%/1% w/w) was used as a reference system. In fact, dyes could only initiate a polymerization of monomers in combination with co-initiators such as EDB or Iod. The specific chemical mechanism is given in section 3.10. Considering that the three-component photoinitiating systems showed higher photoinitiation abilities than their two-component analogues, the amounts of co-initiators EDB/Iod (1%/1% w/w) were fixed to 1 wt% by the control variable method in this study, and the influence of different contents (relative to the monomer) of dyes on photopolymerization of the three-component system was studied. As shown in Fig. 5(a–d), the photopolymerization profiles of thick samples with different contents of dyes (1 wt%, 0.5 wt%, 0.1 wt% and 0.05 wt%) were different, and the FCs of acrylate functional groups are summarized in Table 3.

For dye-B1, by decreasing the dye content, the formulations became clearer and more transparent, and the conversions increased from $\sim 60\%$ to 80%, which finally showed an upward trend. When the dye contents were set to 0.1% and 0.05%, the conversions were almost similar to that obtained with the commercial initiator ITX ($\sim 80\%$), which was much higher than 55% for the reference EDB/Iod (1%/1% w/w) system in the blank control group. Moreover, for the blank, a long inhibition time is found, showing the role of the dye in efficient polymerization processes. This is undoubtedly the most effective photoinitiator among the series of dyes investigated in this work. For dye-B6, the monomer conversions decreased with the reduction of the dye contents. When the concentration was set to 1%, the highest conversion reached 79%. For dye-B2, B3, and B4, when the content was set to 1 wt%, they cannot be completely dissolved in the monomer, which led to poor light...
Fig. 4 Fluorescence quenching of (a) dye-B1 and Iod and (b) dye-B2 and Iod in acetonitrile. Stern–Volmer treatment for fluorescence quenching of (c) dye-B1/Iod and (d) dye-B2/Iod.

Fig. 5 FRP profiles of TMPTA for the thick sample (about 2 mm) under LED@405 nm irradiation initiated by (a) dye/EDB/Iod 1%/1%/1% w/w/w; (b) dye/EDB/Iod 0.5%/1%/1% w/w/w; (c) dye/EDB/Iod 0.1%/1%/1% w/w/w; and (d) dye/EDB/Iod 0.05%/1%/1% w/w/w.
penetration, and thus the monomer conversion was extremely low. When the contents were set to 0.5 wt%, 0.1 wt%, and 0.05 wt%, the conversions basically remained between 56% and 68%, which were lower than that of ITX, but slightly higher than that of the blank control group EDB/Iod (1%/1% w/w) by 55%. The conversions of dye-B5 in all content gradients were between 50 and 60%, which were close to those obtained with dye-B2, B3, and B4. Due to the fact that the conversions obtained with these four dyes were lower than those obtained with dye-B1 and B6, these four dyes were excluded from the follow-up research.

3.5 Metal-free cationic free radical polymerization of EPOX

The photoinititation ability of the three-component system based on dye-B1 in EPOX was examined at 405 nm and the results are shown in Fig. 6(a–d). The conversions obtained with the different dyes and ITX are summarized in Table 4. The dye-B1/EDB/Iod 0.1%/1%/1% w/w (relative to the monomer EPOX) three-component system showed a higher photoinitiation ability than the commercial initiator ITX in both thin and thick samples. It is worth mentioning that a high monomer conversion rate could still be achieved when the dye content was only 0.1 wt%. Among them, the monomer conversion for thin samples (see Fig. 6(a)) was more than 60% after 100 seconds of irradiation, and the maximum monomer conversion in thick samples (see Fig. 6(c)) was close to 40% after 600 seconds. In addition, under the same conditions, the blank control EDB/Iod (1%/1% w/w) could not initiate the polymerization of EPOX, indicating that dye-B1 played a crucial role in the cationic photopolymerization (all operations were carried out at room temperature). The possible reason is that dye-B1 reacts with EDB and Iod to produce radical cations (dye*+). The chemical mechanism is shown in section 3.10.

### Table 3

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<th>Dye (0.5%) + EDB (1%) + Iod (1%)</th>
<th>Dye (0.1%) + EDB (1%) + Iod (1%)</th>
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3.6 High-performance sunlight-induced polymerization under air in three-component systems of TMPTA

Based on the high performance of the six dyes upon excitation at 405 nm, the experiment of sunlight-induced polymerization was performed on December 15, 2023 at 10 am–2 pm in Mulhouse, France. The specific experimental conditions were as follows: for the thin samples in laminate (about 100 microns), the three-component system dye/EDB/Iod 0.1%/1%/1% w/w (relative to the monomer EPOX) three-component system showed a higher photoinitiation ability than the commercial initiator ITX, and the monomer was TMPTA. As shown in Fig. 7(a), the conversions of all samples reached the maximum within 5 minutes, especially the conversion of dye-B1 was as high as 90% within 5 minutes, which was much higher than that obtained with the commercial initiator ITX (71%) and the
blank (EDB/Iod 2%/2%, w/w) group (42%). For thick samples, as shown in Fig. 7(b), the maximum conversions of samples containing dye-B1 and dye-B6 were 60% and 50% respectively within 60 minutes when the 2 mm thick resin sample in an open mold (no protection against oxygen inhibition) was exposed to outdoor sunlight. More interestingly, when the open mold of the thick sample was closed and isolated from oxygen, it was found that the polymerization rates of dye-B1 and B6 were obviously accelerated under sunlight, and the FCs were also improved; the maximum conversions were 71% and 64% for the samples containing dye-B1 and dye-B6 within 60 minutes (see Fig. 7(c)). The conversions of all samples under sunlight are summarized in Table 4. Markedly, for the polymerized samples shown at the bottom of Fig. 7, it can be seen that the photocuring was complete, which proved that the six dyes examined in this study showed an excellent photoinitiation ability under sunlight and thus under mild irradiation conditions and can be used as efficient photoinitiators.

3.7 Steady state photolysis experiments of dye alone, dye/EDB and dye/Iod photoinitiation systems

To reveal the interactions existing between the dyes and EDB or Iod more comprehensively and the stability of individual dyes, photolysis experiments were carried out for dye-alone, dye/EDB, and dye/Iod in acetonitrile under LED@405 nm. The results are shown in Fig. S10, S11, and S12.† It is worth noting that the concentration of dye was set to $2.5 \times 10^{-5}$ M, and the concentrations of EDB and Iod were set to $5 \times 10^{-5}$ M. From Fig. S10,† it can be seen that after irradiation for 25 minutes, the intensity of the UV spectra of all dyes in the absence of a co-initiator (dye-alone) basically did not decrease, indicating that a dye alone demonstrated good light stability. Remarkably, for the dye/EDB system after a long time of irradiation, the photolysis was not obvious (Fig. S11†), indicating that the photochemical interaction between the dye and EDB was very slow. In the dye/Iod system, only dye-B1 showed an obvious dramatic decrease in the absorption spectra after being irradiated with LED@405 nm for 25 minutes (Fig. S12[a]†). Therefore, dye-B1 can be considered as the most effective dye among all the six dyes, which was verified during the photopolymerization with TMPTA and EPOX.

3.8 Sunlight stability experiments

The stability of photoinitiators is essential for practical application. To verify the stability of the six dyes under sunlight, their stabilities were tested upon exposure to sunlight for 120 minutes. As shown in Fig. S13,† all dyes demonstrated excellent stability in acetonitrile, and after a long period of steady-state photolysis, their UV-visible absorption spectra
<table>
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<th>FCs (%) of the thick sample under air</th>
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hardly changed. It thus revealed that the different dyes exhibit good stability under sunlight, which is the basis for long-term storage, transportation, and use under sunlight.

3.9 ESR-ST experiments

To study the free radicals produced by interaction between dyes and additives during photopolymerization, ESR-ST experiments were carried out at room temperature under LED@405 nm. As shown in Fig. 8, phenyl tert-butyl nitroxide (PBN) successfully captured the radical of dye-B6/Iod in tert-butylbenzene solution (under a nitrogen atmosphere), and its hyperfine coupling constants were $\alpha_N = 14.3$ G and $\alpha_H = 2.1$ G (accuracy $\pm 0.1$ G), which may be assigned to aryl radicals.36 In particular, ESR-ST experiments done on the dye-B6/EDB system revealed no obvious signals (see Fig. S14†), consistent with the steady-state photolysis experiments done under the irradiation of LED@405 nm (see Fig. S11(f)†) and the low photopolymerization conversion.

3.10 Photoinitiation mechanisms and theoretical calculations of dyes

According to our previous study, the chemical mechanism of photopolymerization was determined and is summarized in Scheme 2. The chemical mechanism mainly involved a redox reaction between the excited state of the dyes and EDB and Iod. Firstly, the dye in the ground state was promoted to its excited state (dye*) upon light irradiation (see r1), and then the dye* reacted with $\text{Ar}_2\text{I}^+$ (see r2). Interestingly, dye* produced in r2 can be reduced by EDB to the ground state dye for regeneration (see r3), thus completing the catalytic cycle. And ami-

Fig. 7 Sunlight polymerization profiles of TMPTA for (a) the thin sample (about 100 microns) in laminate, (b) the thick sample (about 2 mm) under sunlight and under air and (c) the thick sample (about 2 mm) under sunlight in laminate initiated by dye/EDB/Iod 0.1%/2%/2% w/w/w.

Fig. 8 (a) ESR-ST spectra of the PBN radical adduct in tert-butylbenzene for an irradiated solution of dye-B6/Iod for 0 s and 50 s under a nitrogen atmosphere and (b) ESR-ST spectra of the PBN radical adduct in tert-butylbenzene for an irradiated solution of dye-B6/Iod for 50 s and simulated under a nitrogen atmosphere.

Scheme 2 The photoinitiation mechanisms (r1–r3) of the prepared dye as a photoinitiator.
noalkyl free radicals can be produced. In the whole reaction process, free radical polymerization was initiated by free radicals, while cationic polymerization was initiated by cations generated in the reaction process.

It was worth noting that in the case of the three-component system based on the different dyes, the initiation behavior in FRP and CP processes may be different, and the oxidation and reduction cycles experienced by the dyes can be discussed not only thanks to the results obtained from theoretical calculations concerning the contour plots of the frontier molecular orbital but also thanks to the different photochemical parameters. One important theoretical parameter was $E_{S1}$, and the second one was $E_{T1}$. Indeed, long-living triplet excited states favor the generation of free radicals by providing more time for the dye to react with the additives so that the polymerization process can be more effectively promoted.\textsuperscript{13} $E_{T1}$ was obtained at a UB3LYP/6-$31G^*$ level of theory. HOMO and LUMO energies were obtained at an MPW1PW91/6-$31G^*$ level of theory (see Table 2). It can be concluded that the excellent photoinitiator ability of dye-B1 can be attributed to its high molar extinction coefficient and even its excellent photochemical reactivity in the excited state. The $E_{T1}$ of dye-B5 was the lowest, which was in good agreement with its poor photoinitiation ability. However, dye-B2, B3, and B4 with high $E_{T1}$ did not show satisfactory photoinitiation ability, which may be due to their low molar extinction coefficients.

3.11 Application in direct laser writing (DLW)

Dye-B1 and dye-B6 were selected as appropriate candidates for practical applications, and formulations (dye-B1/EDB/Iod 0.1 w%/1 w%/1 w% and dye-B6/EDB/Iod 1 w%/1 w%/1 w%) were prepared with co-initiators and irradiated with a laser diode at 405 nm. The whole process was carried out at room temperature. Interestingly, 3D patterns with a high precision and a clear outline (dye-B1 to “DYE” is shown in Fig. 9(a) and dye-B6 to “DLW” is shown in Fig. 9(b)) were obtained within 2 minutes (the printed sizes are 7 mm in length, 5 mm in width and 2 mm in height), and its surface was observed by numerical optical microscopy, and a 3D pattern with a smooth surface and an excellent spatial resolution was successfully manufactured in a short time. The success of the DLW experiments and the possibility to promote sunlight-induced polymerization with these dyes make these structures promising candidates for future applications.

4. Conclusion

In summary, six new metal-free dyes were designed and synthesized, and successfully combined with EDB and Iod to form three-component photoinitiating systems. Notably, under LED@405 nm irradiation, these photoinitiating systems successfully generated active species, initiating the FRP of TMPTA and the CP of EPOX. Particularly noteworthy were their photoinitiation abilities, enabling the initiation of the FRP of TMPTA under sunlight, with dye-B1 achieving an unprecedented 90% acrylate function conversion within 5 minutes. Furthermore, all dyes exhibited remarkable light stability under sunlight, a crucial attribute for practical applications. The photoinitiation properties of the dyes were comprehensively validated through both theoretical and experimental approaches, including steady-state photolysis, excited-state fluorescence quenching, and theoretical calculations. Finally, the dye-B1/EDB/Iod and dye-B6/EDB/Iod three-component systems were successfully applied to 3D printing. This work not only showcases the potential of metal-free dyes to initiate polymerization under sunlight, but also addresses limitations associated with visible light LEDs and the traditional UV light sources in photo-polymerization and photocuring. By saving energy and aligning with the principles of sustainable development in green chemistry, sunlight-induced polymerization holds tremendous promise for diverse applications in photocuring.

Data availability

The data supporting this article have been included as part of the ESL.\textsuperscript{†}

Conflicts of interest

The authors declare no competing financial interest.
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