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Letter

BODIPY-Based Photoacid Generators for Light-Induced Cationic Polymerization

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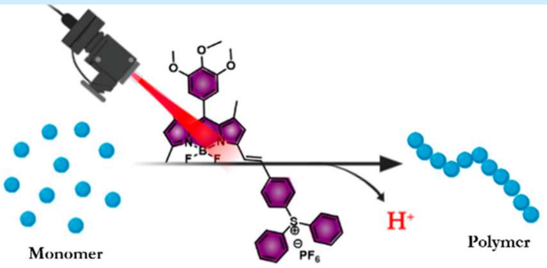
ABSTRACT: Photoacid generators (PAGs) are organic compounds that can generate protons (H^+) upon irradiation with certain wavelengths of light. In this work, we designed and synthesized the first BODIPY-based PAGs with D−A and D−π−A conjugation structures and achieved green and red LED light-induced acid generation. By the use of red-light absorbance, red-LED-triggered cationic polymerization was demonstrated as a proof-of-concept application of these PAGs.



Photoacid generators (PAGs) are light-sensitive organic compounds that produce H^+ upon exposure to certain wavelengths of light. Since the initial studies of PAGs from the 1970s, they have gained enormous interest because of their ability to generate Brønsted superacids in a light-guided way.[1] Using light to activate the formation of H^+ has numerous applications in industry, such as photoinitiation for polymerization,[2,3] lithography,[4] and protecting group chemistry.[5] Furthermore, PAGs recently have been used in biology, including controlling enzyme activity,[6] oxygen inhibition,[7] and photodynamic therapy.[8] Because of their broad applications, many PAGs have been designed, and the area has undergone major shifts with a sharp increase in the number of available PAGs. Aryldiazonium, diaryliodonium, triarylsulfonium, and triarylphosphonium salts have been synthesized for use as PAGs, and their photochemistry has been investigated.[9] For example, triarylsulfonium salts with complex halide anions ($X^- = BF_4^-, PF_6^-$) comprise a class of highly efficient PAGs.[10] Upon light absorption, the sulfonium salts can be excited to the singlet surface, where the excited species (C−S bond) fragments via homolytic cleavage to give a phenyl radical and diphenylsulfinyl radical pair or heterolytic cleavage to give phenyl cation and diphenyl sulfide.[1,11] Consequently, these species undergo secondary reactions, such as radical coupling or H transfer, to produce H^+ (Figure 1a). A main advantage of sulfonium salts is their ability to trigger rapid electron transfer that leads to stable cations and strong acids upon photodissociation.

To date, most of the available PAGs need high-energy (UV to blue) irradiation to generate H^+, which limits their applications, especially in biology, because of the high photon energy and scattering.[9] Though several two-photon PAGs have been reported, conventional PAGs exhibit low two-photon absorption cross sections.[9] Therefore, recent works in the field have focused on developing PAGs that can be excited at longer wavelengths in the visible region. Several sulfonium PAGs have been reported with extended absorption in the blue window, using the approach of conjugating sulfonium salts with various visible-light-absorbing chromophores.[12] For example, Jin et al.[13] and De Waele et al.[14] developed several π-conjugated donor−π−acceptor (D−π−A) sulfonium salts by introducing electron-donating groups at the *para* position of the sulfonium salt (Figure 1b).[15] In addition, Belfield et al.[16,17] conjugated highly thermally and photochemically stable fluorene with sulfonium and formed A−π−A (Figure 1c) and A−π−π−A (with two sulfonium moieties on the fluorene) PAGs. Though these conjugations red-shifted the one-photon absorption wavelengths to some extent, they are still far from green or

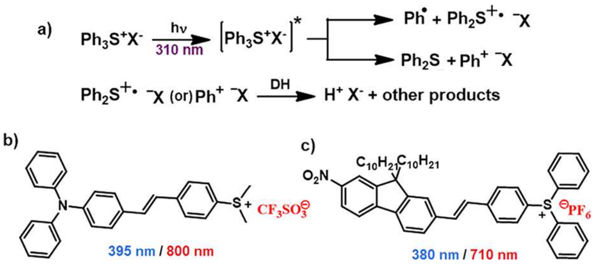


Figure 1. (a) Photolysis mechanism of triarysulfonium-salt-based PAGs (DH = donor of hydrogen) and (b, c) examples of reported PAGs with (b) styryl and (c) fluorene chromophores and their one-photon (blue) and two-photon (red) absorption wavelengths.

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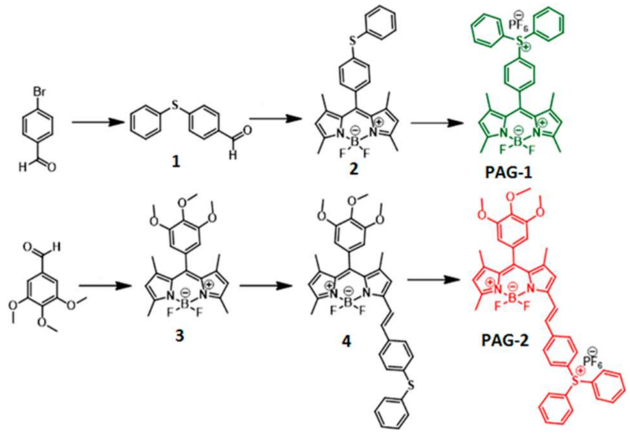
even red, and the design of compounds with satisfying activity in the visible range remains an open challenge.

Boron dipyrromethene (BODIPY) chromophores have promising optical properties, such as high fluorescence quantum yields, large molar extinction coefficients, and narrow emission bands, as well as flexible chemical structures.[18−20] On the basis of previous knowledge,[21−23] we designed PAGs using a BODIPY chromophore as the donor and triarylsulfonium as the acceptor. Here we report the synthesis, characterization, and photophysical and photochemical properties of BODIPY-based **PAG-1** (D−A) and **PAG-2** (D−π−A). We studied the acid-generating ability of the newly synthesized PAGs upon irradiation with green and red LEDs, respectively.

In general, photoinduced polymerization is one of the most exciting technologies for advanced manufacturing of polymers, where one of the key components is a photosensitive moiety that can generate active species upon light absorption. In the past decade, to go beyond photoradical generators, intensive research has been devoted to new structures of PAGs.[10] PAGs are capable of triggering a polymerization process by releasing H^+ upon light irradiation, are insensitive toward oxygen, and can lead to a considerable variety of polymer backbones.[24,25] In this study, we used **PAG-2** to demonstrate the capability to initiate ring-opening cationic polymerization using red LED light.

PAG-1 and **PAG-2** were synthesized following the sequences of chemical reactions shown in Scheme 1. First, thiophenol was reacted with 4-bromobenzaldehyde to afford compound **1**. Then BODIPY diphenyl sulfide (**2**) was obtained by reacting compound **1** with 2,4-dimethylpyrrole. Next, **PAG-1** was synthesized by microwave irradiation of compound **2** with diphenyliodonium hexafluorophosphate in a closed vessel. Next, we synthesized **PAG-2** with the D−π−A structure in a similar way. The BODIPY core (**3**) was synthesized using a literature method by treating 3,4,5-trimethoxybenzaldehyde with 2,4-dimethylpyrrole.[26] Then trimethoxy BODIPY diphenyl sulfide (**4**) was obtained by a condensation reaction between compounds **1** and **3**. Finally, **PAG-2** was obtained by microwave irradiation of compound **4** with diphenyliodonium hexafluorophosphate.

Scheme 1. Synthetic Routes to PAG-1 and PAG-2



Next, the UV absorption and emission spectra of **PAG-1**, **PAG-2**, and their precursor compounds **2** and **4** in methanol were recorded (Figure 2). The absorption spectra of **PAG-1** and **PAG-2** showed an intense peak centered at 509 and 566 nm, respectively, and the emission was centered at 521 and 579 nm, respectively. Compared with **PAG-1**, **PAG-2** has an extended conjugation system and displays red-shifted photophysical properties as well as a larger absorption coefficient (ε). The fluorescence quantum yields (Φ_f) were calculated using fluorescein and crystal violet perchlorate as standards. The Φ_f values for **PAG-1** and **PAG-2** in methanol were 0.11 and 0.02, respectively (Table 1), whereas those of the precursor compounds **2** and **4** were 0.30 and 0.45, respectively. This clearly indicates that the emission decreases dramatically after the formation of the triphenylsulfonium salt as a result of the electron transfer from the BODIPY chromophore to the triphenylsulfonium moiety in both the D−A and D−π−A structures. Furthermore, the decrease in fluorescence intensity correlates well with the decrease in fluorescence lifetime (τ) when the PAGs are compared with their precursors (Figures S1 and S2).

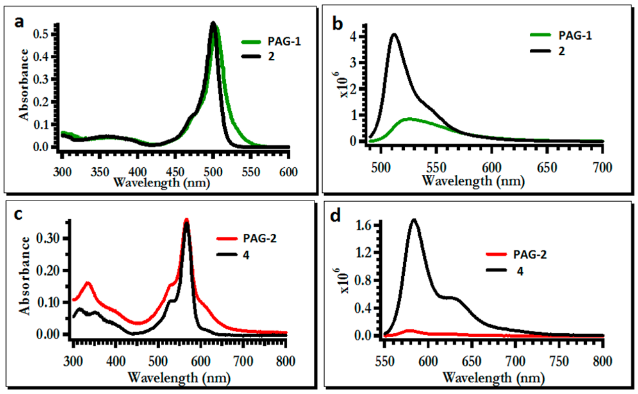


Figure 2. (a) Absorption and (b) emission spectra of **PAG-1** and compound **2** and (c) absorption and (d) emission spectra of **PAG-2** and compound **4**.

Initially the dark stability was checked, and the results showed that after 24 h in the dark both **PAG-1** and **PAG-2** had negligible changes in their UV−vis spectra, indicating high dark stabilities (Figure S3). Then we studied the photochemistry of these BODIPY-based PAGs. On the basis of their maximum absorption wavelengths and the availability of LED light sources, we used a green LED (505 ± 30 nm) to irradiate **PAG-1**, while a red LED (595 ± 30 nm) was employed to excite **PAG-2**. **PAG-1** (2 mL of a 1×10^{-5} M solution in 1:1 v/v MeOH/water) in a quartz cuvette (10 mm path) was placed in front of the green LED light source (Thorlabs M505L3). Upon irradiation, samples were analyzed at regular time intervals by UV−vis spectrophotometry and LC−MS analysis. The absorption peaks of **PAG-1** decreased as the irradiation time increased, indicating the photolysis under LED light exposure. Similarly, under red LED light (Thorlabs M595), the absorption intensity of **PAG-2** decreased in an irradiation-time-dependent manner (Figure S4). Though the light response was obvious, in the dark **PAG-2** is insensitive to the temperature and pH of the solution (Figures S5 and S6). In addition, the photolysis sample solution of **PAG-1** was subjected to study by reversed-phase HPLC. Originally, pure **PAG-1** exhibited a retention time of 0.84 min, but after 10 min under green LED irradiation we observed four other photobyproducts, all having longer retention times than **PAG-1**, and the amounts of the four photobyproduct increased with increasing irradiation time (Figure S7). Furthermore, one of the photobyproducts matched with the standard sample of

Table 1. Photophysical Properties of PAG-1 and PAG-2

	λ_{max}^{abs} (nm)[a]	λ_{max}^{em} (nm)[b]	ε (10^3 M^{-1} cm^{-1})[c]	Φ_f[d]	τ (ns)[e]	Φ_H[f]	$\varepsilon\cdot\Phi_{H^+}$ (M^{-1} cm^{-1})
PAG-1	509	521	61.5	0.11	2.3	0.07	4300
PAG-2	566	579	129	0.02	1.2	0.04	5160

[a] Wavelength of maximum absorption. [b] Wavelength of maximum emission. [c] Extinction coefficient. [d] Fluorescence quantum yield. [e] Fluorescence lifetime. [f] Photoacid generation quantum yield.

compound **2**, suggesting a photolysis pathway similar to that indicated in Figure 1. On the basis of these results, a possible photolysis mechanism is proposed (Scheme S2), in which the benzyl radical (Bz·) attacks the conjugated systems to form the degradation byproducts and release H^+.

Next, we investigated the photoacid generation quantum yield (Φ_{H^+}) using a previously reported steady-state method.[8] The H^+ generation was analyzed using the absorption spectrum of a pH-sensitive dye, 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS). As the pH decreases, HPTS undergoes a pH-dependent shift of the absorption maximum from 455 to 405 nm. **PAG-1** and **PAG-2** (4.0×10^{-4} M and 4.6×10^{-4} M, separately) were dissolved in 0.1 mM HPTS in Locke's solution and subjected to irradiation under the mounted LED with desired wavelength of 505 or 595 nm, respectively. UV–vis spectra of HPTS were measured at different time intervals during LED irradiation of the sample for up to 60 min to generate the calibration curve (Figure S8). The proton generation rate was estimated to be 2.36×10^{-8} and 1.66×10^{-8} mol L^{-1} s^{-1} for **PAG-1** and **PAG-2**, separately. The Φ_{H^+} values for **PAG-1** and **PAG-2** were determined to be 7% and 4%. As a further demonstration that PAGs can generate H^+ in a light-guided manner, we irradiated a pH paper soaked with **PAG-2** in $MeOH/H_2O$ solution under a homemade photomask. After exposure to red LED light, the pH strip clearly showed a color change indicating increased acidity (Figure 3). In addition, the lines and edges of the acidic area demonstrated a highly light-dependent pattern of H^+ release.

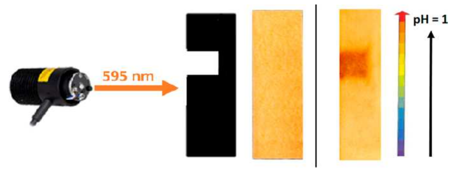
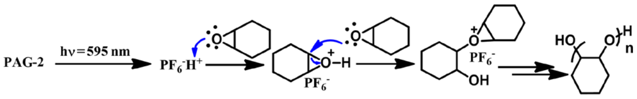


Figure 3. Light-induced pH drop on a pH paper with **PAG-2** (10 mM in $MeOH/H_2O$). The setup of the LED light irradiation on pH paper under a homemade photomask is shown at the left, and the resulting color change of the pH paper is shown at the right.

Compared with **PAG-1**, **PAG-2** exhibited a longer wavelength of maximum absorption as well as a higher $\varepsilon\cdot\Phi_{H^+}$ value, and thus, we picked **PAG-2** for use in the application of photoinduced cationic polymerization of cyclohexene oxide (Scheme 2).[27,28] In brief, photoinitiated cationic ring-opening polymerizations of epoxide monomers are widely used in commercial applications,[29] such as coatings, printing inks, and microelectronic photoresists.[30] The monomers used in cationic polymerization feature low toxicity compared with the acrylate systems employed in radical polymerization.[31] In our study, a solution of cyclohexene oxide and **PAG-2** (0.8% mass ratio) was irradiated with 595 ± 30 nm LED light (80 mW/cm^2) for 30 min, during the course of which we observed a negligible increase in the sample temperature. Then the resulting reaction mixture was analyzed with MS, and the results clearly showed that the cyclohexene oxide started to form oligomers with a periodic pattern of mass peaks with a difference in m/z of 98 (Figure 4). The peaks with m/z from 531.29 to 1119.73 are calculated as repeating units of monomers from number 5 to 11. In the control groups without **PAG-2** and without LED light, we did not find any polymer product in MS analysis. Furthermore, the conversion yield of the polymerization was determined to be around 21% after 30 min of irradiation, and the kinetic curve showed continuous reaction (Figure S9). These data directly showed that cyclohexene oxide oligomers formed by cationic polymerization via proton activation.

Scheme 2. Reaction Scheme for Photoinduced H^+ Generation and Ring-Opening Cationic Polymerization of Cyclohexene Oxide



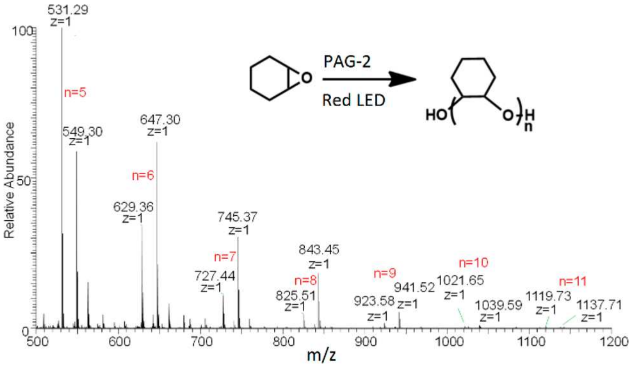


Figure 4. MS of cyclohexene oxide oligomers formed under **PAG-2**-photoinduced cationic reaction upon irradiation with red LED light. Inserted red numbers *n* indicate the calculated numbers of monomer repeating units.

In conclusion, we conjugated the triphenylsulfonium moiety with BODIPY chromophores and developed two new PAGs with D–A and D–π–A configurations. The conjugated PAGs show absorption ability at longer wavelengths in the visible spectrum (green and red). The mechanism of the photoinduced H^+ generation was measured and analyzed. The H^+ formation and ability to lower the pH in a light-dependent manner was demonstrated using a standard pH paper under a photomask. In addition, photoinduced cationic polymerization was tested as a proof of concept of the application, and we observed oligomer formation in MS. While PAGs have been available since the 1970s, in the last decade the interest in light-activated chemical reactions has led to significant advances. Overall, the extended absorption wavelengths of these PAGs should allow them to perform more applications in polymerization to create complex materials using simple methods.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00118.

> Experimental procedures, compound characterization, photophysical measurements, and proposed photodegradation mechanism (PDF)

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Notes

The authors declare no competing financial interest.

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