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Self-Contained Photoacid Generator for Super Acid Based on Photochromic Teraylene

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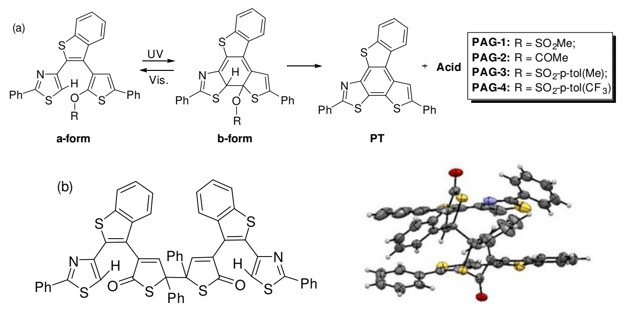
Self-contained photoacid generator for super acid along with the photoinduced 6π-electrocyclization reaction of terarylene backbone is demonstrated. Photoinitiated cationic polymerization of epoxy-monomers is achieved with efficient photochemical quantum yield, Φ_{acid} = 0.47.

Photoacid generators (PAGs) which release strong acids with light exposure have gained enormous interest over the past few decades.[1] The acid generated from the PAG is a key element for the bio-stimulation systems and the photopolymer systems such as those in photoresists for very large scale integration (VLSI)-fabrication[2,3] and photo-curable resins having acid-polymerizable epoxy units[1,2,4,5]. In the practical photo-curable polymer systems, for example, the photo-generated acid induces either polymerization of monomers or cross-linking between polymer chains leading to the less-soluble and robust resins. The acid-induced hydrolysis reaction is also practically used in the chemically amplified photoresist systems, in which the polymers in the exposed part become soluble to the developing solvents for making the positive-mode photo-patterning. New PAG backbones and their chemical modifications are still extensively studied for improved sensitivity to the deep- and near-UV light, visible light, and near-IR with two photon excitation.[8-14] Whereas previous ionic and non-ionic PAGs release the anionic part upon photoexcitation, H^+ ions and/or H radicals are extracted from coexisting hydrogen-sources such as moisture, monomers and/or polymers. This causes in the environmental dependent sensitivity of usual PAGs, in unpredictable and less reproducible by-product and also in partly incomplete acid generation, which restrict their applications[8,15,16].

Recently, the authors have proposed new class of PAGs, which is triggered by photochemical cyclization of hexatriene to cyclohexadiene structure[17-19]. Since some of terarylenes are possible to show a photon-quantitative reactivity with photochemical quantum yield close to unity,[20,22] it is facile to expect improvement in the photochemical quantum yield for photo-acid releasing reaction. Their highly photosensitive acid-releasing capability is partly because of their “self-contained” nature. That is, the compound readily release an anion and, then, H^+ ion after photochemical ring-cyclization reaction, quantitatively. Although the alkyl sulfonic acids is sufficiently strong acid for polymerization of epoxy monomers, release of super acids, such as triflic acid, CF_3SO_3H, is still challenging. Super acids are crucially demanded for some practical photo-polymers such those based on the mono-substituted epoxy, e.g. SU-8, an epoxy-based negative resist material based a resin with pending epoxy groups used for crosslinking. Some of the monomers further throw a critical demand for non-ionic PAGs and still limited number of PAGs are compatible for them. In the present manuscript, we report on a new self-contained PAG, which releases triflic acid as a super acid with high photo-chemical quantum yield.

In our former PAGs, shown in Scheme 1a, the RSO_3-and H-units were introduced at the two reactive carbon atoms of photochromic terarylene scaffold, which convert their configuration from sp^2 to sp^3 upon photocyclization and release



Scheme. 1 Previous self-contained PAGs (a) and formation of a dimer (b).

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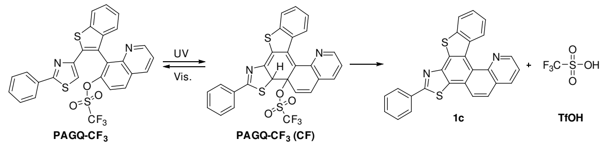

Scheme 2. Photocyclization reaction of **PAGQ-CF_3** to **PAGQ-CF_3(CF)** and the release of triflic acid forming the annulated compound **1c**.

the acids forming condensed aromatic structure.[18] That is, these PAGs are based on the photo-activation of the ionic bond-cleavage at the reaction center carbon atoms. It is associated with the relative stability of carbocation formed after releasing the RSO_3- anions. This hypothesis is supported by the expanded π-conjugation in the ring-closed form and the adjacent electro- donating sulfur atom. In the present study for the super-acid generator, unfortunately, all attempts for introducing triflateunit, CF_3SO_3-, to the terarylene backbone were failed, but we obtained a dimeric derivative (Scheme 1b, Scheme S2 and Figure S3). These results strongly suggested us the instability of CF_3SO_3- binding even in the ring-open form and motivated us to alter the aromatic unit of lower reactivity instead of thiophene, thiazole and benzo-thiophene. We here designed **PAGQ-CF_3** (Scheme 2), in which a less reactive quinoline unit was introduced for stable binding of CF_3SO_3- in the open-ring form and facile release of super acid (CF_3SO_3H) from the ring-closed form, **PAGQ-CF_3(CF)**. We expected the CH/N and S/N tethering interactions between the quinoline and the benzothiophene units and the thiazole and the benzothiophene units, respectively, for stabilizing the reactive conformation and higher photochemical reactivity. DFT calculations with ϖB97XD/ 6-31G(d) functional predicted the reactive C_2-symmetric conformation as a most stable structure associated with the CH/N and the S/N interactions. The calculated distance between CH/N atoms and S/N atoms were 2.70 Å and 3.21 Å, respectively, which are shorter than the sum of the van der Waals radii of H, N, and S atoms (Figure S13). The synthetic procedure is summarized in the supporting information.

A reference compound, **PAGQ-OMe**, showed reversible photochromic coloration and bleaching upon UV and visible light irradiation in hexane solution (Figure 1a). Clear isosbestic point at 335 nm suggested two component photochromic nature and the absorption band at 560 nm is typical for the ring-closed form isomers of diarylethene and terarylene derivatives. The reaction was *quasi*-reversible with alternative UV and visible light irradiation along with gradual decrease in the maximum absorption peak at 560 nm. UV light irradiation of a methanol solution displayed significantly different behaviour, with increasing absorption bands between 250nm-350nm and an isosbestic point at 270 nm but no absorption band in the visible range. The irreversible two component reaction in methanol is assigned to the formation of annulated compound, **1c**, after spontaneous release of methanol. The annulated compound **1c** was isolated from the irradiated solution and characterized with X-ray crystallography (Figure S13). Absorption spectrum of the **1c** (Figure S10) coincided well with the steady state absorption spectrum of Figure 1b, suggesting formation of **1c** as the major photoproduct in methanol. These results are similar to those of the terarylene derivatives based on the five-membered aromatic rings with MeO- and H- units, indicating minor effect of quinoline unit on their photochemical behaviour.

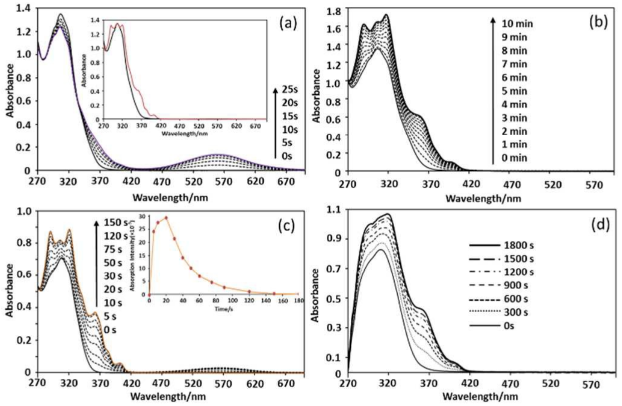

Figure 1. a) Absorption spectral change of **PAGQ-OMe** upon UV (313 nm) irradiation in hexane at r.t. (c = 5.1 × 10^{-5} M. Inset: before irradiation and after 30s irradiation followed by storing in dark for 3 min); b) in methanol at r.t. (c = 4.9 ×10^{-5}M) upon UV (313 nm) irradiation; c) Absorption spectral change of **PAGQ-CF_3** in hexane at r.t. upon UV irradiation ($\lambda_{irra.}$ = 313 nm, c = 1.98 × 10^{-5} M, Inset: change of absorbance at 564 nm); d) Absorption spectral change of **PAGQ-CF_3** in toluene (c = 2.45 × 10^{-5} M) upon UV irradiation (λ = 313 nm) at 60 °C.

Critical impact of quinoline units was observed upon preparation of **PAGQ-CF_3**. That is, we could successfully introduce a CF_3SO_3- group at the reacting center carbon atom. **PAGQ-CF_3** showed similar photo-induced coloration in pale yellow under UV light irradiation in hexane accompanying with weak absorption band at 564 nm (Figure 1c). Interestingly, this absorption band became diminishing with further UV-light irradiation. The final absorption band after the prolonged UV-light irradiation was similar to that of Figure 1b. **1c** was also isolated from the UV-irradiated solution of **PAGQ-CF_3** with HPLC. The spectral feature suggested that the **PAGQ-CF_3(CF)** formed as the intermediate before the final products **1c** and CF_3SO_3H. The acid elimination process was conveniently monitored by the pH paper with clear color change upon light irradiation (see Figure S6), and also by ^{1}H NMR measurement of **PAGQ-CF_3** in DMSO-d_6 (Figure S15). Comparing the acid-releasing capabilities of **PAGQ-CF_3** and **PAGQ-OMe** in hexane, stable $CF_3SO_3^-$ anion seems to dissociate easily in comparison with MeO^- anion. The rate-determining step should thus involve the dissociation of these anions. The CF_3SO_3- unit seems to dissociate easier than the MeO- unit, resulting in gradual formation of **1c**. Similar gradual release of CF_3SO_3H was also observed in toluene and the spontaneous reaction of **PAGQ-CF_3(CF)** was studied in dark condition after UV-light irradiation for 60 sec. The absorption band at 564 nm indicated typical first-order exponential decay with a rate constant of 1.50 × 10^{-3} s^{-1} at room temperature (Figures S11, S12). As shown in Figure 1d, **PAGQ-CF_3** immediately releases CF_3SO_3H at the elevated temperature even in toluene forming **1c** under UV light irradiation. This temperature dependent acid

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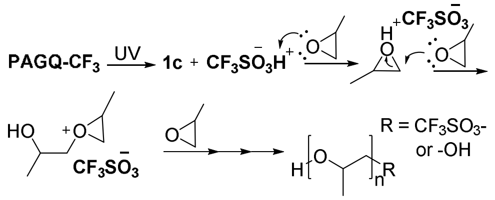
releasing capability is not a practical disadvantage, since most of cationic photo-curing process need heating the sample after photo-irradiation for facile progression of polymerization. Since the acid releasing reaction from **PAGQ-CF$_3$(CF)** proceeds quantitatively, the apparent photochemical quantum yield of acid releasing process is determined by the initial photo-chemical cyclization reaction. The apparent photochemical quantum yield from **PAGQ-CF$_3$** to **1c** was 0.47 in toluene, which is among the highest values for PAGs for super acids so far reported. Those in chloroform and methanol were 0.40 and 0.3, respectively, which are still higher than the previous non-ionic PAGs for super acids. [8,16,23] Although the acid releasing reactivity depends on the environment and may be less at lower temperature, the self-contained elimination reaction guarantees for a high overall efficiency of acid formation that exceeds that of other PAGs. The decrease of the quantum yield with increasing the solvent polarity is consistent with our previous reported,[17,18] where the hydrogen binding like CH-N interaction and CH/π interaction play a certain role to support the photoreactive conformation.[19,20] Photochemical and photo-physical data of **PAGQ-CF$_3$** and **1c** were summarized in ESI (Table S3).



Scheme 3. Reaction scheme of photo-induced cationic polymerization of propylene oxide

We then investigated capability of **PAGQ-CF$_3$** for triggering the cationic polymerization of propylene oxide. After UV irradiation to a mixture of propylene oxide and 0.2 mol% of **PAGQ-CF$_3$**, formation of polymerized products was confirmed as a series of mass peaks with the interval of 58 (Scheme 3, Figure S16). This result displayed significant contrast with our previous PAGs releasing CH_3SO_3H, which served as a photo-initiator of polymerization for cyclohexane oxide but not for the mono-substituted epoxy such as propylene oxide.[17,18] We further demonstrated capability of **PAGQ-CF$_3$** for photo-polymerization patterning of SU-8 (Figure S17). In this procedure, we conducted pre- and post-curing for well-defined photo-patterning formation, which indicates thermal stability of **PAGQ-CF$_3$** in the non-irradiated area.[18]

The nitrogen atom at the quinoline unit seems not to inhibit the cationic polymerizations of epoxy monomers, which must be associated with the specific CH/N hydrogen bonding suggested in the structure given by X-ray analysis and DFT-calculation of **1c** (Figures S13 and S14). The distance between H and N atoms is about 0.22 nm, which is markedly shorter than the sum of van der Waals radii (0.27nm). Significant ^{1}H-NMR shift was observed (Figure S15) due to the strong non-covalent interaction. These results suggest tightly binding CH/N interaction in **1c**, suppressing proton-binding capability of the quinoline unit.

In summary, newly designed self-contained photoacid generator with quinoline group was synthesized, which releases CF_3SO_3H as super acid. **PAGQ-CF$_3$** showed apparent photochemical quantum yield from 30% to 47 %, highest among the PAGs for super acids. Cationic polymerization of epoxy monomers and photo-polymerization patterning of SU-8 were successfully induced by UV-light irradiation for **PAGQ-CF$_3$**.

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Super acid is efficiently released from self-contained photoacid generator based on triangle terarylene backbone upon photoinduced 6π-electrocyclization reaction.