



Production of three radical cations from a single photon using a photo acid generator



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ABSTRACT

Efficient generation of the organic radicals is a fundamental technology for preparing the spintronic materials. In this Letter, we present the chemical reaction of the three radical generation from a single photon. A photo acid generator which can release the multiple acid molecules via the automatic amplification mechanism was synthesized. The synthesized acid generator immediately released methanesulfonic acid by UV irradiation. Due to the amplification system, a maximum of three acid molecules can be produced from the single acid generator. In addition, the release of acid is induced by UV irradiation and automatically proceeds until the release of three acid molecules is finished. Finally, by employing the acid-catalyzed radical generation of tetrathiafulvalene, we also demonstrate the efficient radical generation triggered by UV irradiation in the polymer film.

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Introduction

Corresponded to development in spintronics, the robust materials involving the spin sources have been strongly desired to prove the theoretical predictions and apply the material functions for the practical devices. In particular, organic radicals based on the small molecules and polymeric materials have attracted much attention as a spin source because of the diversity of molecules and the tunable properties.^{1,2} To expand the applicability of the organic radical species, the fundamental technologies for the facile generation and the restrictedly control of the amount of the radical species are required. To satisfy the demands for the control of the generation, we have reported that the gradient materials with the radical concentration can be obtained in the polymer matrices with the photo-acid generator.^{3,4} Based on the acid-catalyzed radical generation via intermolecular electron transfer between tetrathiafulvalenes (TTF),⁵ variable radical concentrations can be realized in the polymer films simply by changing the light-irradiation time. Because of various advantages in the photoreaction such as the minimum requirement to additives and time- and site-specificity, chemically-active species can be localized based on the preprogrammed design in the material. However, because of the intrinsic strong light-absorbing ability of TTF cation radical in the UV and visible region, the efficiency of the photoreaction was suppressed.⁶

The further elaboration for progress of the transformation of TTF to the radical cation is necessary.

Photo acid generators are valid for the modification of the polymer-based materials.⁷ As a practical example, on the fabrication of the integrated circuits, photo acid generators are used to prepare the patterning at the substrate by mixing to the resist materials.⁷ Triggered by light irradiation, photo acid generators can play a role in the creation of the different polarity regions. For the improvement of the reaction yield, conventional photo acid generators can produce the acid species via the self-amplification system.⁸ After the initial release of acid via the photoreaction, another photo acid generator can release acid via the acid-catalyzed reaction. As a result, releasing rates should be drastically enhanced, and finally all acid generators can be consumed. Such self-catalytic mechanism can significantly contribute to the improvement of the reaction yields. Whereas, the regulation of the reaction rate and amounts of the acid species are difficult in the self-catalytic system. It is expected that the restricted control of the acid generation involving the amplification mechanism is promised to contribute not only to the efficient radical generation with TTF in the materials but also to the precise regulation of the amount of the radical species in the materials.

Herein, we present the photo acid generator for the efficient production of TTF radical cation. Our acid generator can absorb UV light and subsequently release the acid molecule. In particular, this acid generator can automatically produce a maximum of three acid molecules without assistance of the released acids. Finally, we demonstrate the acid generation can proceed not only in the

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solution but also in the film states, resulting in the generation of the TTF radical cation. This is the first example, to the best of our knowledge, to offer the amplification of the radical production from a single photon.

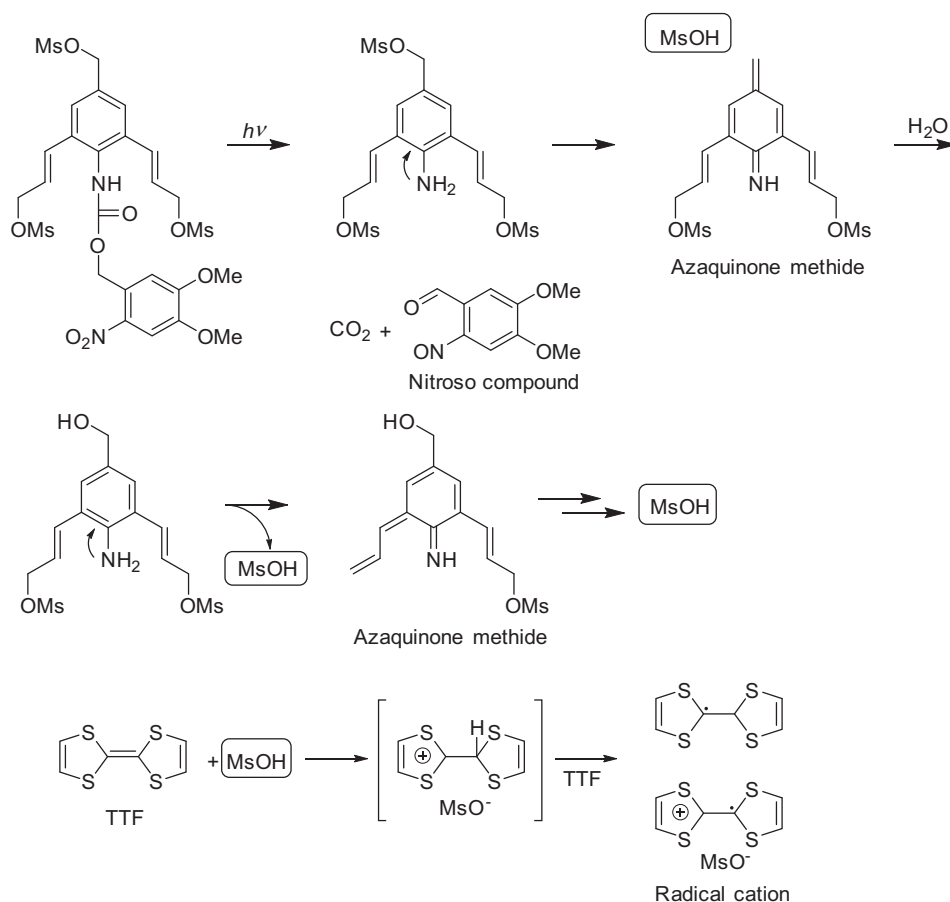
Results and discussion

The photo acid generator **7** was designed to release three equivalents of methanesulfonic acid from the single photon (Scheme 1). By UV irradiation, the *o*-nitrobenzyl ether moiety is released, followed by the generation of the amino group. Electron donation of the amino group can tandemly facilitate the release of the mesyl groups, resulting in the formation of the azaquinone methide skeleton. Subsequently, the mesyl groups at the side chains are released after the restoration of the amino group by employing residual water. Finally, three mesyl groups can be produced from a single molecule of **7**. TTF can be protonated, followed by the formation of the radical cation via the intermolecular electron transfer.⁹ Based on this reaction sequence called ‘self-immolative mechanism’, the multiple radical cations can be generated.¹⁰ Although the neutral radical could be decomposed immediately, the TTF radical cation can exist in the solution and films and show the characteristic absorption band in the visible regions. The synthesis of **7** was performed as outlined in Scheme 2. The intermediates and compound **7** were prepared from commercially available materials according to the previous reports.^{11,12} The deprotection of the *tert*-butyldimethylsilyl (TBS) group was conducted in 1 wt % HCl/THF to prohibit the degradation of the carbamate group by tetrabutylammonium fluoride (TBAF).¹³ When the reaction of **6** with mesyl chloride was conducted at room temperature or 0 °C,

chlorination occurred instead of mesylation to aryl alcohol and benzyl alcohol.¹⁴ The total value of the peak integration in the ¹H NMR spectrum of **5** was corresponded to the theoretical value. At 120 °C, the peak pattern was once simplified, and the same spectrum was reversibly detected after cooling to 25 °C. These data represent that in the synthesis of compound **5** the *cis* isomer was also generated.¹⁵

Initially, to check the photo reactivity of the compound **7**, the time-course of the spectrum change in UV–vis absorption of **7** was examined with variable time of UV irradiation (Fig. 1). By increasing UV irradiation time, the absorption band around 350 nm assigned as the nitro group decreased.^{16–18} In addition, the absorption band around 400 nm increased. These data mean the generation of the nitroso compound which is the degradation product from *o*-nitrobenzyl ether in the photoreaction. Within 30 min, the starting material was consumed. From these results, it was indicated that **7** can be activated by UV irradiation.

Next, the production of acid from **7** was investigated. To detect the existence of acid molecules, TTF was used as an indicator. It is known that TTF derivatives can be immediately transformed to TTF radical cation in the presence of acid via the intermolecular electron transfer,^{19,20} leading to characteristic absorption bands at 434 nm and 579 nm from the TTF radical cation.^{4,21} Based on these changes in the optical properties, the amount of TTF radical cation can be evaluated quantitatively.⁴ Significantly, by adding TTF to the sample, the amount of the released acid can be estimated at this moment. After UV irradiation, the TTF/acetonitrile solution was added to the photoreacted mixtures and measured UV–vis absorption spectra (Fig. 2). Significant absorption bands with the peaks at 434 nm and 579 nm were observed from the UV-irradiated sample.



Scheme 1. Plausible mechanism for the production of TTF cation radical with photo acid generator **7**.

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