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Synthesis and Properties of Novel i- and g-Line Sensitive Photoacid Generators Based on 9-Fluorenone Derivatives with Aryl–Ethynyl Units

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Imino sulfonate photoacid generators (PAGs) sensitive to i- and g-line were synthesized using 9-fluorenone derivatives with aryl–ethynyl units as starting materials. The PAGs exhibited good thermal stability and photoreactivity at 365 (i-line) and 436 nm (g-line) compared with that of an imino sulfonate PAG synthesized from unfunctionalized 9-fluorenone.

Photoacid generators (PAGs) play an important role in many fields such as photoinduced acid-catalyzed polymerization systems (photoinduced curing systems) and photoresists.[1] PAGs sensitive to 365 nm light (i-line) or 436 nm light (g-line) have been getting much attention recently, because of their application to UV curing and chemically amplified photoresists for i- and g-line lithography.[2] However, practical i- and g-line sensitive PAGs are still limited, and therefore, much effort has been devoted for the development of new i- and g-line sensitive PAGs by ourselves and other groups.[2a,3] Among i- and g-line sensitive PAGs, nonionic PAGs have received attention, because of their better solubility in organic solvents and polymer films compared with that of ionic PAGs.[4] In addition, PAGs with an ability to generate superstrong acids such as CF_3SO_3H or $C_4F_9SO_3H$ have been desirable for the application of highly photosensitive resists. We reported the synthesis of 9-fluorenylideneimino trifluoromethanesulfonate (FITf).[3q] Although FITf was sensitive to i-line, the molar extinction coefficients (ε) of FITf at 365 nm was relatively low, and FITf was not thermally stable. After the investigation of the synthetic methods of the new PAGs, we successfully found an entry of i- and g-line sensitive imino sulfonate PAGs **1a**, **1b**, **2a**, and **2b** (Figure 1) obtained using 9-fluorenone derivatives with aryl-ethynyl units as starting materials.

Here we report the synthesis of the PAGs **1a**, **1b**, **2a**, and **2b** and the photochemical properties of the PAGs.

Synthesis of PAGs **1a** and **1b** was performed as shown in Scheme 1. A 9-fluorenone derivative **3** was synthesized by the Sonogashira coupling reaction of arylacetylene derivatives and 2-bromo-9-fluorenone. Next, an oxime derivative **4** was obtained by the reaction of **3** with hydroxylamine hydrochloride, followed by esterification of **4** using trifluoromethanesulfonic anhydride to afford **1a**. Synthesis of **1b** was also achieved by the reaction of **4** with nonafluorobutanesulfonic anhydride. In addition, PAGs **2a** and **2b** were obtained by a similar synthetic procedure as shown in Scheme 2.

Characteristics of the PAGs are shown in Table 1. The thermal decomposition temperatures of **1a**, **1b**, **2a**, and **2b** (158–187 °C) were higher than that of FITf (135 °C). The PAGs **1a**, **1b**, **2a**, and **2b** exhibited high molar absorptivity at 365 nm (i-line). Especially, the ε values at i-line of **2a** and **2b** were about sixty times larger than that of FITf. Furthermore, the PAGs **1a**, **1b**, **2a**, and **2b** showed a strong absorption at 436 nm (g-line). Thus, the PAGs **1a**, **1b**, **2a**, and **2b** can work not only as i-line sensitive PAGs but also as g-line sensitive PAGs.

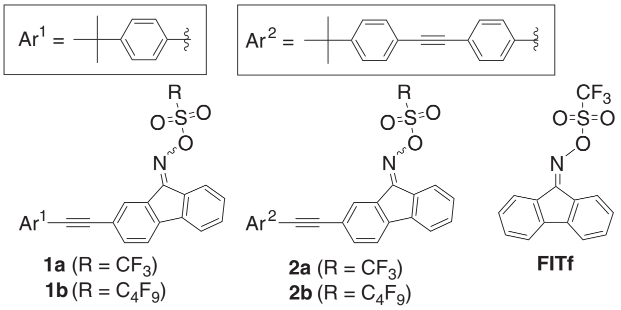
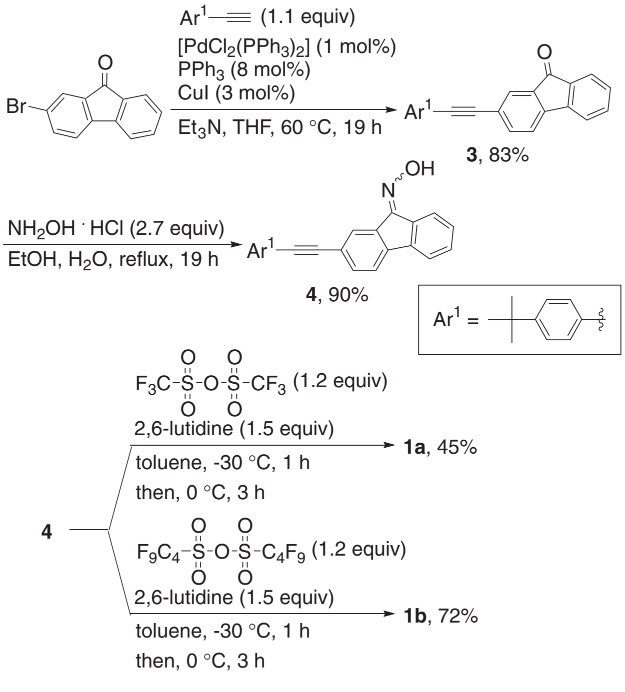
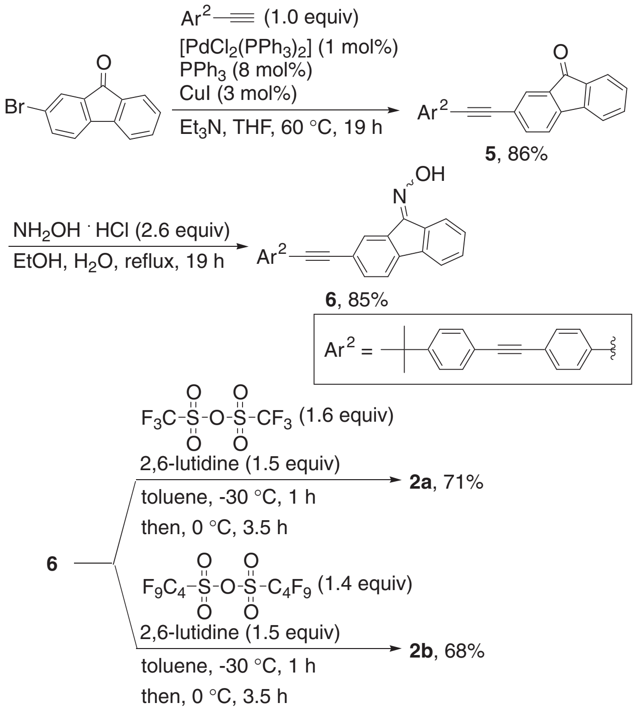


Figure 1. Structures of PAGs **1a**, **1b**, **2a**, **2b**, and FITf.



Scheme 1. Synthesis of PAGs **1a** and **1b**.

Photolysis of PAGs **1a**, **1b**, **2a**, and **2b** was examined in acetonitrile. The UV spectral changes of **1a** and **2a** on irradiation at 365 nm are shown in Figure 2. In the case of **1a**, the absorption band at 290 nm decreased on irradiation. The spectral change in photolysis of **2a** was also observed, and the absorbance at 310 nm decreased. The photolysis of PAGs **1b** and **2b** was also investigated, and similar spectral changes were



Scheme 2. Synthesis of PAGs **2a** and **2b**.

Table 1. Characteristics of PAGs

Sample	T_d/°C[a]	ε (365 nm)[b]	ε (436 nm)[b]
1a	167	773	1810
1b	158	1150	1740
2a	187	18500	3250
2b	180	17100	2880
FITf	135	300[c]	—[c,d]

[a]Determined by TG-DTA measurement under nitrogen. Heating rate; 10 °C min^{-1}. [b]In THF. [c]In acetonitrile. [d]Negligibly low.

observed. These results suggest that photolysis of PAGs **1a**, **1b**, **2a**, and **2b** proceeds via the same reaction mechanism. The photolysis of PAGs **1a**, **1b**, **2a**, and **2b** also occurred on irradiation at 436 nm. Photolysis was done at lower exposure doses to avoid side reactions at higher exposure doses.

The photolysis rate of FITf, **1a**, and **2a** was examined in acetonitrile on irradiation at 365 nm. The first-order plots for the photolysis of these PAGs are shown in Figure 3. Photoreactivities of **1a** and **2a** were from four to eight times higher than that of FITf. Furthermore, **1a** and **2a** strongly absorbed light at 436 nm compared with FITf, and therefore, the photolysis rates of **1a** and **2a** were also higher than that of FITf as shown in Figure 4. PAGs **1b** and **2b** exhibited similar photolysis rates in acetonitrile on irradiation at 365 or 436 nm compared with those of **1a** and **2a**.

Acid generation of **1a** and **2a** in acetonitrile on irradiation at 365 nm was examined using the sodium salt of tetrabromophenol blue (TBPBNa) as an indicator.[5] TBPBNa reacts with acids causing a decrease in the absorption band at 618 nm. The acetonitrile solution of PAGs **1a** or **2a** was irradiated at 365 nm for the appropriate times, and the solution of TBPBNa was added to the solution of the photolyzed PAGs. As a result, the decrease of the absorption band of TBPBNa was observed (Figure 5). These results suggest that **1a** and **2a** decompose and generate acids on the irradiation at 365 nm. The photoinduced acid generation of **1b** and **2b** was also confirmed by a similar experiment described above.[6]

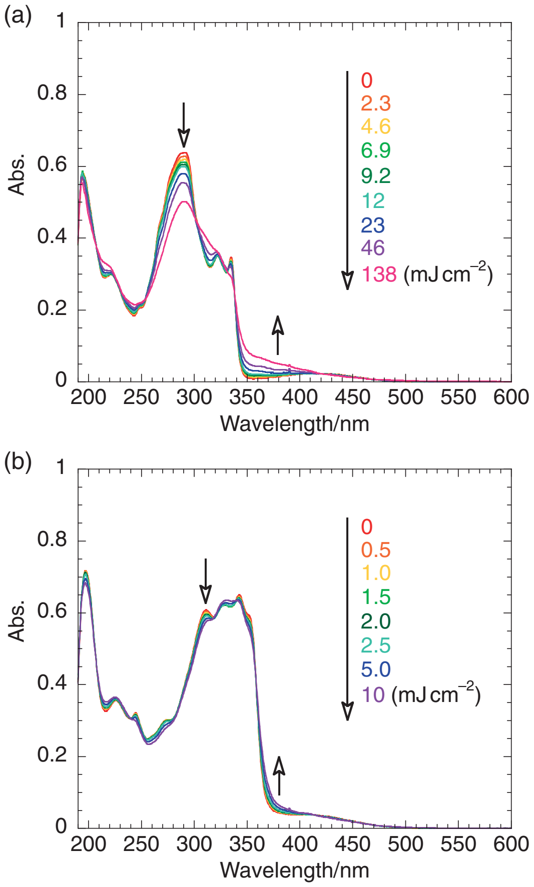


Figure 2. UV–vis spectral changes of (a) **1a**, (b) **2a** in acetonitrile on irradiation at 365 nm. [**1a**] = 1.20 × 10^{-5} M, and [**2a**] = 1.23 × 10^{-5} M.

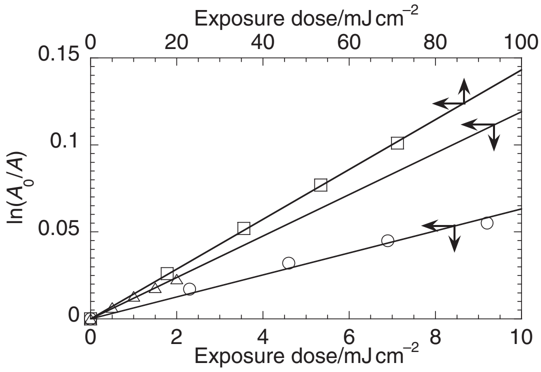


Figure 3. Photolysis of **1a** (○), **2a** (△), and FITf (□) in acetonitrile on irradiation at 365 nm.

A proposed reaction mechanism of photolysis of imino sulfonate PAGs is shown in Scheme 3.[1a] After the cleavage of

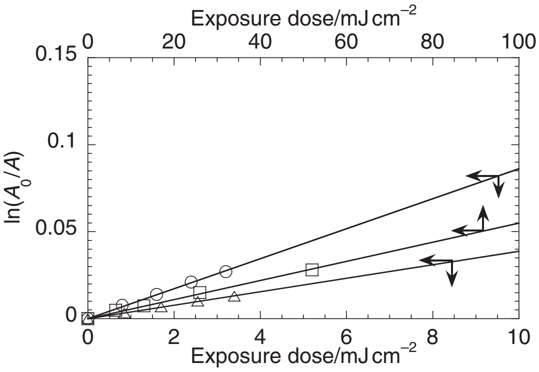


Figure 4. Photolysis of **1a** (○), **2a** (△), and FITf (□) in acetonitrile on irradiation at 436 nm.

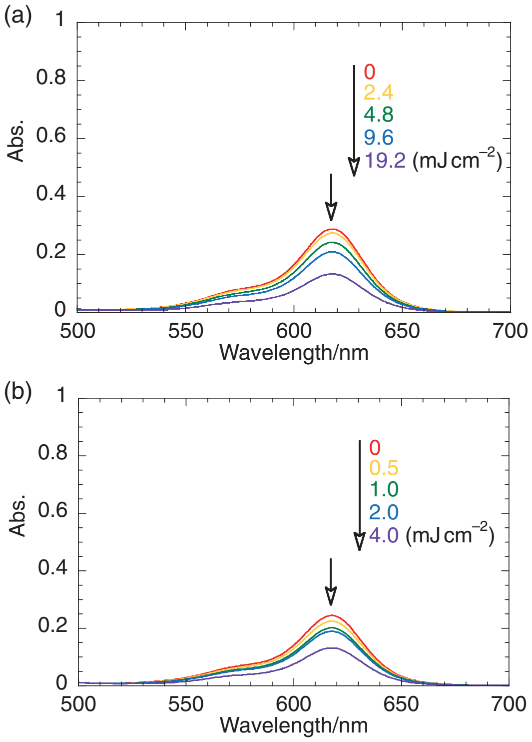
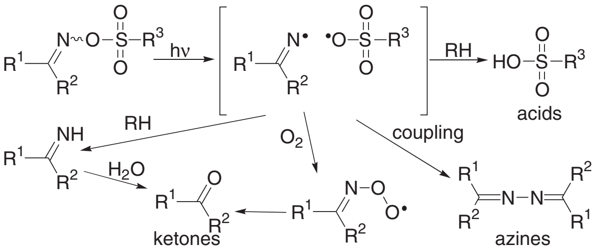


Figure 5. UV–vis spectral changes of the acetonitrile solution of tetrabromophenol blue monosodium salt (TBPBNa) by photogenerated acid from (a) **1a** or (b) **2a** on irradiation at 365 nm. [TBPBNa] = 2.70×10^{-5} M, [**1a**] = 1.20×10^{-5} M, and [**2a**] = 1.23×10^{-5} M.

–O–N= bonds on UV irradiation, sulfonic acids are formed by subsequent hydrogen abstraction from solvents with the generation of ketones and azines. The increase in absorbance around 380 nm indicates the formation of azines (Figure 2).

In conclusion, we synthesized **1a**, **1b**, **2a**, and **2b** as new i- and g-line sensitive PAGs using fluorenones functionalized with aryl–ethynyl units as starting materials.[7] The thermal stabilities and photoreactivities on irradiation at 365 or 436 nm of **1a**, **1b**, **2a**, and **2b** were superior to those of FITf. To the best of our knowledge, this is the first example of the PAG synthesis via the introduction of aryl–ethynyl units to the chromophore to improve their ability of i- and g-line sensitive PAGs. We believe that the present synthetic approach of PAGs is an efficient method to develop a variety of new PAGs. Further studies are in progress in relation to the application of PAGs **1a**, **1b**, **2a**, and **2b** to the polymeric photosensitive systems and the synthesis of other new PAGs with aryl–ethynyl units.



Scheme 3. Photolysis mechanism for imino sulfonate PAG.

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6 No UV–vis spectral change of the mixture of TBPBNa and **1a**, **1b**, **2a**, or **2b** in acetonitrile was observed under dark conditions at room temperature.

7 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.