

SHORT COMMUNICATIONS

Diphenyliodonium Salts with Environment-friendly Dye for a Photo-acid Generator in Chemically Amplified Resist

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Chemically amplified resists based on acid catalyzed reaction have been widely utilized in the development of semiconductor technology and resists.

Photo-acid generator (PAG) that generated acids upon irradiation with light has been played an important role on the progress of chemically amplified resist.

In general, the required properties for PAGs are high sensitivities, high thermal stability, strong acid generation and high solubility in solvents and matrices. In addition, it is important that PAG and precursor of acid are non-mutagen.

PAG's molecules were classified into ionic structure such as onium salts of sulfonate derivatives and non-ionic structure such as sulfonate derivatives of *N*-hydroxynaphthaleneimide.

In the PAGs, onium salts have advantage of easy structure modification to alter their spectral absorption characteristics.

Then various onium salts were applied as a PAG in photolithography.^{1–8} The PAGs that have photosensitivity at 193 nm or 248 nm have been studied, however, there were a few reports about the onium salt's PAGs for 365 nm light^{9–13} and moreover, few reports about PAGs and the precursor of acid considered the safety and environmentally sensitive technology.

In this study, we reported a new type PAG with environment-friendly dye that has photosensitivity at 365 nm light. The PAG is triiodonium salt of 9-hydroxypyrene-1,4,6-trisulfonic acid (PC-DPI, **1**). The dye (**2**) is referred to as pyranine conk that contained cosmetic and shampoo, recently.

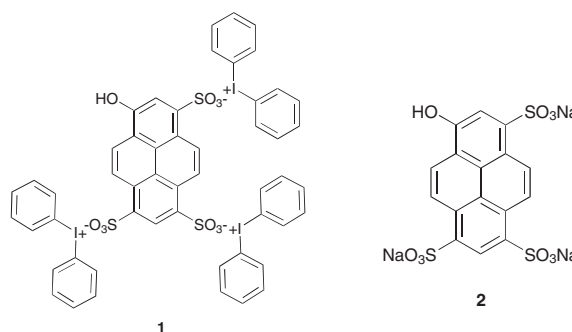


Figure 1. Structure of PAG (**1**) and Dye (**2**).

EXPERIMENTAL

Reagent

All of the solvents used in this study were commercially available, and used after being dehydrated with molecular sieves.

Materials

Pyranine conk, **2** (Hodogaya Chemical) and diphenyliodonium chloride (Tokyo Kasei, DPI-Cl) were used as received. Tetrabromophenol blue (TBPB) and *p*-toluenesulfonic acid was purchased from Wako Pure Chemicals. Tetrabutylammonium hydroxide (TMAH) 2.38 wt % solution was purchased from Tama Chemical Company.

Preparation of tris(diphenyliodonium)9-hydroxy-pyrene-1,4,6-trisulfonate · 3H₂O PC-DPI (**1**)

An amount of 0.5 g (0.95 mmol) of **2** and 0.97 g (3.04 mmol) of DPI-Cl were dissolved in water each other. Pyranine conk solution was dropped into DPI-

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Cl solution. Stirring at 40 °C was continued for 2 h, and filtrated. PC-DPI was then recrystallized two times from water (1.02 g, 79.4%) No attempt was made to maximize product yields. mp 199.9 °C (Decomposition temp.) *Anal.* Calcd for C₅₂H₄₃I₃O₁₃S₃: C, 46.17; H, 3.20; I, 28.14; S, 7.11. Found: C, 45.57; H, 3.17; I, 28.03; S, 7.14. ¹H NMR (400 MHz, DMSO) δ 2.54 (s, 6H), 7.52 (t, 12H), 7.64 (t, 6H), 8.15 (s, 1H), 8.24 (d, 12H), 8.28 (d, 1H), 8.86 (d, 1H), 8.98 (m, 3H) and 10.63 (s, 1H); IR (KBr pellet) 3250 cm⁻¹, 1475 cm⁻¹, 1440 cm⁻¹, 1200 cm⁻¹, 1060 cm⁻¹, 975 cm⁻¹, 740 cm⁻¹ and 670 cm⁻¹.

Measurement

Ames test examined the mutagenesis of PC-DPI and pyranine conk.

The test is one of the mutagenic test for chemicals. The bacterium used in the test is a strain of *Salmonella typhimurium* that carries a defective gene making it unable to synthesize the amino acid histidine from the ingredients in its culture medium. However, some types of mutations can be reversed, a back mutation, with the gene regaining its function. These revertants are able to grow on a medium lacking histidine.

A suspension of a histidine requiring strain of *Salmonella typhimurium* had been plated with a mixture of rat liver enzymes on agar lacking histidine. The disk of filter paper was impregnated with DMSO solution in 10 or 50 mg of the chemical (PC-DPI or pyranine conk). The control disk of filter paper was impregnated with DMSO only. The mutagenic effect of the chemical caused two bacteria (TA-100, TA-98) to regain the ability to grow without histidine, forming the colonies seen around the disk. If the number of the scattered colonies was more than that of the control, the chemical was a mutagen. If the number of the scattered colonies was equal or less than that of the control, the chemical was not a mutagen.

UV-visible spectra were recorded in 1.00 × 1.00 cm quartz cells by a HITACHI U-3000 spectrophotometer.

Steady-state fluorescence spectra were recorded with samples in 1.00 × 1.00 cm quartz cells in a HITACHI MPF-2A fluorescence spectrophotometer.

Redox Potentials were measured by cyclic voltammetry with Hokuto-Denko Function Generator HB-104 and a potentiostat/galvanostat HA-301. Electrochemical measurements were carried out using a three-electrode cyclic voltammetric cell. The working electrode was a platinum wire and the reference electrode was calomel electrode. The electrolyte was 0.1 M tetrabutylammonium perchlorate in DMF. The voltammograms were scanned at 50 mV s⁻¹. All potentials are calculated vs. SCE as E_{1/2} values, where E_{1/2} = 0.5(E_{pa} + E_{pc}); E_{pa} and E_{pc} are the anodic

and cathodic peak potentials, respectively.

The acid generation yield was measured using TBPB as an acid indicator.¹² The acetonitrile solution of PAG (1.41 × 10⁻⁵ mol dm⁻³) in quartz cell was irradiated at 365 nm wavelength light with a filter from super high-pressure mercury lamp (365 nm, 2.8 mJ/cm²). After irradiation, 3 mL of the solution was mixed with 1 mL of 5.59 × 10⁻⁵ mol dm⁻³ acetonitrile solution of TBPB and the absorption spectrum of the mixture was measured. Changes of absorption spectra of TBPB at 618 nm were compared.

Lithographic Evaluation

The photolithographic evaluation of the photopolymer involved a PAG was showed by the relationship between the exposure dose and the normalized film thickness after development. The 1.0 mm thickness film consisted of poly(4-*t*-butoxycarbonyl-styrene) and 3 wt % PAG for photopolymer was prepared on silicon wafer and pre-baked at 110 °C for 2 min. The exposure was carried out using a super high-pressure mercury lamp (365 nm, 2.8 mJ/cm²). Exposed resists were post-exposure baked at 110 °C for 5 min on a hot-plate and developed in a 2 wt % TMAH solution for 12 s.

RESULTS AND DISCUSSION

The results of Ames test were described in Table I.

The number of revertant colonies for pyranine conk and PC-DPI was equal to that for control. The results indicated that pyranine conk and PC-DPI were not mutagens.

Figure 2 shows the absorption spectra of pyranine conk and DPI-Cl and the fluorescence spectrum of pyranine conk in oxygen-free MeOH.

Pyranine conk has the strong absorption peaks at 230 nm, 280 nm and a broad absorption with vibrational structure in the wavelength region of 310–420 nm and a broad and structureless fluorescence spectrum in the wavelength region from 380 to 530 nm. The absorption of pyranine conk extends to longer wavelength than that of DPI-Cl. From these spectra, the lowest excited singlet state energy (ΔE₀₀) of pyranine conk was estimated to be 69.56 kcal/mol.

PC-DPI was synthesized by reaction of pyranine

Table I. Ames test of pyranine conk and PC-DPI used two bacteria (TA-100 and TA-98).

	The number of revertant colonies	
	TA-100	TA-98
DMSO	149	59
Pyranine conk	137	60
PC-DPI	123	61

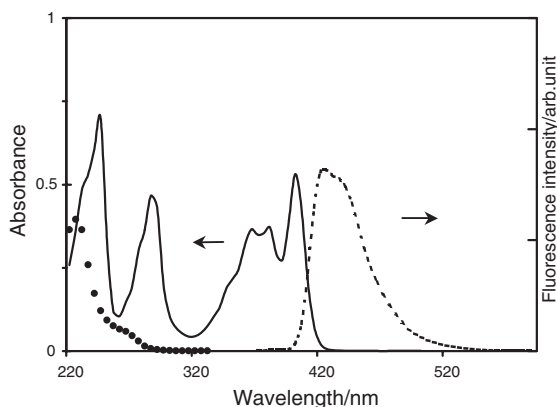


Figure 2. Absorption (—) and fluorescence (---) spectra of pyranine conk in MeOH. Absorption spectrum of DPI-Cl (●) in MeOH. The concentration of pyranine conk and DPI-Cl were 2.18×10^{-5} and 2.28×10^{-5} mol dm $^{-3}$, respectively; the excitation wavelength was 365 nm in the fluorescence spectrum.

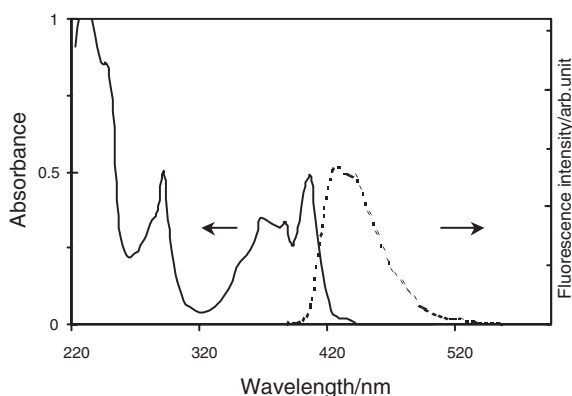


Figure 3. Absorption (—) and fluorescence (---) spectra of PC-DPI in MeOH. The concentration of PC-DPI was 1.47×10^{-5} mol dm $^{-3}$; the excitation wavelength was 365 nm in the fluorescence spectrum. Absorption coefficient of PC-DPI at 365 nm: 2.36×10^4 M $^{-1}$ cm $^{-1}$.

conk and DPI-Cl in water. Figure 3 shows the absorption and fluorescence spectrum of PC-DPI in oxygen-free MeOH.

The electrochemical behavior has been studied in DMF solution with tetrabutylammonium perchlorate as the supporting electrolyte. The oxidation potentials ($E_{1/2ox}$) of pyranine conk were -0.79 V *vs.* SCE and the reduction potentials ($E_{1/2 red}$) of DPI-Cl were -0.81 V *vs.* SCE. Based on these values of redox potentials, the free-energy changes (ΔG) accompanying the electron transfer from the lowest excited single state of pyranine conk to DPI's can be calculated according to the Rehm–Weller equation, where

$$\Delta G = 23.06\{E(D/D^{+\bullet}) - E(A^{-\bullet}/A) - C\} - \Delta E_{00}E(D/D^{+\bullet})$$

is the oxidation potential of the donor. $E(A^{-\bullet}/A)$ is the

reduction potential of the acceptor. ΔE_{00} is the electronic energy corresponding to the excited singlet state of the donor and C is the Coulombic interaction energy of 1–2 kcal/mol in the polar solvent.

In the case between pyranine conk anion and DPI cation in the PC-DPI molecule, the value of ΔG is calculated to -28 kcal/mol without considering the coulombic interaction. The results indicated that the intramolecular electron transfer from anion to cation can take place quantitatively.

The acid generation yield was measured using TBPB as an acid indicator. Absorption band of TBPB at around 618 nm was changed by the addition of an acid quantitatively. Absorption changes of TBPB using *p*-toluenesulfonic acid as a standard material were calibrated. Quantum yield was determined from absorption changes at 618 nm due to acid generation. The quantum yield of acid generation from PC-DPI was 0.72.

The quantum yields of diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate, *N*-trifluoromethylsulfonyloxy-1,8-naphthalimide and fluorenylideneimino trifluoromethanesulfonate that is recent representative PAGs are 0.18, 0.17 and 0.32, respectively.^{10–12} The PAG's quantum yields was much higher than that of these PAGs. The results were associated that the higher acid generation yield of PC-DPI has relation with the more reaction point.

We carried the photolithographic evaluation of the PAG in photopolymer. Figure 4 shows the relationship between the exposure dose and the normalized film thickness after development. The sensitivity at 365 nm of the new PAG was 30.7 mJ/cm 2 . The photopolymer has sufficient sensitivity in the non-optimized step.

This is a positive working resist which shows solu-

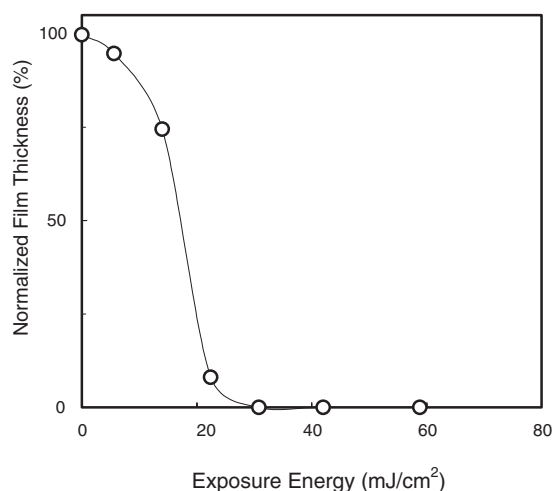


Figure 4. Characteristic curves of the photopolymer involved PC-DPI 3 wt %.

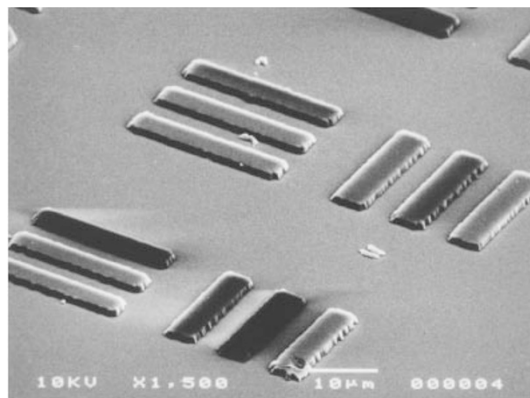


Figure 5. The SEM photograph of pattern from poly (4-*t*-butoxycarbonyl-PHS) with PC-DPI 3 wt %.

bility change due to deprotection by the acid from PAG and subsequent bake.

The SEM micrograph of pattern from the photopolymer with 3 wt % PC-DPI is shown in Figure 5.

CONCLUSIONS

We designed and presented the new environment-minded PAG with non-mutagenic dye for 365 nm chemically amplified resist.

The quantum yield of acid generation by irradiation of the 365 nm was 0.72. The photo-acid generating efficiency in polymer bearing *t*-butoxycarbonyl protecting group was 30.7 mJ/cm². The PC-DPI was examined to be non-mutagen by Ames test. These results show that the PC-DPI has sufficient potential for

365 nm chemically amplified resists and low-damaging materials for environment and human.

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