

フェロセニル基をクロモフォアに有するスルホニウム光酸発生剤の開発

Development of Sulfonium Photoacid Generators
with a Ferrocenyl Group as the Chromophore

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1. Introduction

Photoacid generators (PAGs) are compounds with the ability of acid generation upon irradiation. They play an important role in many fields of materials science such as photoinduced acid-catalyzed polymerization systems and photoresists.¹ In particular, studies utilizing PAGs in semiconductor micromachining have actively been conducted, and therefore most of the commercially available PAGs are sensitive only to UV light. In contrast, visible light sensitive PAGs are attracting considerable attention in recent years, not only because visible light is safer than UV light, but also because of increasing demands for new PAGs applicable to the 3D printing and laser direct imaging systems.

PAGs are composed of a chromophore and an acid precursor, and therefore development of visible light sensitive PAGs requires synthesis of an appropriate chromophore unit responsible for absorption of the target visible light. However, such a chromophore often possesses a complicated π -conjugated structure, which has made the molecular design of new visible light sensitive PAGs costly and time-consuming. In this study, the author reports novel *g*-line (436 nm light) sensitive sulfonium salt PAGs² with a ferrocenyl group as the chromophore unit, which can control acid strength by changing the counter anion.

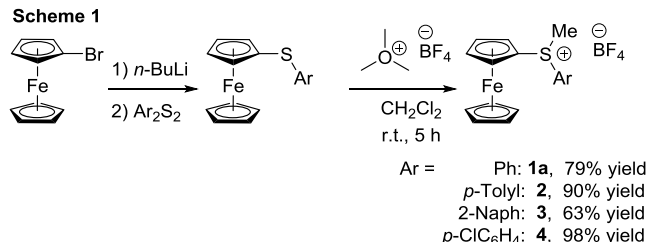
2. Experimental Section

All syntheses of complexes were carried out under an inert atmosphere by using standard Schlenk techniques, while photopolymerization by using capped vial. Organometallic products were characterized by NMR, IR, X-ray diffraction, UV-vis spectroscopy and elemental analyses.

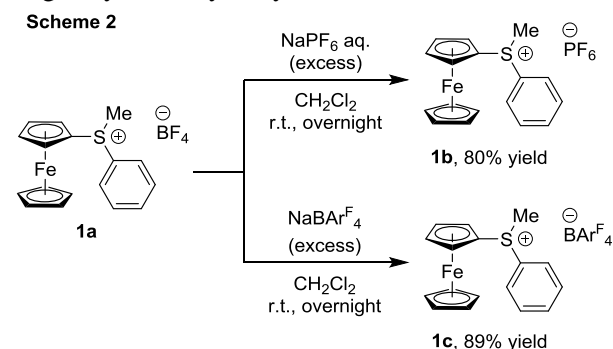
3. Results and Discussion

Synthesis of sulfonium salt type PAGs 1a and 2–4

Synthesis of PAG **1a** was performed as shown in Scheme 1. Treatment of bromoferrocene with *n*-BuLi followed by reaction with Ph₂S₂ led to the formation of ferrocenyl phenyl sulfide, whose methylation with trimethyloxonium tetrafluoroborate afforded the novel ferrocene **1a** having a sulfonium moiety in the side chain as yellow crystals in 79% yield (Scheme 1). Introduction of methyl group was confirmed by ¹H NMR spectroscopy. Likewise, analogs of **1a** (**2–4**) which have a substituent on the aryl group were obtained in good yield.

Counter anion exchange reaction of PAG 1a

The PF₆⁻ and BAr₄^F (Ar^F = 3,5-(CF₃)₂C₆H₃) analogs of **1a** (**1b** and **1c**) were successfully obtained by the anion metathesis of **1a** with NaPF₆ and NaBAr₄^F (Scheme 2). These PAGs are also obtained as crystals in good yield, and complete exchange of the counter anion was confirmed by ¹⁹F NMR spectroscopy and single-crystal X-ray analysis.



Measurement of absorption properties of PAGs

To investigate the photoacid generating properties of the novel ferrocene derivatives, UV-vis spectra were confirmed. PAGs **1–4** have an absorption suitable for photodegradation by *g*-line, and the ϵ values at 436 nm are 270–309 [M⁻¹cm⁻¹] (Figure 1).

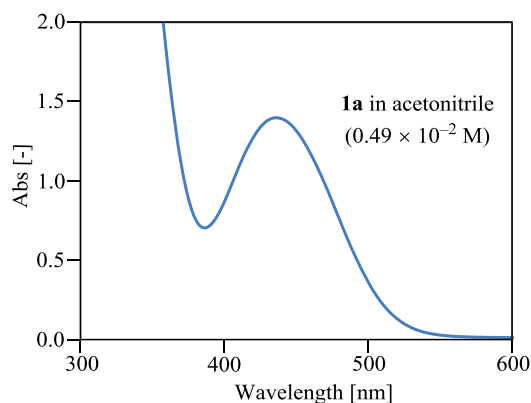


Figure 1. UV-vis spectrum of PAG **1a**.

Evaluation of photoacid generation

Acid generation from **1a** on irradiation at 436 nm was examined by using sodium salt of tetrabromophenol blue (TBPBNa).³ TBPBNa reacts with acids to cause a decrease in the absorption at 618 nm. When a CH₃CN solution of **1a** was irradiated at 436 nm for an appropriate period of time, and then a constant amount of TBPBNa solution was added to the irradiated solution of **1a**, a constant decrease of the absorption intensity of TBPBNa was observed (Figure 2). This clearly indicates that **1a** generated an acid upon irradiation at 436 nm. The acid generation of other PAGs was also confirmed by similar experiments described above. **1a–c** showed nearly the same reactivity, while **2** was less sensitive to 436 nm light.

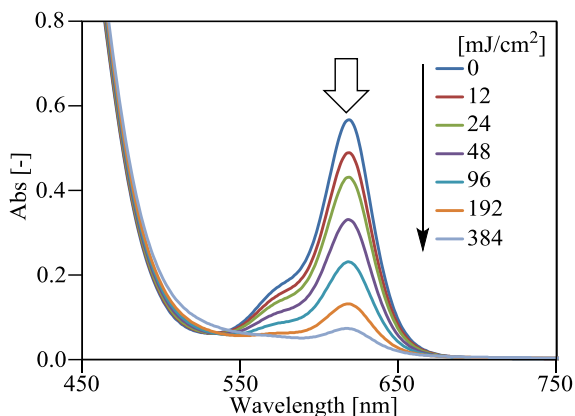


Figure 2. UV-vis spectral changes of TBPBNa by photogenerated acid from **1a**.

Photopolymerization of cyclohexene oxide

Finally, the activities of PAGs **1a–c** as an initiator for cationic photopolymerization of cyclohexene oxide (CHO) have been evaluated. A CH₂Cl₂ solution (3 mL) of CHO (1.056 g) and PAG (0.5 mol%) was irradiated at 436 nm for an appropriate period of time, and then the reaction mixture was added to aqueous NH₃/MeOH to obtain poly(cyclohexene oxide) (PCHO).

Figure 3 shows the plots of weight yield of PCHO against irradiation time. In the case of **1a**, PCHO was hardly obtained even after 50 h, whereas PAG **1c** afforded PCHO in 99.5% yield after 50 h. PAG **1b** exhibited moderate activity. These results are consistent with the strength of the generated acid.

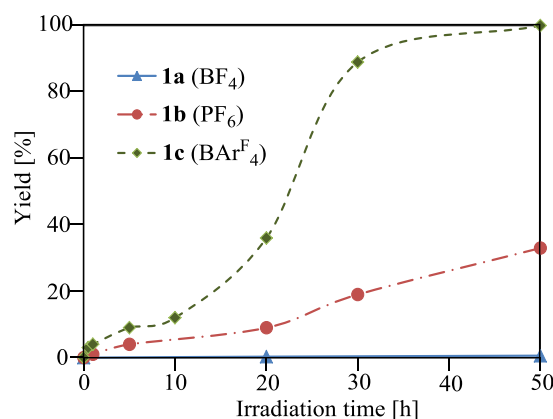


Figure 3. Plots of yield of PCHO against irradiation time.

4. Conclusion

Novel sulfonium salt type PAGs **1–4** with a ferrocenyl group as a chromophore unit were synthesized and found to have the ability of acid generation upon irradiation of 436 nm light.

References

- (a) Shirai, M.; Tsunooka, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2483. (b) Shirai, M.; Tsunooka, M. *Prog. Polym. Sci.* **1996**, *21*, 1. 2) Crivello, J. V.; *Photopolym. Sci. Technol.* **2008**, *21*, 493. 3) Allen, N. S. *et al. J. Photochem. Photobiol. A* **1997**, *111*, 229.

Presentations List

- (1) 97th CSJ Annual Meeting, 1G2-15 (2017). (2) Symposium on Organometallic Chemistry, P2-25 (2017).