

## Article

# Visible-Light Photoredox Catalyzed Formation of Triarylethylenes Using a Low-Cost Photosensitizer

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**Abstract:** Visible-light photoredox catalysis using biacetyl (**BA**) as a low-cost photosensitizer enables the efficient formation of triarylethylenes (TAEs) via a Mizoroki–Heck-type coupling. The reaction proceeds efficiently in acetonitrile upon blue LED irradiation under anaerobic conditions. Alternatively, supramolecular viscoelastic gels have also been explored as reaction media, allowing the possibility of working under aerobic atmosphere. Mechanistic investigations by means of transient absorption spectroscopy and quenching experiments support a charge-separated intermediate pathway. Reaction quantum yield measurements further validate the efficiency of **BA**, demonstrating its potential as an alternative to transition-metal catalysts. Overall, this work presents a sustainable and scalable strategy for TAEs synthesis, integrating photoredox catalysis with soft material engineering. These findings pave the way for broader applications in green chemistry and functional materials.

**Keywords:** biacetyl; photoredox catalysis; visible light; triarylethylenes; gel medium



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## 1. Introduction

Triarylethylenes (TAEs) are key structures in organic chemistry and are present in a number of molecules and materials with broad applications across various disciplines. From a synthetic point of view, TAEs serve as building blocks for constructing sophisticated molecular structures due to their versatility and reactivity. Materials science has contributed to the development of polymers, liquid crystals, and organic electronic materials with tailored properties, such as conductivity, optical activity, or thermal stability [1–3]. TAEs also play a role in medicinal chemistry, serving as scaffolds for the design and development of pharmaceuticals with enhanced biological activities and target selectivity [4]. In addition, this core has been extensively used for the design of photochromic materials [5,6]. Some examples of relevant TAE-based compounds are shown in Figure 1.

The synthesis of TAEs has attracted considerable interest in recent years, and different approaches have been explored to obtain chemical structures containing this polyaromatic core [7–10], such as those depicted in Scheme 1: (a) McMurray coupling between carbonyl compounds in the presence of Ti(IV) salts [11–17]; (b) catalyzed hydroarylation of 1,2-diaryl alkynes with arenes or heteroarenes [18–21]; (c,d) reactions with 1-aryl halides following

Heck coupling [22–26]; (e) light-mediated photoreactions between aryl azo sulfones or aryl halides and 1,1-disubstituted alkenes [27,28]; and (f) catalytic Mizoroki–Heck reactions [29]. These reactions have led to TAE targets with different scopes, yields, and limitations (Scheme 1).

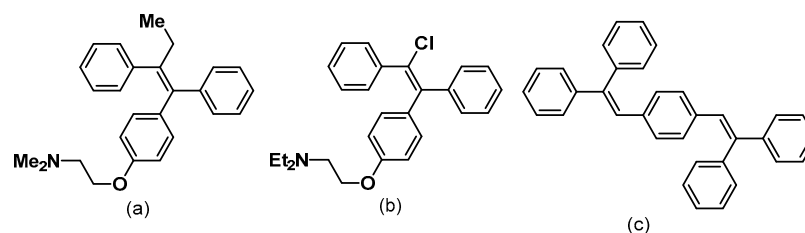
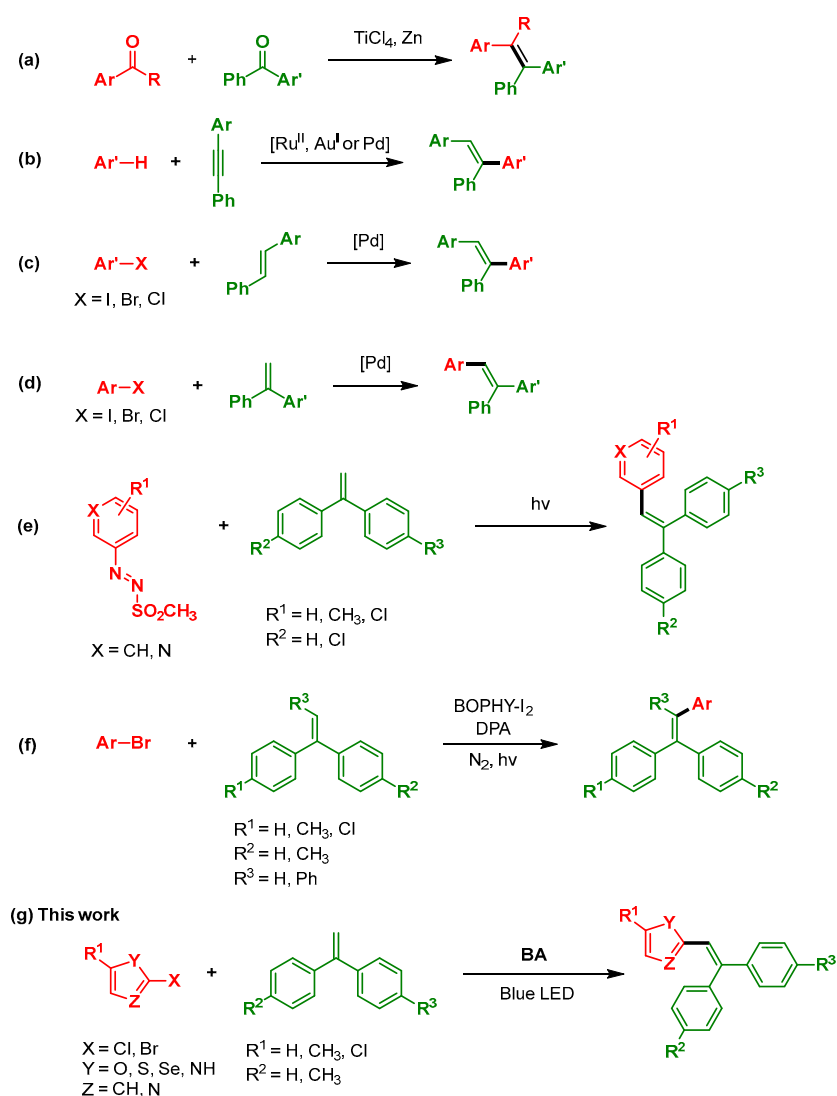


**Figure 1.** Relevant compounds containing the triarylethylene core: (a) tamoxifen, used to treat breast cancer; (b) clomifene, a drug employed for the treatment of infertility in women; (c) extended  $\pi$ -systems with emitting properties that are part of functional materials.



**Scheme 1.** Synthetic strategies for the synthesis of TAEs.

In this context, visible-light photoredox catalysis has emerged as a powerful tool for organic synthesis, enabling chemical reactions under environmentally sustainable and cost-effective conditions and increasing the efficiency and economy of the synthetic process.

Recently, we have employed this strategy in order to obtain TAEs using a bimolecular system as a photoredox catalytic system via the desired Mizoroki–Heck coupling [29].

In the present work, we introduce the use of biacetyl (**BA**, butane-2,3-dione) as a photoinitiator for the synthesis of different TAEs (Figure 2); **BA** is a versatile compound with low toxicity and is commercially available at a relatively low cost. The process involves a clean Mizoroki–Heck-type coupling reaction between 1,1-diphenylethylene and five-membered-ring heteroarenes as starting materials (Scheme 1g). The procedure operates under very mild conditions, with visible light irradiation under an aerobic atmosphere at room temperature and ambient pressure. Different media (organic solvents and supramolecular viscoelastic gels) have been explored to investigate the effects of different types of environments. Moreover, mechanistic studies have been conducted via transient absorption spectroscopy and “light-dark” experiments.

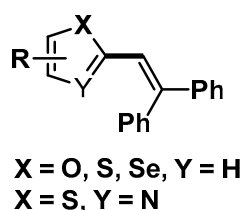


**Figure 2.** Chemical structures of the TAEs synthesized in this work.

## 2. Materials and Methods

### 2.1. General

Biacetyl (**BA**, 2,3-butanedione), 2-acetyl-5-chlorothiophene (**1a**), 1,1-diphenylethylene (**2**), dodecanenitrile, and low molecular weight (LMW) gelator 1,3:2,4-bis(3,4-dimethylbenzylidene)-sorbitol (for G3 gel formation) were purchased from suppliers: Merck (Madrid, Spain), Indagoo (Barcelona, Spain), Fluorochem (Hadfield, UK), TCI (Eschborn, Germany), stored properly and employed directly from the container. Acetonitrile (ACN, p.a. grade) was used as the solvent without further purification. LMW gelators *N,N'*-bis(octadecyl)-L-Boc-glutamic diamide (for the G1 gel) and (*S,S*)-dodecyl-3-[2(3-dodecylureido)cyclohexyl]urea (for the G2 gel) were synthesized according to the literature procedures and yielded spectroscopic data in agreement with those published [30–32].

Thin-layer chromatography (TLC) was performed on commercial SiO<sub>2</sub>-coated aluminum sheets DC60 F254, Merck. Visualization was performed via UV light (254 nm). Purification was performed via reversed-phase HPLC preparative chromatography on silica gel (Merck, mesh 35–70, 60 Å pore size). Yields were determined via quantitative GC-FID measurements on an Agilent 8860 GC-System (Madrid, Spain) with N<sub>2</sub> as the carrier gas, with 1-dodecanenitrile used as an internal standard in the GC-FID.

Products were characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopies. For unknown products, high-resolution mass spectrometry (HRMS) experiments were also conducted. Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker Avance 400 (Madrid, Spain) (400 MHz for <sup>1</sup>H and 101 MHz for <sup>13</sup>C) equipment at 20 °C. Chemical shifts are reported in δ/ppm and coupling constants *J* are given in hertz. The residual solvent peaks were used as internal standards for all the NMR measurements. The quantification of <sup>1</sup>H cores was obtained from integrations of appropriate resonance signals. Multiplet analysis was performed assuming only first-order coupling. The abbreviations used in the NMR spectra are s = singlet, d = doublet, t = triplet, q = quartet, hep = heptet, and m = multiplet. High-resolution mass spectrometry (HRMS) was performed on a UHPLC and mass spectrometer QTOF 6600+ (TRIPLETOFT6600+/Exion LC AD Pump, by SCIEX (Framingham, MA, USA) in the facility of SCSIE University of Valencia. The abbreviations used in the MS spectra are M = molar mass of the target compound and EI = electron impact

ionization. A full collection of spectroscopic data and spectra of the isolated products can be found in the Supplementary Materials (pp. S2–S23).

## 2.2. Steady-State Irradiation

Irradiation was carried out in a Metria<sup>®</sup>-Crimp Headspace clear vial with a flat bottom (10 mL, Ø 20 mm) sealed with a Metria<sup>®</sup>-aluminum crimp cap with a molded septum butyl/natural PTFE (Ø 20 mm). The irradiation source was a 3 W blue LED system (455–460 nm) from Avonec, Wesel, Germany.

### 2.2.1. Irradiation in Homogeneous Media

The five-member heteroarene halide, diphenylethylene, and biacetyl at the concentrations indicated in each experiment were introduced in a vial with a magnetic stir bar containing 2 mL of MeCN. 1-Dodecanenitrile was added as an internal standard. The vial was crimped with a cap septum, and 3 cycles of vacuum/argon were performed on the vial. The mixture was irradiated with the LED system previously described with constant stirring and temperature (20 °C) at different reaction times. Then, ethyl acetate (2 mL) was added to the photolizate. The organic phase was washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under vacuum before final purification by HPLC (Agilent) or preparative chromatography.

### 2.2.2. Irradiation in Supramolecular Viscoelastic Gel Media

The heteroarene halide, diphenylethylene, **BA**, and gelator at the concentrations indicated in each experiment were dissolved in 2 mL of MeCN in a vial. 1-Dodecanenitrile was added as an internal standard. The vial was crimped with a cap septum and heated with a heat pistol (~100 °C) until the complete solution of the gelator was obtained. The mixture was allowed to cool, and gel formation was evident to the naked eye. The mixture was irradiated with the LED system previously described with constant stirring and temperature (20 °C) at different reaction times, with two needles piercing through the septum to allow air to enter the vial. Then, ethyl acetate (2 mL) was injected into the gel and the vial was shaken to break the gel. The mixture was washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under vacuum before final purification by HPLC or preparative chromatography.

## 2.3. Characterization of the Supramolecular Viscoelastic Gel Media

In the corresponding samples, the microheterogeneous media provided by gelation were characterized via standard protocols, including determination of the *gel-to-sol* transition temperature ( $T_{\text{gel}}$ ), oscillatory rheology and scanning and transmission electron microscopy.

### 2.3.1. $T_{\text{gel}}$ Determination

$T_{\text{gel}}$  values were determined via the reverse flow method. For that purpose, a sealed vial containing the gel was placed in an alumina block mold and heated at 2 °C/min using a hotplate equipped with a pair of temperature controls. After several heating and cooling cycles, the  $T_{\text{gel}}$  was determined with an estimated error of  $\pm 2$  °C. Each measurement was performed in triplicate, and the average values are reported.  $T_{\text{gel}}$  values for the gels under different composition conditions are shown in the Supplementary Materials (Figure S35, p. S24).

### 2.3.2. Oscillatory Rheology

Oscillatory rheology was performed with a Discovery HR-2 hybrid rheometer (TA Instruments). The experiments were performed using 2 mL total gel volume: (a) dynamic

frequency sweep (DFS)—variation in storage modulus ( $G'$ ) and loss modulus ( $G''$ ) with frequency (from 0.1 to 10 Hz at 0.1% strain); (b) dynamic strain sweep (DSS)—variation in  $G'$  and  $G''$  with strain (from 0.01 to 100%); (c) dynamic time sweep (DTS)—variation in  $G'$  and  $G''$  with time while keeping the stress and frequency values constant and within the linear viscoelastic regime previously determined in DSS and DFS (strain = 0.1% stress; frequency = 1 Hz).

The rheological measurements were performed for the undoped gel ( $[G1] = 5.5$  g/L,  $V_{\text{MeCN}} = 2$  mL) and the doped gel ( $[G1] = 5.5$  g/L,  $[BA] = 0.03$  M,  $[2\text{-acetyl-5-chlorothiophene}] = 0.01$  M,  $[1,1\text{-diphenylethylene}] = 0.1$  M,  $[\text{dodecanenitrile}] = 0.01$  M,  $V_{\text{MeCN}} = 2$  mL) before and after irradiation with blue LEDs for 24 h. Figures S36–S38 with the results of the oscillatory rheological experiments are shown on p. S25 in the Supplementary Materials.

### 2.3.3. Scanning Electron Microscopy (SEM)

The samples were observed with a JEOL JSM 6400 scanning electron microscope (Madrid, Spain) (resolution 3.5 nm). The samples were prepared by prior freezing at  $-20$  °C for 24 h and then removing the solvent under high vacuum for 12 h. Images were taken at the University of Zaragoza (Servicio General de Apoyo a la Investigación-SAI) and are shown in Figures S39–S41 on pp. S26–S27 (Supplementary Materials).

### 2.3.4. Transmission Electron Microscopy (TEM)

The samples were observed with a Tecnai T20 transmission electron microscope (0.24 nm resolution) equipped with a thermionic gun (LaB6) and a SuperTwin<sup>®</sup> objective lens. For TEM observation, the samples were shaken manually, and a few drops were deposited on copper grids with a holey carbon coating. A Tecnai T20 transmission electron microscope (TEM) (Thermo Fisher, Rafaelbunyol, Spain) was used at a working voltage of 200 kV. Images were acquired with a  $2K \times 2K$  Veleta CCD camera. Images were taken at the University of Zaragoza (Servicio General de Apoyo a la Investigación-SAI) and are shown in Figures S42–S44 on pp. S28–S29 in the Supplementary Materials.

### 2.3.5. Atomic Force Microscopy (AFM)

AFM experiments were performed on a Ntegra Aura (NT-MDT) instrument in tapping mode at a 1 Hz scanning rate using directly polycrystalline sapphire ( $24 \times 19.3 \times 0.5$  mm) as the substrate and a single-crystal silicon tip N-type ( $0.01\text{--}0.025$   $\Omega/\text{cm}$ , coating: Al; SPM probe model: ACLA) at a 200–400 kHz drive frequency. The drive amplitude ranged from 60 to 100 mV. The resolution limit is dictated by the size of the AFM tip. Preparation of the sample: A drop of hot homogeneous solution was placed on the substrate before gelation and dried with a hot air gun. The sample was prepared by pouring a drop of the hot homogeneous solution onto the substrate and dispersing it before gelling. Images are presented in the Supplementary Materials, Figures S45–S47 on p. S30.

## 2.4. Steady-State and Transient Absorption Spectroscopy

Ultraviolet–visible (UV–Vis) absorption spectra were obtained with a JASCO V-650 spectrometer (Madrid, Spain). For the measurements, the samples were placed into quartz cells of 1 cm path length, and the compound concentrations were fixed as indicated.

Transient absorption spectra and time-resolved spectra were obtained via LFP (laser flash photolysis) via an LP980–KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments, Edinburgh, Scotland), which is a combined system for the measurement of laser-induced transient absorption, emission kinetics and spectra, with the ability to automatically convert and analyze the kinetic and spectral information fully. The pump is an INDI Quanta-Ray Nd:YAG laser equipped with a primoSCAN BB optical parametric

oscillator (OPO) from SPECTRA PHYSICS®. The probe pulse is longer than the recorded time window of a measurement, and a monochromator (TMS302-A, grating 150 lines  $\text{mm}^{-1}$ ) disperses the probe light after it passes through the sample. The probe light is then passed on to a PMT detector (spectral S5 range of 200–870 nm) to obtain a temporally resolved picture. All the components were controlled by the software L900 provided by Edinburgh. To photolyze the samples, OPO was employed to obtain a wavelength of 450 nm to excite **BA**. The data were acquired as an average of several shots to improve the signal-to-noise ratio.

### 2.5. Reaction Quantum Yield Determination

For this purpose, a vial (10 mL) with a stir bar was loaded with 2-acetyl-5-chlorothiophene (3.2 mg, 20  $\mu\text{mol}$ , 1.0 equiv), 1,1-diphenylethylene (10.6  $\mu\text{L}$ , 60  $\mu\text{mol}$ , 3.0 equiv), diacetyl (5.2  $\mu\text{L}$ , 60  $\mu\text{mol}$ , 3.0 equiv), dodecanenitrile (4.4  $\mu\text{L}$ , 20  $\mu\text{mol}$ , 1.0 equiv), and 2 mL of acetonitrile. The vial was sealed with a cap septum, purged with argon for 15 min and irradiated with an external blue LED (avoiding 3 W from 455 to 460 nm) through the plain bottom side of the vial at 20 °C for 24 h. The reaction quantum yield ( $\phi$ ) was obtained according to Equation (1) [33,34]:

$$\Phi = \frac{\text{mol of formed product}}{\text{photon flux} \times t \times f} \quad (1)$$

where the mol of the formed product was determined by GC-FID using 1-dodecanenitrile as an internal standard, the photon flux at 457 nm was obtained following the ferrioxalate actinometry method described in the Supplementary Materials (p. S32),  $t$  is the irradiation time and  $f$  is the fraction of light absorbed at  $\lambda_{\text{exc}} = 457 \text{ nm}$ .

## 3. Results

### 3.1. Optimization of the Reaction Conditions for Photosensitized Irradiation in Organic Solvents

In the first stage, we selected 2-acetyl-5-chlorothiophene (**1a**) as the aryl halide partner and 1,1-diphenylethylene (**2a**) as the diarylalkene to investigate the optimal coupling conditions in the presence of **BA** in organic solvents (Table 1). On the basis of the UV-Vis absorption spectra of all the components (Figure 3), blue light is suitable for the selective irradiation of **BA** in the presence of **1a** and **2a**. Therefore, irradiation was carried out via blue LEDs, which emit mainly at  $\lambda$  maximum of 457 nm.

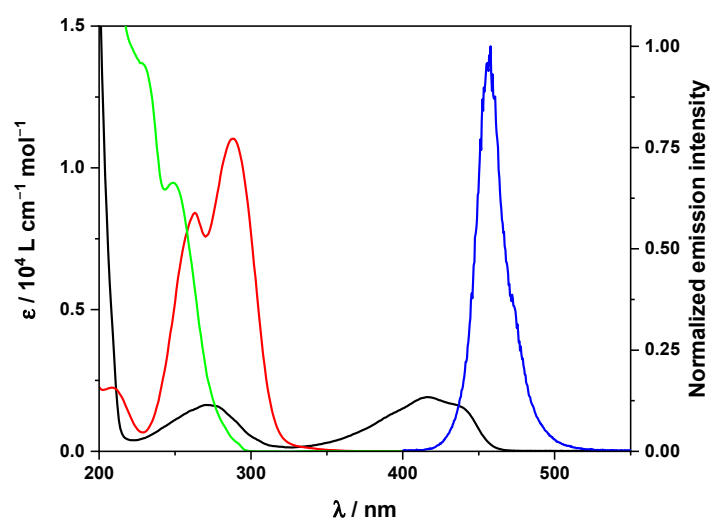


**Figure 3.** UV-Vis absorption spectra of **1a** ( $10^{-4} \text{ M}$ ) in red, **2a** ( $10^{-4} \text{ M}$ ) in green and **BA** ( $5 \times 10^{-3} \text{ M}$ ) in black recorded in MeCN; normalized emission spectrum of the blue LEDs is shown in blue.

**Table 1.** Formation of triarylethylene **3a** via visible-light photoredox catalysis using **BA** in organic solvents <sup>a</sup>.

| Entry           | Solvent               | Time (h) | 2a (equiv) | BA (equiv) | Yield (%) <sup>b</sup> |
|-----------------|-----------------------|----------|------------|------------|------------------------|
| 1               | MeCN                  | 24       | 10         | 3          | 74                     |
| 2               | MeCN                  | 24       | 5          | 3          | 71                     |
| 3               | MeCN                  | 24       | 3          | 3          | 71                     |
| 4               | MeCN                  | 24       | 2          | 3          | 64                     |
| 5               | MeCN                  | 24       | 1          | 3          | 54                     |
| 6               | MeCN                  | 24       | 3          | 2          | 65                     |
| 7               | MeCN                  | 24       | 3          | 1          | 58                     |
| 8               | MeCN                  | 24       | 3          | 0.5        | 50                     |
| 9               | MeCN                  | 24       | 3          | 0.3        | 46                     |
| 10              | MeCN                  | 48       | 3          | 0.3        | 42                     |
| 11              | MeCN                  | 72       | 3          | 0.3        | 53                     |
| 12              | MeCN                  | 96       | 3          | 0.3        | 54                     |
| 13 <sup>c</sup> | MeCN                  | 24       | 3          | 3          | 53                     |
| 14 <sup>d</sup> | MeCN                  | 24       | 3          | 3          | 64                     |
| 15 <sup>e</sup> | MeCN/H <sub>2</sub> O | 24       | 3          | 3          | 55                     |
| 16 <sup>f</sup> | MeCN/H <sub>2</sub> O | 24       | 3          | 3          | 57                     |
| 17 <sup>g</sup> | MeCN/H <sub>2</sub> O | 24       | 3          | 3          | 46                     |
| 18              | DMF                   | 24       | 3          | 3          | 33                     |
| 19              | DMA                   | 24       | 3          | 3          | 21                     |
| 20              | DMSO                  | 24       | 3          | 3          | 39                     |
| 21              | Acetone               | 24       | 3          | 3          | 56                     |
| 22              | AcOEt                 | 24       | 3          | 3          | 45                     |
| 23              | DCM                   | 24       | 3          | 3          | 44                     |
| 24 <sup>h</sup> | MeCN                  | 24       | 3          | 3          | 0                      |
| 25              | MeCN                  | 24       | 3          | 0          | 0                      |
| 26 <sup>i</sup> | MeCN                  | 24       | 3          | 3          | 2                      |
| 27 <sup>j</sup> | MeCN                  | 24       | 3          | 3          | <1                     |

<sup>a</sup> Reaction conditions: [**1a**] = 3.2 mg, 0.02 mmol, V<sub>MeCN</sub> = 2 mL, T = 20 °C, Ar, LED λ<sub>exc</sub> = 457 nm; <sup>b</sup> **1a** conversion determined by GC using dodecanenitrile (4.4 μL, 0.02 mmol) as an internal standard (100% selectivity); <sup>c</sup> V<sub>MeCN</sub> = 1 mL; <sup>d</sup> V<sub>MeCN</sub> = 4 mL; <sup>e</sup> 95/5 ratio; <sup>f</sup> 90/10 ratio; <sup>g</sup> 80/20 ratio; <sup>h</sup> no irradiation; <sup>i</sup> aerobic atmosphere; <sup>j</sup> in the presence of 5 equivalents of TEMPO.

The initial experiment consisted of irradiation using a mixture of **1a** (3.2 mg, 0.02 mmol), **2a** (36 mg, 0.20 mmol), and **BA** (5.2 μL, 0.06 mmol) in 2 mL of MeCN for 24 h at room temperature under an inert atmosphere (Ar). The resulting crude material was analyzed by gas chromatography using dodecanenitrile (4.4 μL, 0.02 mmol) as an internal standard; a new peak was detected, with a 74% yield (Table 1, entry 1). Purification by HPLC (see the experimental section for details) allowed the isolation of 4.5 mg of a white solid. Its chemical structure was unambiguously assigned by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy to 1-(5-(2,2-diphenylvinyl)thiophen-2-yl)ethan-1-one (**3a**).

The reaction was then performed with decreasing equivalents of **2a** (Table 1, entries 2 and 3); under these conditions, the **3a** yield decreased only slightly to 71%. However, at lower **2a/1a** ratios (Table 1, entries 4 and 5), the yield decreased to 64% (when 2 equivalents of **2a**) and 54% (with 1 equivalent of **2a**), respectively. Next, the experiment with 3 equivalents of **2a** or 3 equivalents of **BA** (corresponding to entry 3) was used as the starting point to adjust the equivalents of added **BA** to the reaction mixture. Thus, the **3a** yield decreased

concomitant with the decrease in **BA** equivalents (Table 1, entries 6–9), whereas a slight increment of the **3a** yield was observed at longer irradiation times (Table 1, entries 10–12). The next step was to test the reaction in different solvents, employing the best conditions found in Table 1, entry 4. Modifying the volume of MeCN to increase or decrease the concentration (Table 1, entries 13 and 14, respectively) did not improve the **3a** yield. None of the acetonitrile/water combinations tested (Table 1, entries 13–15) outperformed pure acetonitrile. On the other hand, when irradiation was performed with different solvents such as DMF, DMA, DMSO, acetone, ethyl acetate, or methylene chloride (Table 1, entries 18–23), the results did not improve the formation of **3a** in comparison of that reported in entry 4. Control experiments revealed that, in the absence of light (Table 1, entry 24) or biacetyl (Table 1, entry 25), the reaction did not proceed, and under air atmosphere (Table 1, entry 26), only traces (2%) of **3a** were detected. Therefore, optimal conditions involved acceptable loading reagents (3 equiv of both **2a** and **BA**), with irradiation in the visible range at 440–470 nm with blue LEDs in MeCN for 24 h under anaerobic conditions. This output was found to be comparable to that obtained with other strategies [29], despite the lower addition of trapping agent (**2a**). In the presence of TEMPO as a radical scavenger, yields of **3a** drastically dropped to less than 1%.

### 3.2. Optimization of the Reaction Conditions in Gel Media

The use of an anaerobic atmosphere was crucial for obtaining **3a** in homogeneous solvent. To overcome this requirement and take advantage of previous research using supramolecular viscoelastic gels [30,35–37], we decided to investigate the reaction using a gel medium as a photonanoreactor. Thus, based on the gelator, we tested different gels such as G1 (*tert*-butyl-(*S*)-(1,5-bis(octadecylamino)-1,5-dioxopentan-2-yl)carbamate), G2 (using *N,N'*-((1*S*,2*S*)-cyclohexane-1,2-diyl)didodecanamide), and G3 (obtained from (1*R*)-1-((4*R*,8*aS*)-2,6-diphenyltetrahydro-[1,3]dioxino [5,4-*d*][1,3]dioxin-4-yl)ethane-1,2-diol) to determine whether they could provide a protective environment against oxygen, thereby enabling the synthesis of **3a** under open-air conditions. The chemical structures of the gelators used to prepare gels G1, G2, and G3, along with images of each gel, are shown in Figure 4.

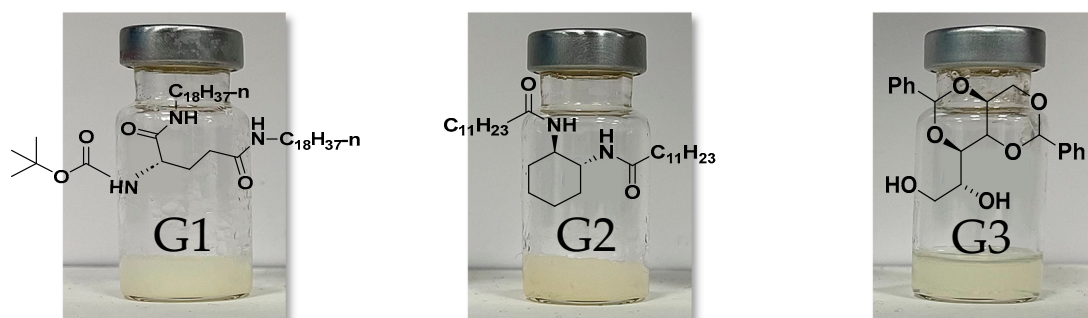


**Figure 4.** Chemical structures of the gelators employed for obtaining gels **G1**, **G2**, and **G3** and images of the gels.

For irradiation with G1, 10 mg of the corresponding gelator was first dissolved in 2 mL of solvent, and then **1a**, **2a**, and **BA** were added at different molar ratios (Table 2) to determine the optimal reaction conditions. All the experiments were performed under an aerobic atmosphere.

**Table 2.** Formation of triarylethylene **3a** mediated by visible-light photoredox catalysis using biacetyl in a gel protective microenvironment <sup>a</sup>.

| Entry | Solvent | Time (h) | 2 (equiv) | BA (equiv) | Yield (%) <sup>b</sup> |
|-------|---------|----------|-----------|------------|------------------------|
| 1     | MeCN    | 4        | 50        | 8          | 48                     |
| 2     | DMF     | 4        | 50        | 8          | 35                     |
| 3     | DMA     | 4        | 50        | 8          | 26                     |
| 4     | AcOEt   | 4        | 50        | 8          | 38                     |
| 5     | Acetone | 4        | 50        | 8          | 43                     |
| 6     | DMSO    | 4        | 50        | 8          | 14                     |
| 7     | MeCN    | 8        | 50        | 8          | 65                     |
| 8     | MeCN    | 24       | 50        | 8          | 87                     |
| 9     | MeCN    | 24       | 25        | 8          | 83                     |
| 10    | MeCN    | 24       | 20        | 8          | 83                     |
| 11    | MeCN    | 24       | 15        | 8          | 82                     |
| 12    | MeCN    | 24       | 15        | 2          | 70                     |
| 13    | MeCN    | 24       | 15        | 3          | 74                     |
| 14    | MeCN    | 24       | 15        | 4          | 74                     |
| 15    | MeCN    | 24       | 10        | 3          | 71                     |
| 16    | MeCN    | 24       | 5         | 3          | 24                     |
| 17    | MeCN    | 24       | 1         | 3          | n.d.                   |
| 18    | MeCN    | 24       | 10        | 3          | 66                     |
| 19    | MeCN    | 24       | 10        | 3          | 61                     |

<sup>a</sup> Reaction conditions: [**1a**] = 3.2 mg, 0.02 mmol, [gelator] = 5.5 mg/mL for G1 (entries 1–17), 5 mg/mL for G2 (entry 18) and 40 mg for G3 (entry 19),  $V_{\text{MeCN}} = 2$  mL,  $T = 20$  °C, air, LED  $\lambda_{\text{exc}} = 457$  nm; <sup>b</sup> **1a** conversion determined by GC using dodecanenitrile (4.4  $\mu$ L, 0.02 mmol) as an internal standard (100% selectivity).

In the first attempt, irradiation of **1a** in the presence of a large excess of **2a** (50 equiv) and **BA** (8 equiv) was employed, using different solvents such as MeCN, DMF, DMA, AcOEt, acetone, or DMSO (Table 2, entries 1–6). The highest yield, assessed by FID-GC, was found to be in MeCN; therefore, we selected this solvent to optimize the reaction conditions. When the irradiation time increased to 8 h (Table 2, entry 7), the yield increased to 65%, and after 24 h of exposure to blue light, 87% **3a** was obtained (Table 2, entry 8). The following experiments were thus performed by irradiating MeCN for 24 h, varying the equivalents of **2a** and **BA**. When 25, 20, or 15 equivalents of **2a** were used in the presence of 8 equivalents of **BA** (Table 2, entries 9–11), the yield slightly decreased to 82–83%. When the amount of **2a** was fixed at 15 equivalents and that of **BA** was 2, 3, or 4 equivalents, a reduction in **3a** yield (70–74%, Table 2, entries 12–14) was observed. When 10 equivalents of **2a** or 3 equivalents of **BA** were maintained, 71% yield of **3a** was obtained (Table 2, entry 15). Finally, reducing the amount of **2** to 5 and 1 equivalents resulted in lower yields of **3a** (entries 16 and 17). The use of G2 or G3 (Table 2, entries 18 and 19, respectively) instead of G1 (while keeping the same conditions as entry 15) did not improve the formation of **3a**. From these results, the optimal conditions using gel medium implied G1, 24 h irradiation, 10 equivalents of **2a**, and 3 equivalents of **BA**.

The properties of the gel media upon doping with the reactant and the effect of the irradiation were established by standard characterization techniques including determination of the *gel-to-sol* transition temperature ( $T_{\text{gel}}$ ), oscillatory rheology, scanning and transmission electron microscopy, and atomic force microscopy (see Section 2 and Supplementary Materials pp. S24–S30). Briefly, oscillatory rheological studies (i.e., DFS, DSS,

and DTS measurements) confirmed the conservation of the gel nature over time and during irradiation. The collapse of all gels took place around 35–45% strain, indicating a good tolerance of the materials to external mechanical forces. In general, the storage modulus  $G'$  was approximately one order of magnitude higher than the loss modulus  $G''$  within the linear viscoelastic regime for all samples. Furthermore, although the *gel-to-sol* transition temperature ( $T_{\text{gel}} = 63 \pm 2$  °C) was not affected by the inclusion of the reactants (Figure S35), the  $\tan \delta$  value increased slightly after doping the gel with the reactants (Figures S36–S38), suggesting destabilization of the network to some extent. However, the irradiation of the samples did not cause any significant detriment in the mechanical damping properties of the gels. In terms of morphological properties, the preservation of the main fibrillar features of the gels, and the absence of artifacts, were confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), with smallest features in the range of ca. 35 nm width and 45 nm height (Figures S39–S47).

### 3.3. Scope of the Reaction

Using the selected optimized conditions, we examined the scope of the reaction, both in solution and in gel medium. These conditions corresponded to the following parameters: **1** (0.02 mmol), **2** (0.06 mmol), **BA** (0.06 mmol), MeCN (2 mL),  $\lambda_{\text{exc}} = 457$  nm (blue LEDs),  $t = 24$  h,  $T = 20$  °C, Ar atmosphere for experiments in the absence of gel; in contrast, in heterogeneous media, the conditions were **1** (0.02 mmol), **2** (0.20 mmol), **BA** (0.06 mmol), **G1** (10 mg), MeCN (2 mL),  $\lambda_{\text{exc}} = 457$  nm (blue LEDs),  $t = 24$  h,  $T = 20$  °C, air.

Thus, several five-membered ring heteroarene halides, were used to be coupled with different 1,1-diphenylethene derivatives (Figure 5, where yields in the absence or presence of **G-1** are indicated in black or blue, respectively). The corresponding heteroarene halides comprised substituted thiophenes (with acetyl, propionyl, (2-methyl) propionyl, formyl, benzyl, methyl formate, cyano, and bromine substituents, products **3a–3h**), furans (with acetyl, formyl, methyl formate, or cyano substituents; compounds **3i–3l**), selenophene (**3m**), and thioimidazole (**3n**). In addition, ring-substituted diphenyl ethylenes were also found to be suitable starting materials for the reaction (final products **3o** and **3p+3p'**). In the case of asymmetric 1-(4-chlorophenyl)-1-phenylethylene, two products were isolated, namely **3p** and **3p'**, since formation of *cis*- and *trans*- isomers is possible; due to the similarity of the NMR spectra of both compounds, it was difficult to clearly distinguish between the two geometrical isomers, and the overall yield is provided.

Comparing the reactions in acetonitrile solution and in supramolecular gel media revealed key differences. In solution, high yields were achieved, but only under strict inert conditions, making scalability challenging. Oxygen interference was a major limitation. In contrast, the gel-based reactions proceeded smoothly even in the presence of air. Additionally, gel stability suggests potential for recyclability, making it a more sustainable option. While solution-phase reactions work well under controlled conditions, the gel-based approach offers a more practical and scalable alternative for photoredox catalysis under ambient conditions.

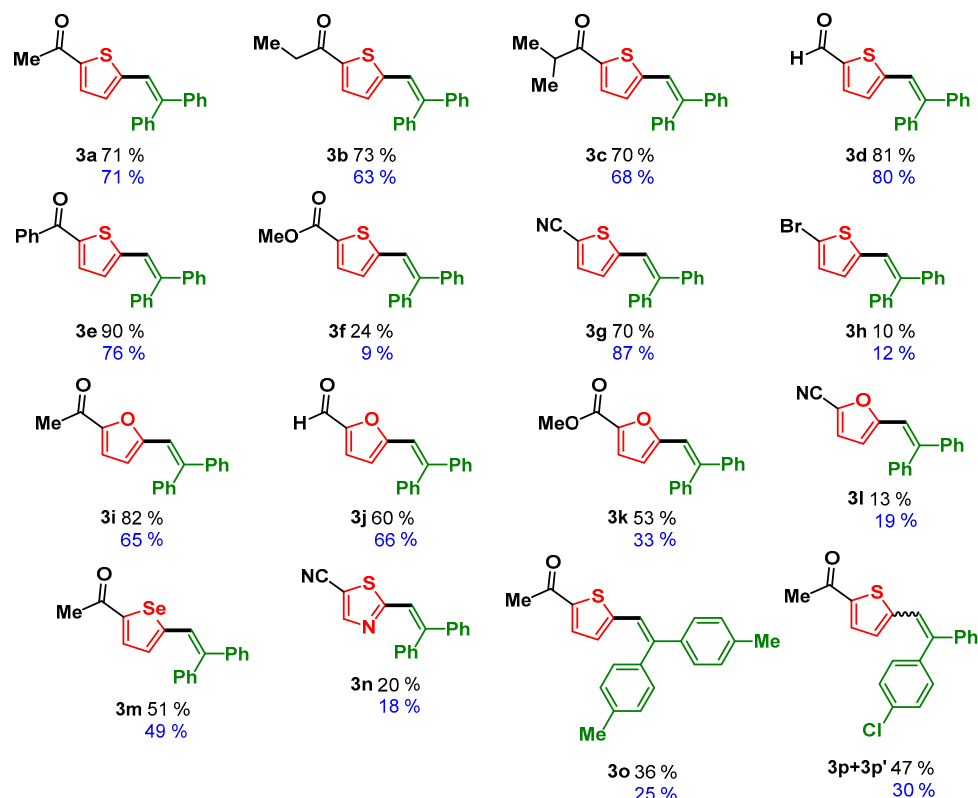


**Figure 5.** Chemical structures of the TAEs synthesized in this work and the yields obtained using the optimized conditions in solution (black) and in gel media (blue).

### 3.4. Laser Flash Photolysis Experiments

To gain insight into the reaction mechanism, laser flash photolysis (LFP) experiments on the microsecond timescale were performed. Hence, a solution of **BA** (0.03 M in MeCN) was excited at  $\lambda_{\text{exc}} = 450$  nm under a  $\text{N}_2$  atmosphere. The spectrum recorded 1  $\mu\text{s}$  after the laser pulse displayed a band with a maximum at  $\lambda = 320$  nm (Figure 6a), which was attributed to the **BA** triplet excited state ( $^3\text{BA}^*$ ), formed with high efficiency, in agreement with the intersystem crossing quantum yield value reported in the literature (ca. 1) [38]. As expected, no transient species were detected when we performed LFP experiments on solutions containing only **1a** or **2a**, as these compounds do not absorb light in the blue region (Figure 3).

Next, the  $^3\text{BA}^*$  decay traces were recorded after the addition of increasing amounts of **2a** to a **BA** solution (0.03 M). A clear quenching of  $^3\text{BA}^*$  was observed, as evidenced by a shortening of the triplet lifetime with increasing amounts of **2a** (Figure 6b). Based on the literature data, triplet energies of **BA** and **2a** are 2.38 eV [39] and 2.57 eV, [40], respectively. Thus, triplet–triplet energy transfer from  $^3\text{BA}^*$  to  $^3\text{2a}^*$  is not thermodynamically feasible. Therefore, the quenching observed agrees with a single electron transfer (SET) process from **2a** to  $^3\text{BA}^*$ , leading to ionic species  $\text{2a}^{+\bullet}$  and  $\text{BA}^{-\bullet}$ . The free energy changes ( $\Delta G_{\text{ET}}$ ) associated with this SET has been found to be an exergonic process ( $\Delta G_{\text{ET}} = -1.5$  kcal/mol), according to the Weller equation [41]. Under these conditions, estimation of the **BA** triplet lifetime value ( $\tau_{\text{T}}$ ) is complex; even in the absence of **2a**, it adequately fits to a sum of two single exponential functions. A longer-lived component of 44  $\mu\text{s}$  and a shorter-lived component of 18  $\mu\text{s}$  were obtained with relative amplitudes of 0.60 and 0.40, respectively. This lifetime heterogeneity in homogeneous MeCN solution precluded the quantitative application of the Stern–Volmer equation,  $I_0/I = \tau_0/\tau = 1 + k_q\tau_0[\text{Q}]$ , to obtain the electron transfer rate constant between **BA** and **2a**. We note that using the steady-state photolumines-

cence intensity quenching data produces a linear Stern–Volmer plot (Figures S48 and S49 on p. S31) with  $K_{sv} = k_q\tau_0 = 2676 \text{ M}^{-1}$ .

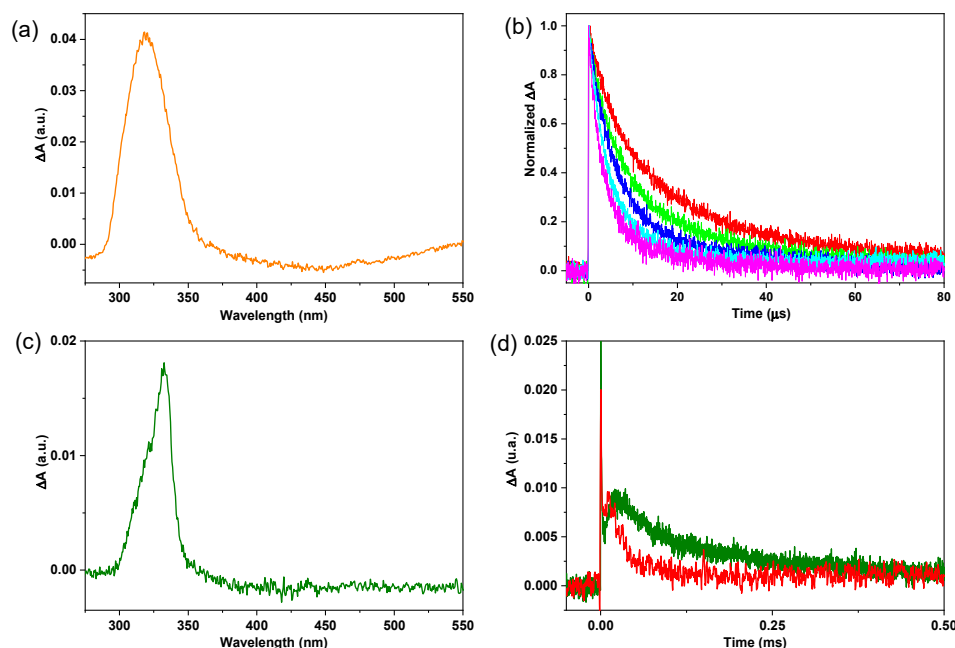


**Figure 6.** Laser flash photolysis experiments ( $\lambda_{exc} = 450 \text{ nm}$ , MeCN/ $\text{N}_2$ ). (a): Transient absorption spectrum of **BA** (0.03 M) recorded at 1  $\mu\text{s}$ , with maxima at  $\lambda = 320 \text{ nm}$ ; (b): quenching of  $^3\text{BA}^*$  (**BA** 0.03 M) monitored at  $\lambda = 320 \text{ nm}$  in the presence of different concentrations of **2a**: 0 mM (red), 0.6 mM (green), 1.2 mM (dark blue), 1.8 mM (pale blue), and 2.4 mM (magenta); (c) transient absorption spectrum of a mixture of **BA** (0.03 M) and **2a** (0.03 M) obtained 45  $\mu\text{s}$  after the laser pulse, with maxima at  $\lambda = 332 \text{ nm}$ ; (d) kinetic traces monitored at  $\lambda = 332 \text{ nm}$  for a mixture of **BA** (0.03 M) and **2a** (0.1 M), in the absence (green) or presence (red) of **1a** (0.003 M).

The transient absorption spectrum of a mixture of **BA** (0.03 M) and **2a** (0.03 M) in MeCN/ $\text{N}_2$  showed a band with a maximum at  $\lambda = 332 \text{ nm}$  (Figure 6c) at 45  $\mu\text{s}$  after laser pulse. This was assigned to the radical  $2a^\bullet$  based on the literature data [42], since this species is likely formed within the reported time scale via  $2a^{+\bullet}$  deprotonation. In another experiment, LFP measurements were performed using a mixture of **BA** (0.03 M), **2a** (0.1 M), and **1a** (0.003 M) (again at  $\lambda_{exc} = 450 \text{ nm}$  in MeCN/ $\text{N}_2$ ). In this way, quenching of the kinetic trace of  $2a^\bullet$  was observed (Figure 6d), revealing a plausible SET process from  $2a^\bullet$  to **1a**, leading to the formation of  $2\text{-H}^+$  and  $1a^\bullet$ . The coupling of these two radicals ultimately leads to **3a**.

### 3.5. “Light–Dark” Experiments

To demonstrate the necessity of light for coupling **1a** with **2a** in the presence of **BA**, a “light/dark” experiment was performed using standardized reaction conditions in an MeCN solution (Table 1, entry 3). The reaction clearly advanced when blue light irradiation was used, whereas no formation of **3a** occurred when the irradiation source was switched off (Figure 7). This result unequivocally indicated that visible light is essential for the reaction; however, it did not definitively exclude a radical-chain mechanism. To rule out this possibility, the reaction quantum yield was determined following the methodology described in Equation (1), where the mol of the formed product was  $0.014 \times 10^{-3}$  (determined by GC-FID using 1-dodecanenitrile as an internal standard), the photon flux at 457 nm was determined to be  $9.38236 \times 10^{-9} \text{ Es}^{-1}$ , following the ferrioxalate actinometry method described in the Supplementary Materials (p. S32),  $t$  was the irradiation time (86,400 s),

and  $f$  was 0.238. In this way, the obtained value for the reaction quantum yield ( $\phi$ ) was 0.07, clearly excluding a radical-chain mechanism.

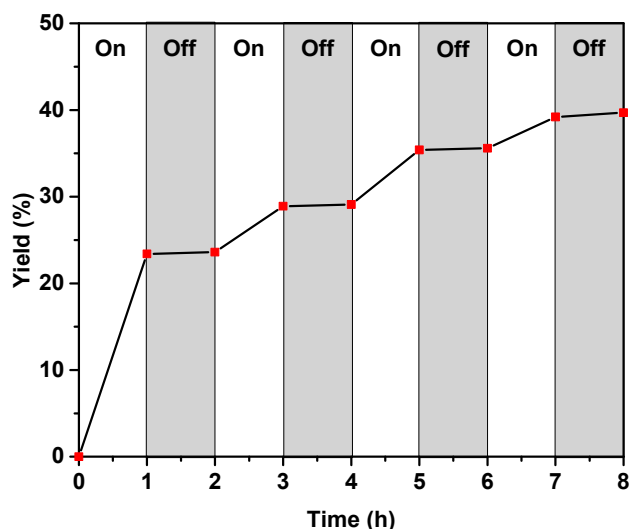


**Figure 7.** Light/dark experiments for coupling between **1a** and **2a** in the presence of **BA** as photoinitiator.

#### 4. Discussion

The results obtained in this work demonstrate the efficiency and versatility of visible-light photoredox catalysis using biacetyl (**BA**) as a low-cost photosensitizer for the formation of triarylethylenes (TAEs). The optimization of the reaction conditions revealed that acetonitrile is the most suitable solvent for achieving high yields under homogeneous conditions, supporting its role in facilitating electron transfer processes. The reaction was dependent on the presence of **BA** and light irradiation, as evidenced by control experiments where the absence of either component resulted in negligible product formation. Variations in the number of **BA** and 1,1-diphenylethylene equivalents directly influenced the reaction efficiency.

The investigation of the reaction kinetics and selectivity in supramolecular gel media provided significant insights into the impact of a microheterogeneous environment. Among the tested gels, G1 exhibited the highest performance, enabling the reaction to proceed efficiently even under aerobic conditions. This protective microenvironment prevented not only quenching of  $^3\text{BA}^*$ , but also oxidative side reactions, such as benzophenone formation, therefore modulating the reaction kinetics. Additional characterization through scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) revealed morphological differences between undoped and doped gels, suggesting structural adaptation upon interaction with the reaction components.

A plausible reaction mechanism is depicted in Figure 8. The involvement of SET processes as well as the presence of transient species such as  $^3\text{BA}^*$  and  $2\text{a}^\bullet$  is supported by transient absorption spectroscopy measurements (Figure 6). Employment of TEMPO as a radical scavenger confirmed the presence of radical species (Table 1, entry 27). Furthermore, a radical chain pathway can be ruled out from the “light-dark” experiments (Figure 7). Concerning **BA** restoring, a redox reaction between  $\text{BA}^{\bullet-}$  and  $\text{H}^+$  would be thermodynamically allowed according to the  $E_{\text{red}}$  values ( $E_{\text{red}}(\text{BA}) = -1.015 \text{ V vs SHE}$ ) [43]. The observed solvent effects and the impact of gel matrices indicate that the stabilization of charge-separated intermediates plays a crucial role in dictating the reaction efficiency. Overall, **BA** undergoes efficient photoexcitation, generating an excited state capable of initiating a Mizoroki–Heck-type coupling.

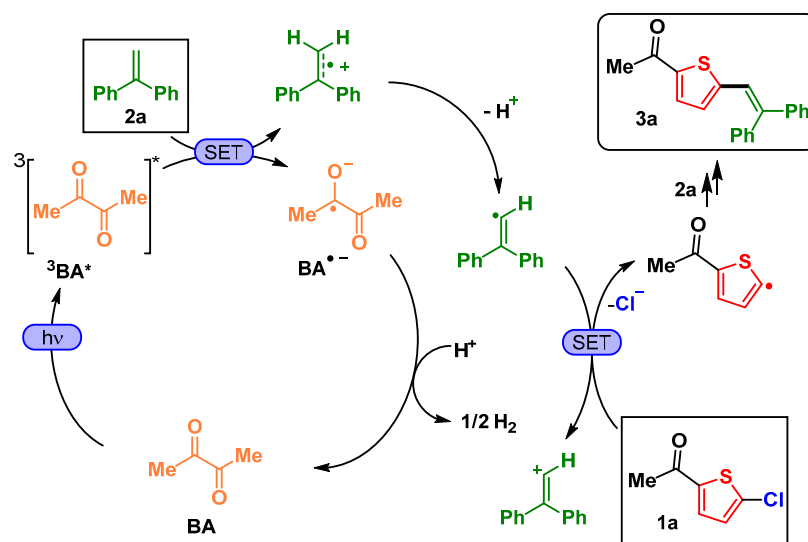


**Figure 8.** Plausible mechanism for the synthesis of TAEs using **BA** as photosensitizer.

The influence of substituents on aryl halides and heterocycles was systematically examined, revealing that electron-withdrawing groups enhance reactivity by facilitating the oxidative addition step. The electronic nature of these substituents dictates the rate of the reaction, with strongly electron-deficient systems exhibiting faster conversion rates than their electron-rich counterparts.

Comparative analysis of different reaction conditions highlighted the advantages of conducting the transformation in gel media. For instance, the selectivity and yield improvements observed in the gel-based system under aerobic conditions demonstrate its potential as a green and scalable alternative for photoredox catalysis. The ability of the gel matrix to regulate oxygen permeability further enhances its practical applicability, reducing the need for an inert atmosphere without compromising the reaction efficiency. The long-term stability of the gels was also evaluated, revealing minimal degradation over extended reaction times, which underscores their suitability for repeated use in synthetic applications.

Additionally, quantum yield measurements provided further validation of the efficiency of **BA** as a photosensitizer. The reaction exhibited a moderate quantum yield, confirming the effective utilization of absorbed photons in promoting the desired transformation. The sustainability aspect of this methodology was also considered, as the use of **BA** presents an attractive alternative to expensive and toxic transition-metal catalysts commonly employed in photoredox reactions. The facile availability and low cost of **BA**, combined with its efficient energy transfer properties, reinforce its potential for broader applications in visible-light-mediated organic transformations.

## 5. Conclusions

Overall, this research highlights the practical advantages of employing **BA** as a cost-effective photosensitizer for visible-light-mediated transformations. The combination of photoredox catalysis with supramolecular gel media opens new avenues for the development of environmentally friendly methodologies, with promising applications in organic synthesis and materials science. The ability to conduct reactions under mild conditions, coupled with the tunable nature of gel systems, presents a robust strategy for expanding the scope of photoredox transformations. Given the promising results, further studies will be performed to explore the applicability of this system to other photochemical transformations, as well as the possibility of further refining gel formulations to optimize reaction rates.

and selectivity. By bridging the fields of photoredox catalysis and soft material chemistry, this work paves the way for innovative approaches in sustainable organic synthesis.

**Supplementary Materials:** The following Supplementary Materials can be downloaded at <https://www.mdpi.com/article/10.3390/photochem5020013/s1>. Spectroscopic characterization of compounds **3a–3p** (pp. S2–S6), <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of compounds **3a–3p** (Figures S1–S34, pp. S7–S23), *T*<sub>gel</sub> values (Figure S35 on p. S24), oscillatory rheology (Figures S36–S38 on p. S25), scanning electron microscopy (SEM) images (Figures S39–S41 on pp. S26–S27), transmission electron microscopy (TEM) images (Figures S42–S44 on pp. S28–S29), atomic force microscopy (AFM) images (Figures S45–S47 on p. S30), Stern–Volmer analysis (Figures S48 and S49 on p. S31) experimental procedures for determining the photon flux at 457 nm via ferrioxalate actinometry (p. S32) [44,45].

**Author Contributions:** Conceptualization, R.P.-R., D.D.D. and M.C.J.; methodology, R.P.-R. and D.D.D.; software, D.Á.-G.; validation, D.Á.-G. and P.D.D.; formal analysis, M.C.J., R.P.-R. and D.D.D.; experimental work, D.Á.-G. and P.D.D.; data curation, D.Á.-G. and P.D.D.; writing—original draft preparation, M.C.J.; writing—review and editing, M.C.J., D.D.D. and R.P.-R.; M.C.J., D.D.D. and R.P.-R. project administration; M.C.J., R.P.-R. and D.D.D. funding acquisition. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare that they have no conflicts of interest.

## Abbreviations

The following abbreviations are used in this manuscript:

|                         |                                                                                                                                 |
|-------------------------|---------------------------------------------------------------------------------------------------------------------------------|
| AcOEt                   | Ethyl acetate                                                                                                                   |
| AFM                     | Atomic Force Microscopy                                                                                                         |
| BA                      | Biacetyl                                                                                                                        |
| DFS                     | Dynamic Frequency Sweep                                                                                                         |
| DMA                     | Dimethylacetamide                                                                                                               |
| DMF                     | Dimethylformamide                                                                                                               |
| DMSO                    | Dimethyl sulfoxide                                                                                                              |
| DSS                     | Dynamic Strain Sweep                                                                                                            |
| DTS                     | Dynamic Time Sweep                                                                                                              |
| G1                      | <i>Tert</i> -butyl-( <i>S</i> )-(1,5-bis(octadecylamino)-1,5-dioxopentan-2-yl)carbamate                                         |
| G2                      | <i>N,N'</i> -((1 <i>S</i> ,2 <i>S</i> )-Cyclohexane-1,2-diyl)didodecanamide                                                     |
| G3                      | (1 <i>R</i> )-1-((4 <i>R</i> ,8 <i>aS</i> )-2,6-Diphenyltetrahydro-[1,3]dioxino[5,4- <i>d</i> ][1,3]dioxin-4-yl)ethane-1,2-diol |
| MeCN                    | Acetonitrile                                                                                                                    |
| SEM                     | Scanning electron microscopy                                                                                                    |
| SET                     | Single electron transfer                                                                                                        |
| TAE                     | Triarylethylene                                                                                                                 |
| <i>T</i> <sub>gel</sub> | <i>Gel-to-sol</i> transition temperature                                                                                        |
| TEM                     | Transmission Electron Microscopy                                                                                                |
| ULL                     | Universidad de La Laguna                                                                                                        |
| UPV                     | Universitat Politècnica de València                                                                                             |

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