Novel Photoinitiators Based on Benzophenone-Triphenylamine Hybrid Structure for LED Photopolymerization

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Two novel photoinitiators (PIs) based on benzophenone-triphenylamine hybrid structures are proposed from the perspective of molecular structure for light-emitting diode (LED) photoinitiating systems. Benzoyl substituents have been introduced on the triphenylamine (TPA) core to form peripheral benzophenone groups. As a result of this specific substitution, compounds with excellent light absorption properties as well as high molar absorption coefficients and red-shifted maximum absorption wavelengths compared to that of benzophenone and triphenylamine considered separately could be prepared. By the advantageous combination of benzophenones and TPA onto the same

structures, photoinitiators that could simultaneously work in oxidative and reductive processes could be obtained. Thus, the generated benzophenone units attached to the TPA core could act as a Type II PI capable to initiate the free radical photopolymerization (FRP) of acrylates when combined with an amine used as the co-initiator. Conversely, the triphenylamine moiety could act as an electron-donating group and efficiently interact with an iodonium salt to generate free radical and cationic species for FRP and cationic photopolymerization (CP) respectively. The interactions of PIs and additives (amine and iodonium salt) were investigated through steady state photolysis, fluorescence quenching and cyclic voltammetry experiments. The proposed chemical mechanisms are also discussed. Three-dimensional (3D) printing experiments were carried out to evidence the high reactivity of the newly proposed photoinitiating systems and the resulting 3D patterns were characterized by numerical optical microscopy. It revealed that the novel versatile photoinitiators based on benzophenone-triphenylamine hybrid structures have great potentials for future industrial applications.

1. Introduction

Photopolymerization has a widespread application in many research fields such as inks, coatings, biomaterials and microelectronics.[1, 2] Photoinitiator (PI) is the key-component of the photosensitive systems as this molecule is in charge to absorb light and in turn induce the formation of initiating species by mean of various mechanisms. Therefore, the design and development of PIs constitute an active research field of photopolymerization.[3, 4] In addition, to optimize the light absorption efficacy,

adequation between the PI absorption and that of the light sources is also an important issue. At present, UV light sources (e.g. Hg lamp) are still widely used in industry but suffer from several drawbacks. Thus, these devices are characterized by their high costs, the release of heat and ozone during device operation, which negatively impact the development of photopolymerization.[5] In recent years, light-emitting diodes (LEDs) have drawn increasing attention as light sources due to their low cost, lightweight and compact structures facilitating their incorporation in various setups. LEDs demonstrate tremendous potentials as an effective visible light alternative to the traditional UV irradiation sources.[6] However, at present, most of the Type I cleavage systems (e.g. hydroxyl-ketone photoinitiators) and Type II H-abstraction systems (e.g. benzophenone/amine) based on benchmark PIs can only be activated under UV irradiation and cannot be even used in the near UV/visible range, even if these wavelengths are now widely employed for the industrial production and scientific research.[7-9] Nowadays, the irradiation @405 nm is the new standard in three-dimensional (3D) printing for both stereolithography (SLA) and digital light processing (DLP) approaches. Therefore, search for new PISs perfectly matching the emission of LEDs is the focus of numerous research efforts.

Dye-photosensitized systems display a lively interest in photopolymerization under LEDs irradiation for the free radical photopolymerization (FRP) of (meth)acrylates and cationic photopolymerization (CP) of epoxides. Interestingly, in the excited state, organic dyes can act as an electron acceptor when opposed to amines to generate aminoalkyl radicals or act as an electron donor with onium salts to generate aryl radicals

and cationic species.[10, 11] Thanks to the wide range of organic dyes reported in the literature and the variety of absorption spectra, it provides a unique opportunity to develop high performance PISs under LEDs irradiation. Thus, numerous photoinitiating systems based on carbazole, pyrene, anthracene, etc. have been reported in the literature.[3, 12, 13]

In order to improve the photochemical reactivity or obtain additional properties, dyes are usually modified with various substituents through chemical engineering. Traditional UV sensitive PIs are commonly introduced in the backbone of dyes absorbing in the visible range due to their well-established photochemical reactivities, the chromophores onto which these UV sensitive PIs are attached being in charge to red-shift their absorption toward the visible region and provide high molar extinction coefficients (e.g. @405 nm) at wavelengths these PIs do not naturally absorb. Benzophenone (BP) and thioxanthone (TX) have been exploited widely for this purpose[3, 14] and the photoinitiation mechanism of BP is shown in Scheme 1. Notably, BP and TX units covalently linked to truxenes or pyrenes respectively, and BP units introduced onto naphthalimides were notably reported in the literature, evidencing the interest of this approach.[15-18] Due to a strong molecular orbital coupling, the new derivatives exhibit red-shifted absorptions and high molar absorption coefficients which led to efficient photopolymerization upon near UV/visible light irradiation. Beyond the simple combination of PIs and dyes by forming covalent bonds between the two structures, hybrid structures where the PI and the dye share in common an aromatic ring were also proposed. Thus, a one-component Type II PI TCX-EC based

on thioxanthone-ethylcarbazole hybrid structure was proposed as an innovative approach for the design of photoinitiators. [19] The absorption of TX-EC was extended towards the visible wavelength region ($\lambda > 400$ nm, where the TX and EC chromophores are almost transparent when considered separately) and good polymerization performances could be found in the visible range by mean of this combination.[19] A thioxanthone-anthracene (TX-A) PI was also proposed in 2011 and this molecule exhibited a high molecular absorption coefficient (~14000 $M^{-1}cm^{-1}$ at 368 nm) which ensured effective light absorption upon near UV irradiation.[20] A series of benzophenone-pyrene hybrid structures was proposed and absorption spectra extending between 200 and 420 nm could be determined.[21] Recently, bifunctional benzophenone-carbazole PI (BPC) and monofunctional benzophenone-carbazole PI (BPC1) have been reported in the literature.[22, 23] Compared to the BPC1, BPC has a red-shifted absorption and a higher molecular absorption coefficient which was ascribed to the additional benzophenone-carbazole hybrid structure.

In this study, one and three benzoyl substituents were introduced onto the triphenylamine core to obtain a monofunctional benzophenone-triphenylamine PI 4-(diphenylamino)phenyl)(phenyl)methanone (MBP-TPA) and a trifunctional benzophenone-triphenylamine PI nitrilo*tris*(benzene-4,1-diyl))*tris*(phenylmethanone (TBP-TPA) respectively. The synthesis and characterization of MBP-TPA and TBP-TPA are described in supporting information. TBP-TPA has been previously reported in the literature, in the context of nanoporous organic frameworks for CO_2 storage,[24] and MBP-TPA as photo and electroluminescent materials or as candidate for

mechanistic investigations.[25-31] To the best of our knowledge, both MBP-TPA and TBP-TPA have never been used as PIs. The high molecular weight of TBP-TPA and its trifunctional character can also be very interesting for its migration stability.

As a result of these hybrid structures, red-shifted absorption wavelengths and high molar absorption coefficients are expected. FRP experiments were carried out to evaluate the photoinitiation ability of MBP-TPA and TBP-TPA-based systems, and compare them with well-known and established BP-based and 2-isopropylthioxanthone (2-ITX)-based systems. CP of epoxides in the presence of two-component PI/Iod systems was also investigated. *Bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod) and ethyl 4-(dimethylamino)benzoate (EDB) were used as co-initiators. Chemical structures of PIs and other compounds used in this study are shown in Scheme 2.

2. Results and discussion

2.1. Light Absorption Properties of Photoinitiators

UV-Visible absorption spectra of MBP-TPA, TBP-TPA, BP and 2-ITX in acetonitrile are presented in Figure 1. The maximum absorption wavelengths (λ_{max}), molar absorption coefficients at maximum absorption wavelength (ε_{max}) and molar absorption coefficients at 405 nm (ε_{405} nm) are also summarized in the Table S1. According to the literature, the maximum absorption wavelength of neat triphenylamine (TPA) is 300 nm and there is almost no absorption at 405 nm.[32] Compared to the BP, 2-ITX and TPA, MBP-TPA and TBP-TPA clearly exhibit better absorption properties. Because of the strong π-conjugation extension effect, the

absorption band shifts towards long wavelengths when the benzoyl substituent is introduced on the TPA core. Interestingly, the maximum absorption wavelengths of monofunctional benzophenone-triphenylamine PI MBP-TPA and trifunctional benzophenone-triphenylamine PI TBP-TPA shift to 361 nm and 375 nm respectively. Meanwhile, remarkable molar absorption coefficients at 405 nm of MBP-TPA ($\varepsilon_{max} = 3100$ $M^{-1}cm^{-1}$) and TBP-TPA ($\varepsilon_{max} = 8700$ $M^{-1}cm^{-1}$) are observed. The benzophenone-triphenylamine hybrid structures increase thus significantly the light absorption properties which ensure a good overlap with the emission spectra of the near UV or visible LEDs.

2.2. Free Radical Photopolymerization and Cationic Photopolymerization

Different PISs were investigated for FRP and CP experiments upon LED@405 nm irradiation in laminate and the resulting polymerization profiles are presented in Figure 2. The contents of photoinitiators, Iod and EDB were calculated from the monomer content. Remarkably, benzophenone-triphenylamine PIs exhibited a better photoinitiation activity than BP and 2-ITX in the presence of Iod, which is agreement with the improved absorption properties of PIs (Figure 2a). Especially, for TBP-TPA/Iod system, fast polymerization rates and high acrylate function conversions (69%) were obtained. EDB as co-initiator (H donor) was also added to study the photoinitiation ability of PIs (Figure 2b). The BP/EDB system, used as a benchmarked Type II system, had a poor performance, resulting from the bad absorption of BP at 405 nm. Compared with the well-established 2-ITX/EDB Type II system, the MBP-TPA/EDB system showed a lower polymerization rate, but interestingly, a better

polymerization performance was found for TBP-TPA/EDB system. Remarkably, TBP-TPA/EDB system also exhibited a better performance than the 2-ITX/EDB system upon LED@365 nm irradiation (Figure S1a). The same holds true with 2-ITX. A H-abstraction behavior from EDB could be also observed on MBP-TPA and TBP-TPA. The high molar absorption coefficients of MBP-TPA and TBP-TPA at 405 nm ensure that the benzophenone moiety in benzophenone-triphenylamine hybrid structure keeps a high capacity for H-abstraction under irradiation. In addition, TBP-TPA has a better bimolecular reactivity with EDB than MBP-TPA, which demonstrates that the benzophenone moiety contributes to the FRP very well. Three-component PI/Iod/EDB systems were also investigated in the same conditions (Figure 2c). Remarkably, the TBP-TPA/Iod/EDB system had the fastest polymerization rate and the highest final function conversion (71%) than the other three-component systems. In addition, without additives, MBP-TPA or TBP-TPA can initiate the polymerization of TMPTA upon LED@405 nm irradiation in laminate (Figure S1b), which might occur thanks to the H-abstraction from the monomer (TMPTA).

The cationic photopolymerization of EPOX in the presence of two-component MBP-TPA/Iod and TBP-TPA/Iod systems were carried out under air upon LED@405 nm irradiation (Figure 2d) where the final epoxy function conversions at 200 s were 38% and 45% respectively. It indicates that MBP-TPA and TBP-TPA exhibit a versatile behavior for FRP and CP. The final function conversions are gathered in Table S2.

2.3. Photoinitiation Mechanisms

Iod and EDB as additives play the role of electron acceptor and electron donor

respectively in the associated photoinitiating systems. PIs interact with additives under irradiation to produce active species for FRP and CP. These interactions can be observed in steady state photolysis and fluorescence quenching experiments. The steady state photolysis of TBP-TPA-based systems were thus carried out (Figure S2). The UV-Visible absorption spectra were mostly unchanged in the presence of TBP-TPA alone. Obvious photolysis was observed in the presence of Iod and EDB, which demonstrated that there were effective interactions between TBP-TPA and additives in the excited states. An isosbestic point is observed for these photolyses suggesting a photochemical reaction without by-side processes. As shown in Figure 3, the fluorescence quenching of TBP-TPA in acetonitrile was observed in the presence of Iod (and EDB) with different concentrations (Table 1). Interaction constant (K_{sv}) between TBP-TPA and additives were calculated by Stern−Volmer treatment. The electron transfer quantum yields in the excited singlet state (Φ^{et}) which reflected the PI/additives reactivity were extracted from these K_{sv} data. Fluorescence quenching experiments of MBP-TPA were also carried out (Figure S3). The results are summarized in Table 1. The Φ^{et}_{Iod} and Φ^{et}_{EDB} of TBP-TPA are higher than those of MBP-TPA. It demonstrates that TBP-TPA has a higher reactivity with additives than MBP-TPA which is in full accordance with the results of polymerization.

Based on the results of steady state photolysis and fluorescence quenching experiments, the proposed photoinitiation mechanism of benzophenone-triphenylamine PIs is depicted in Scheme 3. Using the redox potentials (E_{ox}, E_{red}) and excited singlet state energy (E_{s1}), the free energy change ($\Delta G^{et(S1)}$) for the electron transfer reaction

between PIs and additives in the excited singlet state were calculated. The redox potentials were determined from cyclic voltammetry experiments (Figure S4, Table S3) and the excited singlet state energies were evaluated from the crossing point between absorption and fluorescence spectra (Figure S5, Table S3). Under irradiation, PI is converted from its ground state to its excited state (r1, Scheme 3). The interaction of PI/Iod corresponds to an electron transfer reaction generating aryl radical Ar$^\bullet$ and cation PI$^{\bullet+}$ which are considered as the initiating species for the radical polymerization and the cationic polymerization respectively (r2, Scheme 3). Favorable free energy changes ΔG are found (MBP-TPA/Iod: $\Delta G^{et(S1)}_{Iod} = -0.88$ eV; TBP-TPA/Iod: $\Delta G^{et(S1)}_{Iod} = -1.08$ eV) in agreement with a strong PI/Iod interaction (see fluorescence quenching above). EDB as an electron donor and a H donor reacts with PI to generate EDB$_{(-H)}^{\bullet}$ which is regarded as efficient active species for free radical polymerization (r3, Scheme 3). The negative free energy change (MBP-TPA/EDB: $\Delta G^{et(S1)}_{EDB} = -1.59$ eV; the reduction potential of TBP-TPA was not observed in the detection range from 0 to -2000 mV) demonstrates that H abstraction of MBP-TPA from EDB is available. In addition, minor triplet state pathways for r2 and r3 can not be ruled out but high Φ^{et} from S_1 suggest a major singlet state pathway. The consumption rate during the photolysis of TBP-TPA in TBP-TPA/Iod/EDB system is slower than that in TBP-TPA/Iod system (Figure S2e). It could be ascribed to the photoredox catalytic cycle in three-component PI/Iod/EDB system (r4 and r5, Scheme 3). The regeneration of PI in r4 and r5 contributes to the high photoinitiation ability of TBP-TPA to some degree.

3. 3D Printing Experiments

The FRP in the presence of TBP-TPA/Iod/EDB system and CP in the presence of TBP-TPA/Iod systems were used for 3D printing due to the high performance in photopolymerization. The polymerization profiles in these conditions for thick samples are given in Figure S6. 3D printing experiments were carried out upon laser diode irradiation at 405 nm under air and the 3D patterns were analyzed by numerical optical microscopy. As shown in Figure 4, high spatial resolution could be observed. Indeed, the high performance of TBP-TPA-based PISs for FRP and CP allowed an efficient polymerization process in the irradiated area during 3D printing.

4. Conclusion

In this study, the PIs MBP-TPA and TBP-TPA based on benzophenone-triphenylamine hybrid structure are designed for the development of novel high-performance PISs. Benzoyl substituents connecting with triphenylamine moiety not only contribute to the red-shifted wavelength but build up the molar absorption coefficient notably. As a result, both high final conversions and polymerization rates are achieved in FRP. Remarkably, TBP-TPA owning trifunctional benzophenone group exhibits a better Type II PI behavior than well-known 2-ITX for photopolymerization under LED @ 365 and 405 nm exposure. FRP and CP of TBP-TPA-based systems are applied on 3D printing experiments, and good profiles of the 3D patterns are observed which demonstrates that the PIs based on benzophenone-triphenylamine hybrid structure exhibit great potential for application. In addition, favorable free energy

changes of electron transfer reaction for PI/additives are found and the proposed photoinitiation mechanism is discussed. The high molecular weight of TBP-TPA associated with it trifunctional character can also be very interesting for a better migration stability of PIs that is a huge challenge. The development of other photoinitiators based on benzophenone hybrid structure is in progress.

5. Experimental Section

Bis(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod), ethyl 4-(dimethylamino)benzoate (EDB), 2-isopropylthioxanthone (2-ITX) and benzophenone (BP) were obtained from Lambson Ltd (Wetherby, United Kingdom). Trimethylolpropane triacrylate (TMPTA) and (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) were purchased from Allnex (Ivry sur Seine, France). The UV−visible absorption spectra were obtained using a JASCO V730 spectrophotometer (JASCO, Lisses, France). The conversion of the monomers was continuously monitored by Real-Time Fourier Transformed Infrared Spectroscopy JASCO FTIR-4100 (JASCO, Lisses, France). For the thin samples, the characteristic peaks for the acrylate groups of TMPTA and epoxy groups of EPOX are ~1630 cm^{-1} and ~790 cm^{-1} respectively; for the thick samples, the characteristic peaks for the acrylate groups of TMPTA and epoxy groups of EPOX are ~6160 cm^{-1} and ~3700 cm^{-1} respectively. The fluorescence properties of the compounds were studied using the JASCO FP-6200 spectrometer (JASCO, Lisses, France). A computer-controlled laser diode (Thorlabs, Exceter, United Kingdom) (spot size around 50 μm) was used to obtain

the specific 3D patterns on the basis of the photosensitive resins under air. The obtained

3D patterns were analyzed by a numerical optical microscope (OLYMPUS DSX-

HRSU).

Conflict of Interest
The authors declare no conflict of interest.

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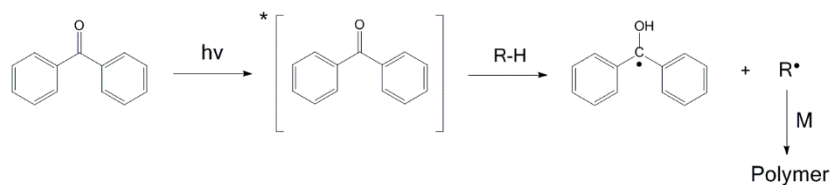
Scheme 1. The photoinitiation mechanism of BP.
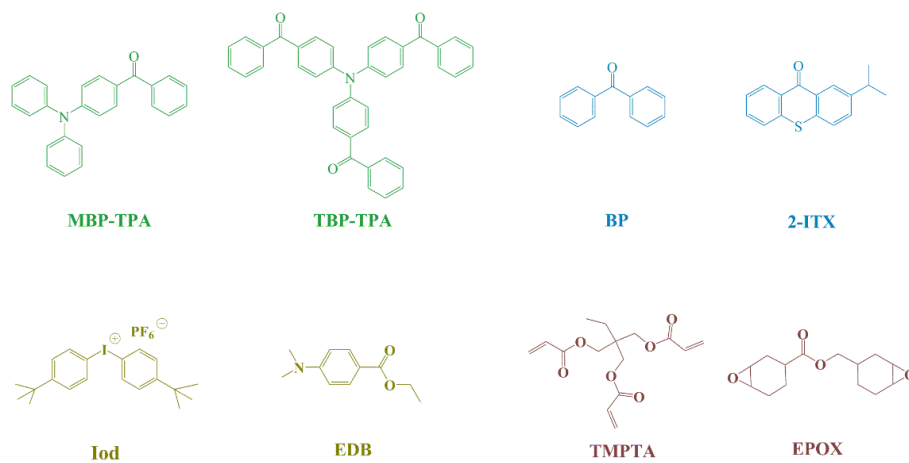
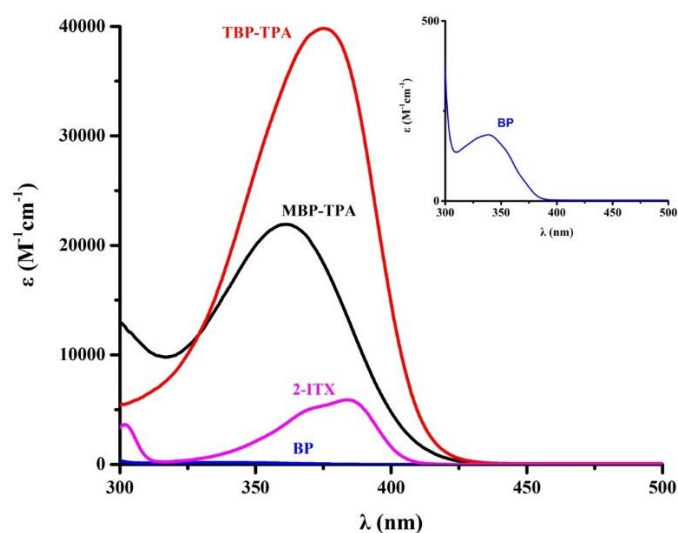**Scheme 2.** The structures of PIs and other compounds used in this study.

Figure 1. UV-Vis absorption spectra of MBP-TPA, TBP-TPA, BP and 2-ITX in acetonitrile; inset: amplification for UV-Vis absorption spectra of BP.
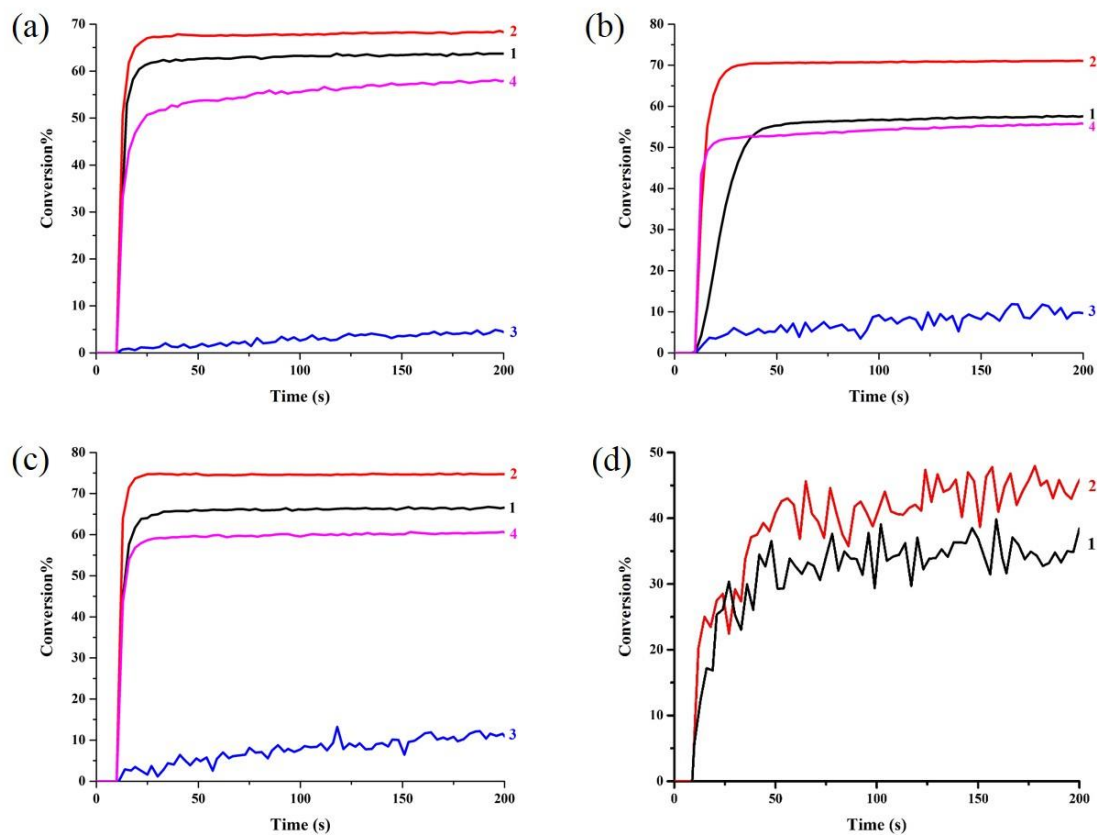
Figure 2. Photopolymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) in laminate (~ 25 μm) upon LED@405 nm irradiation in the presence of **(a)** PI/Iod (0.3%/1%, mol/mol), **(b)** PI/EDB (0.3%/1%, mol/mol), **(c)** PI/Iod/EDB (0.3%/1%/1%, mol/mol/mol); Photopolymerization profiles of EPOX (epoxy function conversion vs. irradiation time) upon LED@405 nm irradiation under air (~ 25 μm) in the presence of **(d)** PI/Iod (0.3%/1%, mol/mol): curve 1: PI = MBP-TPA; curve 2 : PI = TBP-TPA; curve 3 : PI = BP; curve 4 : PI = 2-ITX. The irradiation starts from t = 10 s.
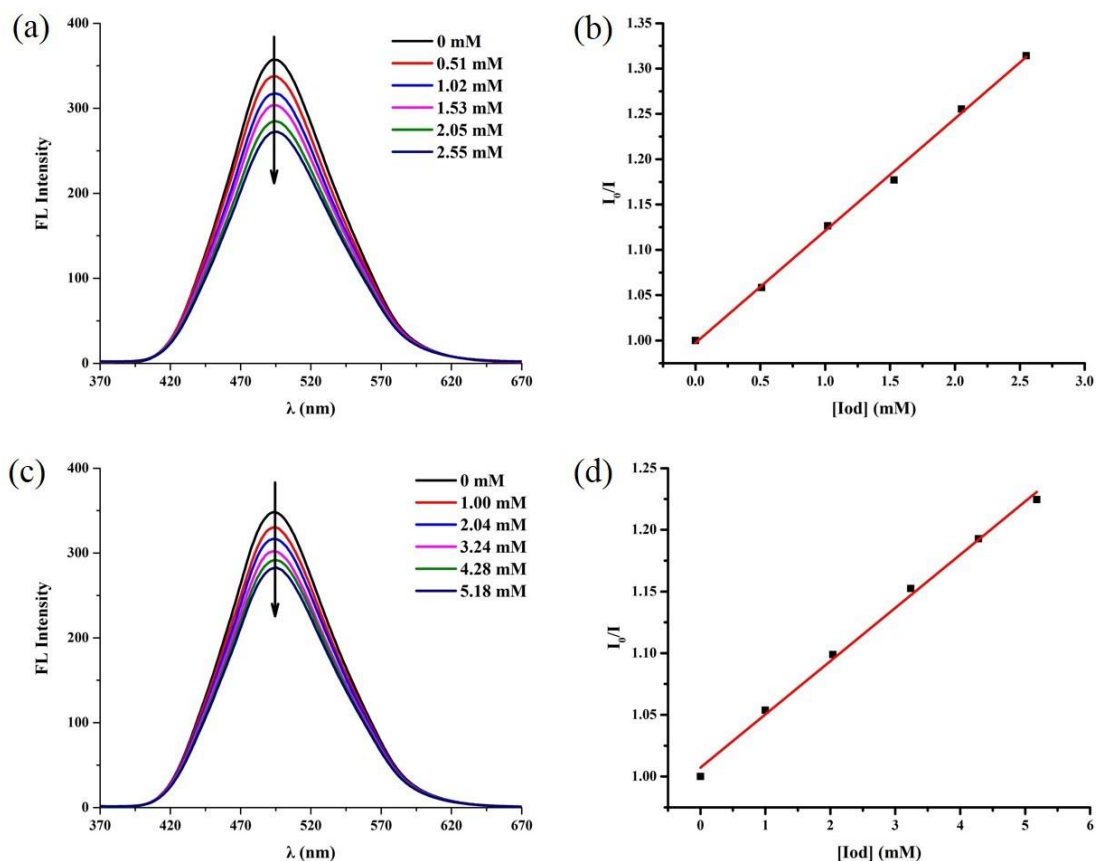
Figure 3. (a) Fluorescence quenching of TBP-TPA by Iod in acetonitrile; **(b)** Stern–Volmer treatment for TBP-TPA/Iod fluorescence quenching; **(c)** Fluorescence quenching of TBP-TPA by EDB in acetonitrile; **(d)** Stern–Volmer treatment for TBP-TPA/EDB fluorescence quenching.

$$PI \xrightarrow{\ h\nu\ } {}^{1,3}PI \tag{r1}$$

$${}^{1,3}PI \ + \ Ar_2I^+ \longrightarrow PI^{\bullet +} \ + \ Ar^{\bullet} \ + \ ArI \tag{r2}$$

$${}^{1,3}PI \ + \ EDB \longrightarrow PI\text{-}H^{\bullet} \ + \ EDB_{(-H)}{}^{\bullet} \tag{r3}$$

$$PI\text{-}H^{\bullet} \ + \ Ar_2I^+ \longrightarrow PI \ + \ Ar^{\bullet} \ + \ ArI \ + \ H^+ \tag{r4}$$

$$PI^{\bullet +} \ + \ EDB \longrightarrow PI \ + \ EDB^{\bullet +} \tag{r5}$$

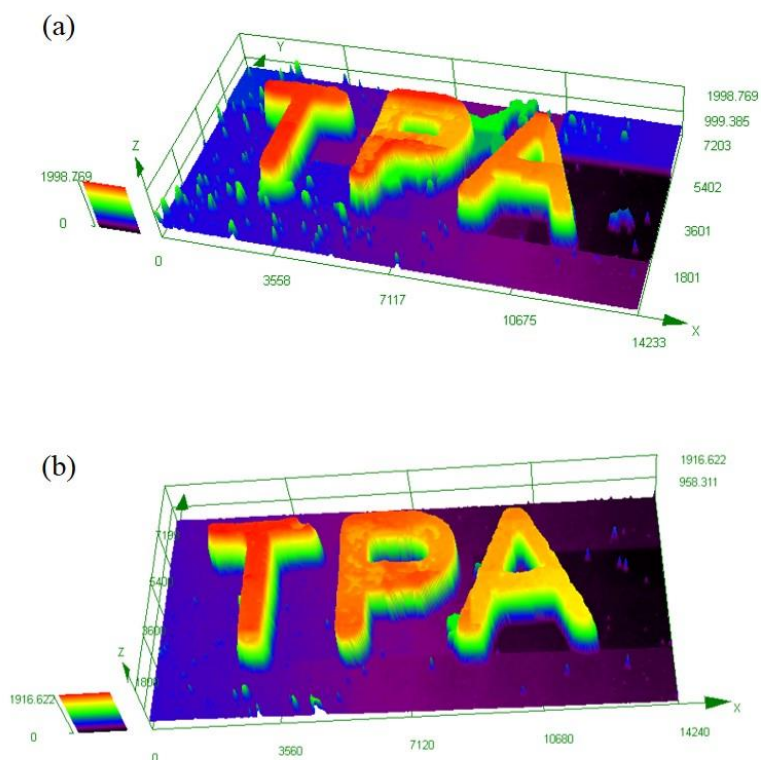**Scheme 3.** Photoinitiation mechanism of the PISs in this study.

Figure 4. Photopolymerization experiments for 3D printing upon laser diode irradiation @405 nm: characterization of the 3D patterns by numerical optical microscopy **(a)** free radical photopolymerization based on TBP-TPA/Iod/EDB system in TMPTA; **(b)** cationic photopolymerization based on TBP-TPA/Iod system in EPOX.

Table 1. Electron transfer quantum yields ([a] Φ^{et}) and free energy changes ([b] $\Delta G^{et(S1)}$) between PIs and additives in excited singlet state.

| PI	Φ^{et}_{Iod}	Φ^{et}_{EDB}	$\Delta G^{et(S1)}_{Iod}$ [eV]	$\Delta G^{et(S1)}_{EDB}$ [eV]
MBP-TPA	0.77	0.45	-0.88	-1.59
TBP-TPA	0.82	0.61	-1.08	—

a) $\Phi^{et} = K_{SV}[\text{additive}]/(1+ K_{SV}[\text{additive}])$;

b) calculated from $\Delta G^{et(S1)} = E_{ox} - E_{red} - E_{S1}$, oxidation potential of EDB is 1.0 V,[1] reduction potential of Iod is -0.7V.[33]

Novel Photoinitiators Based on Benzophenone-Triphenylamine Hybrid Structure for LED Photoinitiating Systems

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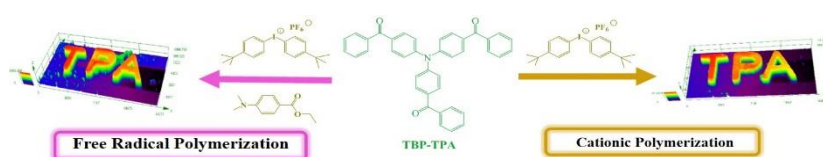
Because of the benzophenone-triphenylamine hybrid structure, excellent light absorption properties are achieved for TBP-TPA and the benzophenone moieties contribute to the Type II H-abstraction behavior well. As a result of this, TBP-TPA has better performances than the well-known isopropylthioxanthone in FRP experiments. Using TBP-TPA-based PISs in both FRP and CP, 3D patterns with high spatial resolution could be obtained.