



## Short communication

## Design of novel photobase generators upon violet LEDs and use in photopolymerization reactions



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## ABSTRACT

Two new near-UV and visible-light-sensitive photobase generators (PBGs) are synthesized and investigated. They are built on a near-UV and visible light sensitive (*E*)-3-(2,2'-bithiophen-5-yl)-2-cyanoacrylic acid chromophore and a latent strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Upon irradiation, decarboxylation occurs and the base is released. The anionic curing of epoxy/thiol as well as thiol/divinylsulfone formulations in the presence of these PBGs under LEDs at 385 and 405 nm is studied. More than 60% of conversion of the thiol and epoxy functions is achieved upon LED@385 nm without any post baking.

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## 1. Introduction

In the field of photochemical processes and photopolymerization reactions, the use of acid catalyzed processes is already well known and well established [1]. For example, different photoacid generators (PAGs) (e.g. iodonium salts, sulfonium salts, non salt compounds ...) are already commercially available but also used in high tech applications (photolithography, 3D printing ...) [2]. Several researches and a huge amount of work have been carried out for the use of base catalyzed processes and different photobase generators (PBGs) were already proposed [3–23]. These PBGs can be very suitable for the curing of resins that are not easily accessible by other processes (e.g. epoxy/thiol). However, many of them remain restricted to UV light and can more hardly be used with near-UV or visible Light Emitting Diodes (LED).

In fact, the photochemical process of the base release under near-UV or visible LED and/or soft irradiation conditions is still the subject of huge research efforts and elegant works have been

already reported [8–20]. As pointed out in earlier studies, visible PBGs must have nowadays a progressing need to push the boundaries of UV-ones to longer excitation wavelengths. Indeed, near UV or visible PBG upon LED could be a useful tool to overcome the problems of UV lamp's toxicity, reduce the energy employed for the reaction and have a high curing depth [9]. Photobase generators concept can be based on a decarboxylation reaction that generates the reactive base to initiate the polymerization. Therefore, an efficient initiation process can particularly depend on the decarboxylation to enhance the photolysis quantum yield.

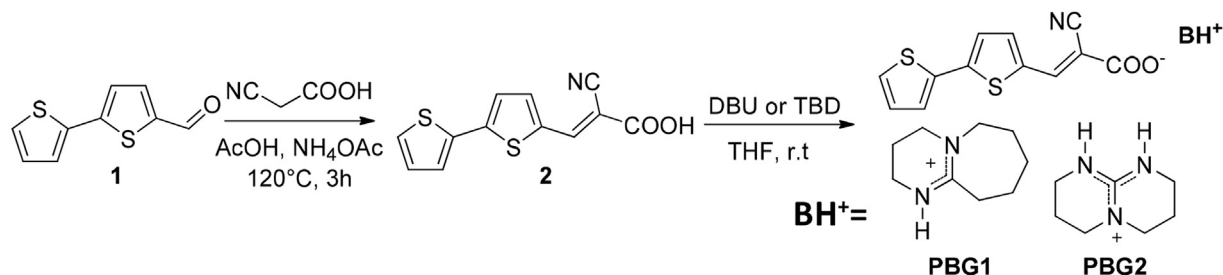
Different organic derivatives were already elegantly used as PBGs such as *o*-nitroaryl carbamate derivatives [4], [(*o*-nitroaryl)oxy] carbonyl [5], *N*-{[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl}-2,6-dimethylpiperidine [6], 7-hydroxy-4-methyl coumarin [10], curcumin [11], xanthinol [12], bicyclic guanidium tetraphenylborate where a strong 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) base [7] is generated [13], but also others [14–20]. For the use of PBGs, high light intensity and higher irradiation time than for classical radical polymerization are often required. Many other compounds have been also reported in the literature as efficient PBGs based on a decarboxylation reaction [21–23].

In the present paper, we propose novel PBGs i. e. (*E*)-3-(2,2'-bithiophen-5-yl)-2-cyanoacrylic acid as a chromophore associated with a latent strong base such as 1,8-diazabicyclo[5.4.0]undec-7-

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Scheme 1. Synthesis of PBG1 and PBG2.

ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). The resulting photobases PBG1 and PBG2 are shown in Scheme 1. A good to excellent near-UV or violet-blue light absorption is expected as well as a suitable initiation of the photopolymerization of epoxy/thiol or divinylsulfone/thiol resins upon exposure to violet LEDs (LED @ 385 nm or LED @ 405 nm).

## 2. Experimental part

### 2.1. FTIR procedure

The conditions of photopolymerization experiments are given in the figure captions. The photosensitive formulations were deposited (100  $\mu\text{m}$  thick) between two polypropylene films for irradiation with the LEDs. The evolution of the epoxy group content of EPOX, the thiol content of the Trithiol and the vinyl ether content of DVS were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about  $790\text{ cm}^{-1}$  [24],  $2570\text{ cm}^{-1}$  [25] and  $3100\text{ cm}^{-1}$  [9], respectively.

The final conversions can be evaluated from the area of these peaks according to:

$$\text{Conv}(\%) = (A_0 - A_t) / A_0 * 100$$

Where  $A_0$  and  $A_t$  stand for the area of the peak before irradiation and at a given time  $t$ , respectively.

### 2.2. UV-vis spectroscopy

UV-Vis experiments were performed using a UV-Vis spectrophotometer (JASCO V730). Sample solutions were analyzed in quartz cuvettes with 1 cm path length. Data was collected in absorbance mode with a bandwidth of 1 nm and a scan speed of 400 nm/min.

### 2.3. Other chemicals

The synthesis of PBG1 and PBG2 is described in detail below. EPOX, Divinylsulfone and trithiol were obtained from Sigma-Aldrich and used with the best purity available.

## 3. Results and discussion

### 3.1. Synthesis of PBG1 and PBG2

The photobases were obtained efficiently in two steps from 2,2'-bithiophene-5-carbaldehyde **1** as depicted in Scheme 1. All the synthesis are fully described in Supporting information. The first step was a Knoevenagel condensation between compound **1** and 2-cyanoacetic acid to give (*E*)-3-(2,2'-bithiophen-5-yl)-2-

cynoacrylic acid **2**. Then, compound **2** was mixed with either DBU or TBD in THF to furnish PBG1 or PBG2 respectively. It should be noticed that these photobases are thermally stable in solution i.e. heating a solution of PBG2 in deuterated DMSO at  $100\text{ }^\circ\text{C}$  for 2 h didn't lead to any changes in the proton NMR spectra.

### 3.2. Photolysis and photochemical reactivity of PBG1 and PBG2

PBG1 and PBG2 strongly absorb in the 350–450 nm range (Fig. 1). This property is very useful for the use of near-UV, violet or blue LEDs with a good matching between the absorption spectrum of the PBG and the emission spectrum of the source. Both PBG1 and PBG2 exhibit high molar extinction coefficients i.e.  $38100$  and  $43100\text{ M}^{-1}\text{ cm}^{-1}$  at their maximum absorption wavelength (387 nm for both of them).

The frontier orbitals (Highest Occupied Molecular Orbital HOMO and Lowest Unoccupied Molecular Orbital LUMO) associated with the lowest energy transition were calculated at UB3LYP/6-31G\* level (Fig. 1B). A participation of the electron rich carboxylate moiety can clearly be observed for the HOMO while the LUMO is delocalized over the entire  $\pi$  system. Accordingly, for the decarboxylated form (noted **C2** in Scheme 2) a different UV-vis spectrum is expected (see below for the photolysis experiments). The calculated UV-vis absorption spectrum is in excellent agreement with the experimental one (Fig. 1 A vs. B).

Samples containing  $2.4 \times 10^{-6}\text{ M}$  of PBG1 and  $10^{-5}\text{ M}$  of PBG2 were prepared in methanol and then irradiated with a LED@385 nm (Intensity =  $500\text{ mW cm}^{-2}$ ) for 5, 20 and 60 min. The UV-vis spectra were taken after each irradiation time. Interestingly, a clear and significant photolysis is found for both PBG1 and PBG2 (Fig. 2A): the maximum absorption wavelength  $\lambda_{\text{max}}$  is shifted from 390 nm (before irradiation) to 369 nm (after 60 min of irradiation). No isobestic point was observed in the photolysis of PBG1 or PBG2. In Fig. 2B, the UV visible absorption spectrum of the decarboxylated form of PBG1 or PBG2 (noted **C2** in Scheme 2) is very similar to those of the photoproduct generated after photolysis of PBG1 or PBG2 showing that a decarboxylation of the chromophore moiety occurs (see also the FTIR results below). This photoproduct cannot be ascribed to the *Z*-isomer generated after a photoisomerization process (Scheme 3) i.e. the *Z* and *E* forms exhibiting rather similar absorption spectra, no significant change of the maximum absorption wavelength would be expected in photolysis experiments if only photoisomerization occurs.

No isobestic point has been observed in the UV-vis measurements for the photodecomposition behavior of PBG1 or PBG2. This can be ascribed to the decarboxylation reaction that is in competition/parallel to the photoisomerization reaction leading to different photoproducts.

The yield of photolysis determined using the procedure given in Ref. [7] is  $\sim 0.04$  for PBG1. This value can be compared to that

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