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Photochemistry

Efficient Self-Contained Photoacid Generator System Based on Photochromic Terarylenes

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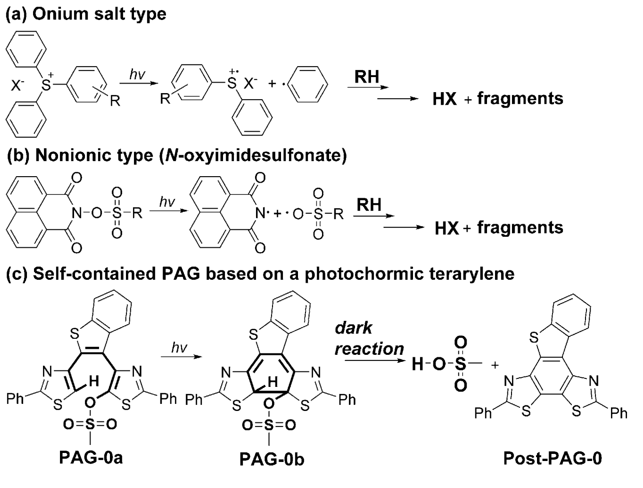
Abstract: A series of highly sensitive neutral photoacid generators (PAGs) based on photochromic terarylenes was prepared. Like the example presented herein, these compounds show a subsequent thermal elimination of a Brønsted acid after a light-triggered 6π-electrocyclization, concomitant with the hexatriene aromatization. A novel type of molecular systems was developed, in which one thiazolyl moiety was replaced by a thienyl group. Depending on the solvents and on the nature of the acid source, the quantum yield (QY) for acid generation could reach up to 0.6. Comparative studies on the acid source clearly showed that aromatic leaving groups tend to extinguish the molecular system photoefficiency. A second type was also prepared, in which the nature of the hetero-aromatic rings were identical to our previous example, but their sequence was modified. Therefore, a second level of improvement was achieved in nonpolar solvents, pushing the QY value up to 0.7. Finally, we demonstrated the mesylic acid-releasing PAG as a photocatalyst in a chemically amplified positive resist system.

Introduction

Photoacid generators (PAGs) are light-sensitive compounds that produce protons upon exposure to light.[1,2] Since the study of PAGs from 1970s, they have gained enormous interest and been widely used in the microlithographic technology[3–5] along with the explosive growth of semiconductor industry. Recently, the applications of PAGs also extended to other domains such as photodynamic therapy,[6] photocontrolling of enzymatic activity,[7] and to photoinduced doping of conjugated polymers.[8–10] Remote activation of fluorescent molecules by photoacid generation[11] was also demonstrated with the view of super-resolution imaging[12] and imprinting of fluorescent patterns.[13] Some applications demand the generation of sufficiently strong acids, for example, photopolymerization initiations. Two types of PAGs are currently used: ionic[14] and nonionic.[15] A large number of onium-salt-based ionic PAGs such as aryldiazonium, diaryliodonium, triarylsulfonium, and triarylphosphonium salts have been used at the forefront of industry for more than three decades and their photochemistry has been investigated in great detail.[16] Meanwhile, nonionic PAGs are exemplified by *N*-oxyimidosulfonates, which produce sulfonic acids.[15,17] More recently, the chemical modifications of ionic PAGs[18–20] and the combinations of sensitizers and nonionic PAGs[21] sensitized them to two-photon activation. Both the onium salt and nonionic PAGs dominantly undergo homolytic bond-cleavage reactions upon light irradiation (Scheme 1 a and b). Photogenerated radical species need to extract a hydrogen atom from solvent molecules or other hydrogen sources (RH) to generate a Brønsted acid, which gives rise to medium-dependent sensitivity and complicated fragments remaining in the systems. As a matter of fact, nitrobenzyl-derivatives representative of caged compounds[22] with photoremovable protecting groups have also been used for a photolithiographic applications.[23] The quantum yield (QY), which mea-



Scheme 1. Various types of photoacid-generation reactions.

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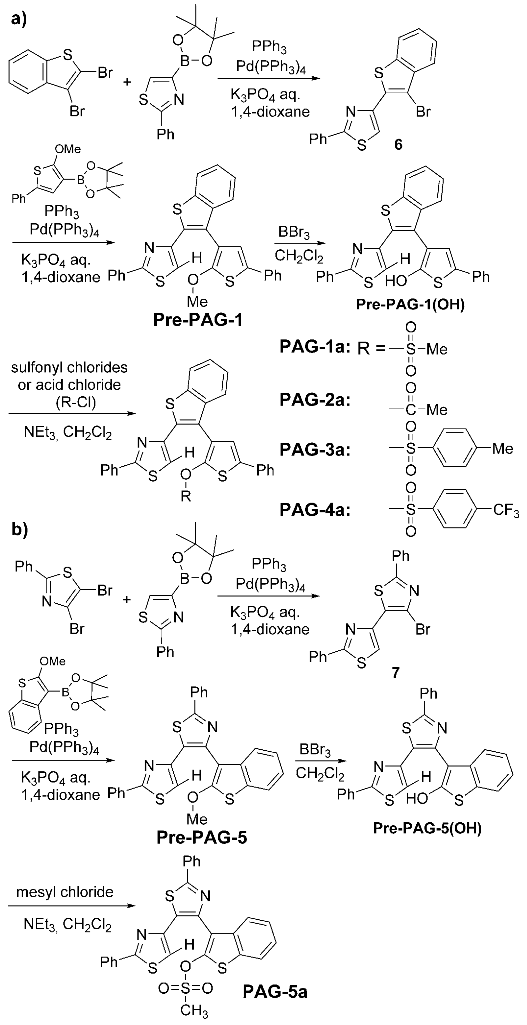
sures the efficiency of the so-far reported PAGs capability to initiate photopolymerization through the acid release, has to the best of our knowledge rarely exceeded 0.5.[19] As a consequence, there is a strong need in new PAG molecular systems to offer higher photosensitivities combined with greater efficiencies and improved thermal stabilities.

The first attempts to photocontrol (modulate or gate) the proton dissociation by modifying the pK_a value was achieved with photochromic diarylethenes[24,25] and spiropyranes,[26–29] in which the photochromic core acted as the conjugate base of the released proton. However, the amplitude of photoinduced modulation in K_a value of most pH-switching photochromic dyes is less than two orders of magnitude, which is too small for applications in photoresist systems. Recently, we reported a self-contained PAG molecule based on a new mechanism for the acid release.[30] An elimination reaction[31,32] of a Brønsted acid molecule was triggered by a photoinduced 6π-electrocyclization reaction in **PAG-0** (Scheme 1 c), as a subsequent thermal reaction. Although the acid-release reaction itself does not involve a photochemical process, the simultaneous formation of multiple aromatic rings through a highly stable arenium carbocation intermediate drove the quantitative elimination of the acid. The QY of acid generation is, therefore, determined by the photoinduced 6π-electrocyclization reaction from **PAG-0 a** to **PAG-0 b**. The first self-contained **PAG-0** was designed based on the bisthiazolylbenzo[*b*]thiophene framework which exhibited a QY of 0.52 for the release of methanesulfonic acid in toluene.[30] Although this value is rather larger than most of practical PAGs, there should be room for substantial improvement considering the capability of the mother compound, which showed a photon-quantitative reactivity (QY = 0.98).[33] As much effort have been devoted to the improvement of ring-cyclization sensitivity of diarylethene and its analogues, we were highly motivated to explore further photosensitive PAGs by developing molecular scaffolds inspired by previous developments in the field, which aim to maximizing the population of the photoreactive conformation in the ground state.[33–38] Although the bisthiazolylbenzo[*b*]thiophene molecule showed much suppressed photoreaction quantum yield in methanol,[33] the replacement of one of the thiazolyl moieties with a thiophene derivative, which formed an asymmetric terarylene, interestingly led to a large improvement of the QY in methanol.[34] We herein report on our challenges to improve the QY of the self-contained PAG system based on the asymmetric terarylene backbones with various types of acid–ester. A first level of improvement was obtained when a thienyl group was introduced (PAGs **1**–**4**, Scheme 2). Four new self-contained PAGs were synthesized from an identical precursor, namely **Pre-PAG-1**, and their properties including the net acid-releasing efficiency were investigated. A second improvement of the photosentivity was obtained when changing the sequence of aromatic rings connection in **PAG-0** (**PAG-5**). As proof of principle and to assess its full potential, the latter was further employed as an acid catalyst in a chemically amplified positive resist system.



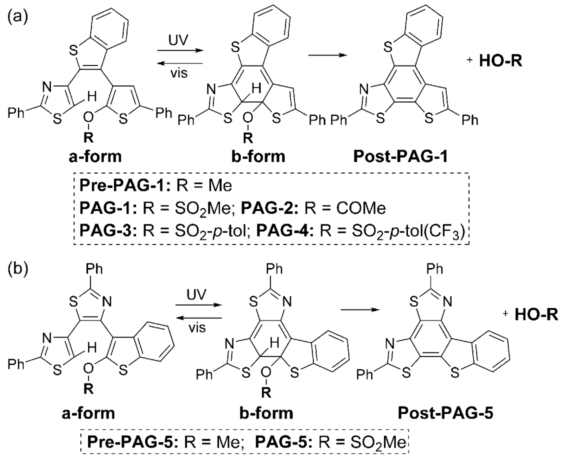
Scheme 2. Synthesis of: a) **PAGs 1 a–4 a**, and b) **PAG-5 a** through their key precursors **Pre-PAGs-1** and **5**, respectively.

Results and Discussion

Five PAG molecules were synthesized according to the synthetic route depicted in Scheme 2. The key precursors **Pre-PAG-1** and **Pre-PAG-5** were synthesized by simple Pd-catalyzed Suzuki–Miyaura cross-coupling reactions between the central and side aryl units under identical conditions.[34] A thiazolyl pinacol borate was first reacted with 2,3-dibromobenzo[*b*]thiophene at the 2-position with the higher reactivity and then a thienyl ring was introduced at the 3-position, giving **Pre-PAG-1** in 68% yield over two steps. The methoxy group of **Pre-PAG-1** was deprotected and converted to the corresponding hydroxyl group by using BBr_3 in CH_2Cl_2. The subsequent esterification reactions of this identical precursor with acetyl chloride or sulfonyl chlorides gave **PAGs-1 a**–**4 a** (about 40% over two steps). **PAG-5 a** was also prepared by a sequential Suzuki-coupling reaction, deprotection of the methoxy group, followed by an esterification with mesyl chloride. Although we also tried to introduce superacids such as triflic or fluorosulfonic acid using their acid chlorides or acid anhydrides, the reactions did not proceed as hoped, and instead gave a dimeric derivative that was clearly identified by X-ray crystallography (see the Supporting Information).

Photoirradiation of Pre-PAG-1 and PAGs 1–4

Upon UV irradiation, the colorless solution of precursor **Pre-PAG-1** in dry hexane turned blue, due to the emergence of an intense absorption band at 600 nm corresponding to the formation of closed ring form (b-form in Scheme 3, Supporting Information, Figure S1). The colored state was reversibly bleached upon visible irradiation and the corresponding spectrum was identical to **Pre-PAG-1**. These spectral changes accompanied isosbestic points, indicating a two-component reversible and clean photochromic reaction in hexane. On the other hand, the photoreaction of **Pre-PAG-1** in polar solvents such as methanol also led first to the same coloration reaction, which was followed by a subsequent bleaching reaction when the solution was kept into the darkness (Supporting Information, Figure S2). This bleaching reaction agrees with the elimination of a methanol molecule reported for analogous molecules.[30,31] Along with the elimination of methanol, a polycyclic compound depicted as **Post-PAG-1** in Scheme 3 was formed, which was isolated by HPLC and its structure was confirmed by ^{1}H NMR and X-ray crystallography (Supporting Information, Figures S3, S4).



Scheme 3. Photochromism of **Pre-PAGs-1**, **5** and **PAGs-1–5**, and subsequent elimination reaction of **PAGs-1–4**.

PAGs-1–4 exhibited very different spectral responses from those of **Pre-1** (Figure 1). After UV irradiation, each of the toluene solution of **PAGs-1–4** presented a pale yellowish color with the emergence of a newly formed absorption band above 350 nm. The absorption profiles of **PAGs-1–4** after the UV irradiation were similar to each other, featuring a maxima located at 375 nm and a shoulder at 398 nm, suggesting the formation of the identical molecule **Post-PAG-1** by the immediate leaving of an acid molecule. In fact, the spectral profiles were identical with that of isolated **Post-PAG-1** in toluene (Supporting Information, Figure S5). It should be noted that **PAGs-3** and **4** gave a residual band with a faint absorbance above 500 nm, which may be attributed to the transient formation of closed-ring b-forms. **PAGs-3** and **4** have a phenyl ring in the leaving group which could interact with the aryl units in the closed-ring form of photochrome through π–π interactions, partly suppressing the elimination reaction. The complete bleaching in the visible region was observed in a few minutes after photoirradiation (Supporting Information, Figures S6, S7).

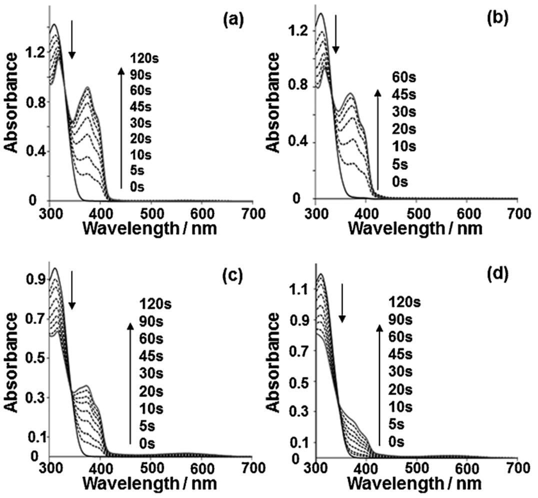


Figure 1. Absorption spectral change of: a) **PAG-1**, b) **PAG-2**, c) **PAG-3** and d) **PAG-4** upon UV ($\lambda = 313$ nm) irradiation in toluene.

Photoirradiation of Pre-PAG-5 and PAG-5

The solution of **Pre-PAG-5** also showed a similar behavior to that of **Pre-PAG-1** (Supporting Information, Figures S8, S9) in the same solvents. The formation of **Post-PAG-5** after the elimination of methanol was confirmed with high resolution MS and ^{1}H NMR spectra after the photoproduct isolation by HPLC (Supporting Information, Figure S10). **PAG-5** bearing a mesyl group showed a similar spectral response to those of **PAGs-1–4** after UV irradiation. Although the degree of redshift in **PAG-5** after the UV irradiation was not as large as those for **PAGs-1–4**, the absorbance at 338 nm increased almost twofold (Figure 2). The absorption spectrum of **PAG-5** after the photoirradiation well accorded with that of isolated **Post-PAG-5** (Supporting Information, Figure S11).

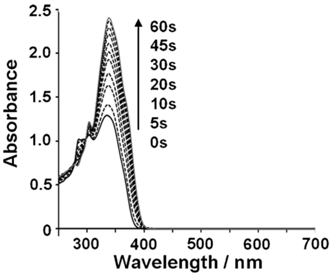


Figure 2. Absorption spectral change of **PAG-5** upon UV ($\lambda = 313$ nm) irradiation in toluene.

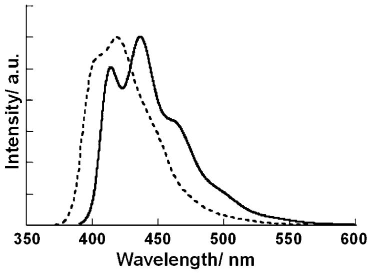


Figure 3. Fluorescent spectra of **Post-PAG-1** (solid line) and **Post-PAG-5** (dash line) in toluene. ($\lambda_{ex} = 338$ nm).

Both **Post-PAGs-1** and **5** have a planer polycyclic structure, showing blue fluorescence with the emission peak at 436 and 423 nm, respectively (Figure 3). The simultaneous formations of acid molecules and Post-PAGs on the photoreaction were confirmed by ^{1}H NMR measurements (Supporting Information, Figures S12–S16).[30]

Table 1 summarized the optical properties of **PAGs-1–5** including the apparent QY for photoacid generation (ϕ_{acid}). Since the elimination of acid from the closed-ring b-forms proceeds quantitatively in a spontaneous manner with $\Delta G < 0$ through an arenium cation intermediate,[30] the ϕ_{acid} value could be determined by the efficiency of 6π-electrocyclization reaction forming b-forms. **PAGs-1–4** featured similar absorption maxima, close values of extinction coefficient in the three used solvents for this study. Interestingly, changing the nature of the leaving group had no influence onto the spectroscopic properties, even though when the leaving group is an aromatic system. Therefore, it suggests that the electronic parameter is controlled by the three aromatic rings and their respective connection. In addition, when going from **PAG-1** to **PAG-5**, one could observe a large change in both maximum of absorption and extinction coefficient, due to the modification in the aromatic type and sequence. A large redshift is observed for **PAG-5**, probably because of the central 2-phenylthiazolyl moiety that extends the system π-conjugation compared with benzo[*b*]thiophene. In addition, a QY of 0.6 was measured for **PAG-1** and **PAG-2** in toluene, which marked a first improvement compare to our previous work. However, introducing aromatic leaving group drastically reduced the photosensitivity. Since the absorption characteristics of **PAGs-3–4** are similar to **PAGs-1–2**, this suggests that bulky aromatic leaving groups probably favored a nonphotoreactive conformation, hence the low values. Moreover, the best ϕ_{acid} value of 0.71 was obtained with **PAG-5**, which is a structural isomer of the first PAG, **PAG-0**.[30] The improvement of the ϕ_{acid} value from 0.52[27] to 0.71 was thus achieved just by changing the sequence in the connectivity of aromatic units consisting of the terarylene framework. To our best knowledge, this is the highest value for PAGs so far reported in the literature. The bathochromic shift of absorption band in **PAG-5** is also an advantage as a candidate of PAGs, since they are usually demanded to be sensitive toward Hg lamps ($\lambda = 365$ nm) and UV-LEDs ($\lambda = 360$–380 nm). The present terarylene-based PAGs are capable for chemical tuning on their sensitive wavelength and extinction coefficient.

Table 1. Photophysical properties of **PAGs** and **Post-PAGs**.

Compd	λ_{abs} [nm] ($\varepsilon \times 10^{-4}$ [M^{-1}cm^{-1}])	ϕ_{acid}[d]
PAG-1	310 (3.54),[a] 309 (3.64),[b] 308 (3.69)[c]	0.58,[a] 0.37,[b] 0.29[c]
PAG-2	311 (3.51),[a] 310 (3.60),[b] 309 (3.62)[c]	0.61,[a] 0.41,[b] 0.31[c]
PAG-3	309 (3.56),[a] 308 (3.64)[b]	0.05,[a] 0.03[b]
PAG-4	311 (3.58),[a] 310 (3.64)[b]	0.04,[a] 0.01[b]
Post-PAG-1	318 (2.95),[a] 375 (2.46),[a] 318 (3.10),[b] 373 (2.56),[b] 315(3.21),[c] 371 (2.68)[c]	–
PAG-5	334 (2.25),[a] 333 (2.29),[b] 328 (2.33)[c]	0.71,[a] 0.47,[b] 0.23[c]
Post-PAG-5	338 (2.33),[a] 337 (2.50),[b] 335 (2.61)[c]	–

Measured in: [a] toluene, [b] in chloroform, [c] in methanol. [d] Apparent quantum yield for photoacid generation.

Interestingly, all PAGs showed solvent-dependent QY for the acid generation, decreasing the ϕ_{acid} with increasing the solvent polarity. The parent molecule bisarylbenzo[*b*]thiophene with methyl groups at both ends of 6π-system showed a photon-quantitative ring-cyclization reaction, which indicates the efficiency of the electrocyclization reaction is predominantly dependent on the geometry around the photoreactive 6π-system in the ground state.[33–39] Since the acid ester groups introduced at a reactive carbon atom have negligible electronic effect on the photoreactive 6π-system, the conformational fluctuation must depend on solvent effects and thus may explain the diversity of ϕ_{acid} values. Furthermore, the lack of methyl groups at the reactive carbon atoms disables mutual intramolecular CH–π interactions and should result in a striking destabilization of the photoreactive C_2-like conformation,[34] which in turn substantially decreased the photochemical reaction efficiency for all PAGs in comparison to those of dimethyl-substituted ones in polar solvents. Regardless of the lack of methyl groups at the reactive carbon atoms, the methyl moiety in the acid ester group may similarly interact with the 2-phenylthiazolyl unit at the opposite site to partly stabilize photoreactive conformers. The downfield shifts of these methyl protons after the photoinduced elimination (Supporting Information, Figures S12, S13) suggested that the ring-current effect of 2-phenylthiazole unit operated on these methyl groups in PAGs **1** and **2**. On the other hand, bulky substituents on the reactive carbon atoms as aromatic leaving groups markedly decrease the efficiency of electrocyclization reaction for PAGs **3** and **4**.[40] In addition for PAG-**5**, the S⋯N interaction operating between the central and the side thiazolyl units,[33] the CH⋯N interaction between the central thiazole and the side benzo[*b*]thiophene unit may contribute to the stabilization of photoreactive conformer. Because of the hydrogen-bonding nature of CH⋯N interaction, the ϕ_{acid} value is expected to significantly drop in protic and polar solvents (0.23 in methanol).

Theoretical investigations

The optimized geometries for the PAGs were simulated by DFT calculations using the Gaussian 09 suite.[41] Prior to the DFT calculation, we searched for possible conformers with the MMFF94s force field using the CONFLEX program[42] and used them as an input structure for DFT calculations. For the DFT calculation, ωB97XD functional with the 6-31G(d) basis set was employed since it is known to give relatively accurate results on diarylethenes.[43] **PAGs-1** and **5** with the high ϕ_{acid} values showed optimized structures with a photoreactive conformation as the most stable geometries (Supporting Information, Figure S17). Nonphotoreactive conformers with a parallel orientation about the side-aryl units were picked up as the second most stable conformers by the conformation search. The photoreactive conformers were more stable than the nonphotoreactive ones by 2.20 and 2.67 kcal mol^{-1} for **PAG-1** and **PAG-5**, respectively, indicating the higher stability of the photoreactive conformer for **PAG-5**. As a result, **PAG-5** possessed the better ϕ_{acid} than other PAGs. Meanwhile, **PAG-3** with the much suppressed ϕ_{acid} value possessed a non-photoreactive conformation as the most stable geometry. The energy difference between the non-photoreactive conformer and a simulated photoreactive one was estimated to be 1.3 kcal mol^{-1}. Thus, the small population of photoreactive conformer should be responsible for the suppressed ϕ_{acid} values for **PAG-3**, which could be the case with **PAG-4**.

Thermal stabilities

Since most photolithographic processes include a prebaking procedure above 100 °C, the thermal stability of PAGs is of importance to avoid acid formation by nonphotochemical pathways.[44] Generally, a decomposition temperature of larger than 150 °C for PAGs is deemed sufficient for the use in photoresist systems. We performed a thermogravimetric (TG) analysis for the most efficient PAG, **PAG-5** (Figure 4). The gradual mass decrease of **PAG-5** started around 200 °C, which was 100 °C lower than that of a representative terarylene with methyl groups at photoreactive carbon atoms (ca. 300 °C, Supporting Information, Figure S18). The introduction of an acid ester group at a reactive carbon atom should be attributed to the decrease in the thermal stability in **PAG-5**, whereas the value of decomposition temperature seems high enough for photolithographic applications. It should be noted that 50 % of overall weight remained even above 500 °C (Figure 4), which was much higher than that observed for the conventional terarylene (Supporting Information, Figure S18). The residue after the TG analysis of **PAG-5** exhibited a black graphitic appearance (Supporting Information, Figure S19). The thermal elimination of acid molecule might lead to the polyaromatization followed by the graphitization.

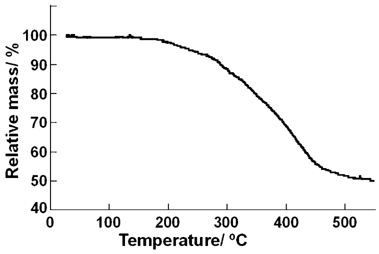
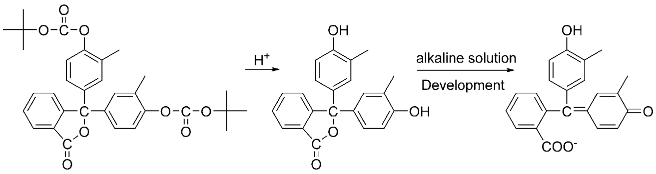


Figure 4. TG curve of **PAG-5** (heating rate: 10 °C min^{-1}).

Application in a chemically amplified resist system

As has been demonstrated by our first self-contained **PAG-0** in our previous developments,[30] mesylic acid-containing PAGs-**1** and **5** could also serve as a photoinitiator of cationic polymerization of cyclohexene oxide (Supporting Information, Figures S20, S21). Since **PAG-5** gave the most efficient QY, we herein employed it as an acid catalyst in a positively acting, chemically amplified resist system to demonstrate the performance of PAG. The system is composed of **PAG-5**, novolak polymer and a dissolution inhibitor.[42] The dissolution inhibitor is a derivative of phthalide bearing *tert*-butoxycarbonyl (Boc)-protected hydroxyl groups, which interact with novolak resin to avoid from development with alkali solution.[45] In the presence of an acid, the acid-catalyzed deprotection reactions of Boc groups take place, giving an unprotected molecule which can be dissolved in an alkaline solution and no longer protect the novolak resin from the development process (Scheme 4). The solution of inhibitor with PAG was cast on the novolak polymer layer to form a bilayer configuration on a glass slide, which was prebaked at 115 °C, irradiated with UV ($\lambda = 365$ nm, 22 mW cm^{-2}) for 10 min through a photomask, postbaked at 115 °C, and then developed in an aqueous solution of tetramethylammonium hydroxide. Figure 4a shows the scanning electron microscope image of a photopattern obtained after the development. The pattern of a photomask was clearly transferred as a topographic pattern of the polymer film, demonstrating **PAG-5** actually performed efficiently as an acid generator upon irradiation to induce the acid-catalyzed deprotection of Boc groups. The film just before the development process was also observed by fluorescence microscope. The blue fluorescent image corresponds to the unmasked area in the photoirradiation process (Figure 5b), demonstrating the formation of **Post-PAG-5** molecule in the UV-exposed area. The simultaneous formation of blue-emitting **Post-PAG-5** by the photoreaction of **PAG-5** thus clearly reported the release of mesylic acid in the exposed area.[46] The further investigations includ-



Scheme 4. Chemical reactions of dissolution inhibitor including deprotection of Boc-groups with acid-catalyst followed by development in an alkali solution.

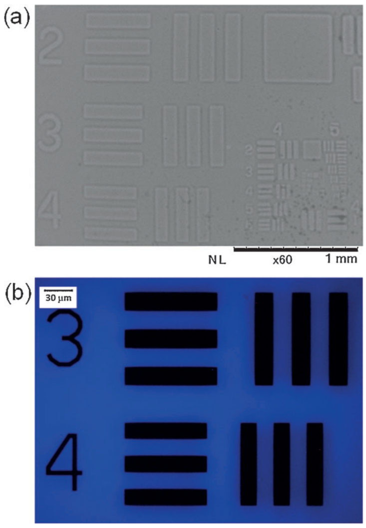


Figure 5. a) SEM image of a photopattern fabricated by a chemically amplified photoresist system containing **PAG-5**. b) Fluorescent microscope image of the film just before the development process.

ing the optimization of conditions may reveal the utility of present PAGs in a chemically amplified photoresist system.

Conclusions

We have demonstrated two levels of improvement of our newly based PAG molecular systems, gaining insight into the structural requirement to improve their photoefficiencies. 1) Non-aromatic acid sources seem to be required if one would keep high level of photosensitivity in solution. For the same acid source, compare to our previous compound, replacing one thiazolyl group by a thienyl one already brought about +10% of enhancement, pushing the QY value to 0.6 in toluene. 2) A higher level of improvement could be achieved in changing the sequence of the heteroaromatic rings while keeping each of them identical to our previous example. Placing the benzothiophene as side-aryl group increased the yield to 0.7 in non-polar solvent. As a proof of principle, we demonstrated that the most efficient **PAG-5** could induce the acid-catalyzed chemical amplification in a positive-tone resist film. Furthermore, the photolysis of self-contained PAGs induced the simultaneous formation of a fluorescent fused aromatic polycycle, which could also report the formation of acid molecule. Since the terarylene framework is prepared simply by controlled Pd-catalyzed aryl–aryl cross-coupling reactions, a combinatorial approach in regard to the type of aromatic units as well as their connection sequences may lead to further improvement in the photoacid generation efficiency.

Experimental Section

General

All compounds were characterized by ^{1}H NMR (400 MHz) and ^{13}C NMR (75 MHz) spectroscopy on JEOL JNM-ECP400 and JNM-AL300 spectrometers, respectively. High-resolution mass spectrometry (HRMS) analyses were performed on a JEOL JMS-700 mass spectrometer. Separative HPLC was performed on a JASCO LC-2000 Plus Series. Quantum yields were measured with QYM-01 photoreaction quantum yield evaluation system ($\lambda = 313$ nm).[47] Absorption and fluorescence spectra in solution were studied with a JASCO V-670 and JASCO FP-6500 spectrophotometers, respectively. DFT calculations were performed with Gaussian 09 at the ωB97XD/6–31(d) level. Conformational search with the MMFF94s force field was performed on the CONFLEX program (CONFLEX Corp.). Thermogravimetric analysis was carried out using a Shimadzu DTG-60. SEM images were taken with a Hitachi TM 3030. Fluorescence microscopic measurements were performed with an Olympus BX-51 optical microscope.

Synthesis

4-(3-Bromobenzo[*b*]thiophen-2-yl)-2-phenylthiazole (6): A 300 mL four-necked flask was charged with 2,3-dibromobenzo[*b*]thiophene (1.9 g, 6.3 mmol), 2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole (1.8 g, 6.3 mmol), PPh_3 (0.19 g, 0.73 mmol), 2 M K_3PO_4 solution (12 mL), and 1,4-dioxane (110 mL). Then $Pd(PPh_3)_4$ (0.548 g, 0.474 mmol) was added to the solution under N_2 flow and the mixture was stirred at 100 °C for 24 h under N_2 atmosphere. The reaction mixture was extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$. After the solvent was evaporated, the crude product was purified with silica gel column chromatography by using a mixture of hexane and $CHCl_3$ as an eluent to afford compound 4-(3-bromobenzo[*b*]thiophen-2-yl)-2-phenylthiazole (1.7 g, 72%) as colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 7.47–7.51$ (m, 5H), 7.81–7.87 (m, 2H), 8.02–8.05 (m, 2H), 8.31 ppm (s, 1H).

4-(3-(2-Methoxy-5-phenylthiophen-3-yl)benzo[*b*]thiophen-2-yl)-2-phenylthiazole (Pre-PAG-1): **Pre-PAG-1** was prepared according to the same condition with the synthesis of compound **6** by using 2-(2-methoxy-5-phenylthiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and **6**. 0.70 g of **Pre-PAG-1** was obtained in 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 3.84$ (s, 3H), 7.13 (s, 2H), 7.35–7.38 (m, 5H), 7.44–7.46 (m, 3H), 7.55–7.60 (m, 3H), 7.87–7.90 (m, 1H), 8.00–8.03 ppm (m, 2H).

Photoacid generators (PAG-1 a–4 a): PAG compounds **1 a** to **4 a** were prepared from the identical precursor **Pre-PAG-1** by using the same method according to our previous work.[30]

PAG-1 a: Yield: 28 mg, 41%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.63$ (s, 3H), 7.18 (s, 2H), 7.39–7.45 (m, 8H), 7.58–7.63 (m, 3H), 7.89–7.92 (m, 1H), 7.95–7.99 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 167.77$, 149.21, 139.95, 139.37, 138.82, 136.65, 133.40, 133.19, 130.61, 129.34, 129.20, 128.58, 126.84, 125.79, 125.58, 125.20, 123.34, 122.61, 122.27, 115.81, 37.70 ppm; HRMS (ESI) *m/z* calcd for $C_{28}H_{19}NO_3S_4Na^+$ $[M+Na]^+$: 568.01455; found: 568.01514.

PAG-2 a: Yield: 25 mg, 39%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.99$ (s, 3H), 7.10 (s, 1H), 7.19 (s, 1H), 7.36–7.46 (m, 8H), 7.57–7.63 (m, 3H), 7.89–7.92 (m, 1H), 7.99–8.02 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 167.56$, 167.16, 149.64, 147.08, 140.38, 138.94, 136.82, 133.90, 133.20, 130.35, 129.10, 129.03, 127.79, 126.70, 125.44, 124.99, 124.57, 123.22, 122.36, 121.27, 115.15, 20.37 ppm; HRMS (ESI) *m/z* calcd for $C_{29}H_{19}NO_2S_3Na^+$ $[M+Na]^+$: 532.04756; found: 532.04576.

PAG-3 a: Yield: 30 mg, 39%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.07$ (s, 3H), 6.70–6.73 (d, 2H), 6.88 (s, 1H), 7.06 (s, 1H), 7.28–7.48 (m, 11H), 7.56–7.59 (m, 2H), 7.78–7.81 (m, 1H), 7.98–8.01 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 166.98$, 149.25, 146.00, 145.53, 139.72, 139.09, 138.64, 136.06, 133.49, 133.26, 131.07, 130.53, 129.30, 129.20, 128.46, 127.95, 126.82, 126.26, 125.66, 125.07, 124.60, 124.01, 123.45, 122.07, 115.15, 21.69 ppm; HRMS (ESI) m/z calcd for $C_{34}H_{23}NO_3S_4Na^+$ $[M+Na]^+$ 644.04585; found: 644.04568.

PAG-4a: Yield: 33 mg, 40%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=$ 7.00 (s, 1H), 7.07 (s, 1H), 7.27–7.48 (m, 12H), 7.56–7.59 (m, 2H), 7.73–7.76 (m, 1H), 7.96–7.99 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta=$167.48, 149.04, 145.49, 139.54, 139.48, 138.44, 138.16, 136.35, 133.30, 133.21, 130.60, 129.35, 129.19, 128.65, 128.21, 126.86, 126.64, 125.75, 125.56, 125.39, 124.82, 123.70, 122.96, 122.32, 122.20, 115.41 ppm; HRMS (ESI) m/z calcd for $C_{34}H_{20}FNO_3S_4Na^+$ $[M+Na]^+$: 698.01758; found: 698.01825.

4′-(2-Methoxybenzo[*b*]thiophen-3-yl)-2,2′-diphenyl-4,5′-bithiazole (Pre-PAG-5): **Pre-PAG-5** (220 mg, 58%) was prepared from the compound **7**[27] according to the same condition with the synthesis of **Pre-PAG-1**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=$3.94 (s, 3H), 6.86 (s, 1H), 7.25–7.30 (m, 2H), 7.43–7.50 (m, 7H), 7.72–7.75 (m, 1H), 7.96–7.99 (m, 2H), 8.06–8.09 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta=$167.28, 166.21, 162.81, 147.62, 143.91, 137.88, 133.91, 133.30, 131.94, 131.24, 130.47, 129.17, 129.11, 126.80, 126.75, 125.34, 123.42, 122.35, 114.21, 110.02, 61.84 ppm; HRMS (ESI) m/z calcd for $C_{27}H_{18}N_2OS_3Na^+$ $[M+Na]^+$: 505.04789; found: 505.04752.

Protocol for chemically amplified photolithography

The inhibitor and **PAG-5** (5 wt% relative to inhibitor) were dissolved in diethylene glycol dimethyl ether (DGDE) and then the solution was filtered through a 0.20 μm PTFE filter (ADVANTEC). The same procedure was subjected to the novolak resin (EP4080G, Asahi-Yukizai, corp.) to give a DGDE solution (20 wt%). The novolak resin was first cast on a glass slide which was further coated by the layer of inhibitor and PAG. The resist film was exposed to the UV light for 10 min after prebaked at 115 °C for 120 s. A high intensity UV lamp (Blak-Ray B-100AP, UVP, LCC, $\lambda=$365 nm, 22 mW cm^{-2}) was used for the UV exposure. The exposed film was then post-baked at 115 °C for 120 s. The development procedure was conducted by soaking the film in an aqueous tetramethylammonium hydroxide solution (TMAH, 2.38%) for 30 s.

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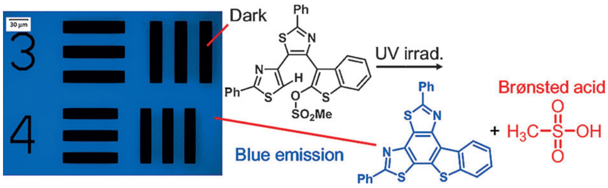
FULL PAPER



Let there be acid: An elimination reaction of an acid molecule was combined as a subsequent reaction of a photochromic 6π-electrocyclization reaction of terarylenes, which was applied in a chemically amplified resist system (see figure).

Photochemistry

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Efficient Self-Contained Photoacid Generator System Based on Photochromic Terarylenes