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A new positive-type photoresist based on mono-substituted hydroquinone calix[8]arene and diazonaphthoquinone

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Mono-substituted hydroquinone calix[8]arenes **1a** and **1b** were synthesized by the debenzylation of *O*-substituted *p*-benzyloxyphenol calix[8]arenes which were prepared by the cyclization of *p*-benzyloxyphenol and paraformaldehyde in the presence of a base, followed by acylation with acetic anhydride or toluene-*p*-sulfonyl chloride. The calixarenes provide highly transparent films from their solutions in ethyl lactate (EL). A new positive-type photoresist based on the calix[8]arene **1b** having toluene-*p*-sulfonate groups as a base-developable matrix and diazonaphthoquinone-4-sulfonate [DNQ(4)] or -5-sulfonate [DNQ(5)] as a photoreactive dissolution inhibitor has been successfully developed. The difference of dissolution rates for this resist system toward 1.5 wt% aqueous tetramethylammonium hydroxide (TMAH) solution reached 1300–5000 times before and after UV radiation (200 mJ cm^{-2}). Thus, the photoresists containing 25 wt% of DNQs showed high sensitivities of 30–37 mJ cm^{-2} (D) and contrasts of 2.5–2.8 (γ) when they were exposed to 365 nm light and post-exposure baked (PEB) at 100 °C for 90 s, followed by developing with 1.5 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature. A fine positive image featuring 1 µm of minimum line and space patterns was also printed on the film which was exposed to 40 mJ cm^{-2} by the contact mode.

Since novolac resin–diazonaphthoquinone (DNQ) photoresist was first introduced for 16 Kbit DRAM production in 1972, UV lithography has begun to be developed as a promising technology for manufacturing DRAMs.[1] The initial advantages of the novolac–DNQ resist are the higher resist contrast and the absence of swelling during development. The characteristics which have led this resist system to the most successful photoresist are their high dry-etch resistance and the environmentally favorable aqueous base developer. Therefore novolac–DNQ resist is still the 'workhorse'.[2]

The growth of the recent resist is supported by the new photo-imaging concept of 'dissolution inhibition' which is fundamentally different from the classic rubber–bisazide system.[1] The 'dissolution inhibition' behavior is based on a kinetic effect which is indicated as a difference in dissolution speeds between exposed and unexposed regions, and not in solubility, while the imaging process for the classic negative resist depends on the insolubility of the fully exposed region. The resist performance is influenced by various factors which are induced by characteristics of novolac resin and DNQ, therefore the influences have been continuously studied to develop higher contrast photoresists.[3] However, the synthesis of novolac resin from *o*-cresol and formaldehyde cannot be well controlled to give products with constant properties. Even small changes in the experimental conditions affect the amount of the different bond types, *o,o*-, *o,o′*-, *p,o*-, and *p,o′*-linkages, which cause branched structures and changing of molecular weight and molecular weight distribution.[4] On the other hand, macrocyclic novolac oligomers or 'calixarenes' which are prepared by the base catalyzed condensation of *p*-alkylphenol and formaldehyde have been found to have definite cyclic structures consisting of the corresponding phenol moieties and *o,o*-methylene bridges.[5] Their highly regular structures, furthermore, allow them to be easily isolated by means of well-controlled preparation conditions and further purification. However, the formation of intramolecular hydrogen bonds between hydroxy groups induces high melting points and low solubility not only in most organic solvents, but also in aqueous bases.[5] The only example of an E-beam photoresist based on *p*-alkylphenol calix[6]arenes has been reported, but *O*-acetylation and an organic developer were required.[6]

Calix[4]resorcinarenes (C4-RAs), which are readily prepared by the acid-catalyzed condensation of resorcinol and aldehydes, have a good solubility in high polar organic solvents such as alcohols and aqueous alkaline bases.[7] Because their optical properties are similar to those of novolac resin, we successfully introduced C4-RAs to the negative working photoresist including a polyfunctional benzylic alcohol as a cross-linker and a photo-acid generator.[8]

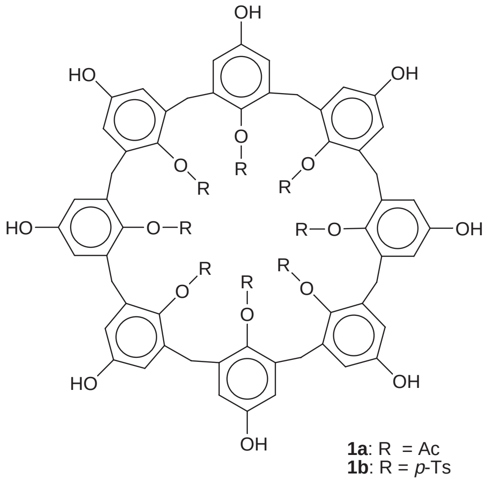
Recently Shirota *et al.* reported guidelines for molecular design of low-molecular weight amorphous materials (called 'amorphous molecular materials'),[9] that is, increasing the number of conformers by lowering the symmetry of non-planar molecules. We are interested in the concept of amorphous molecular materials that provide a new matrix in the resist system in place of polymers. We also have found that *O*-substitution of C4-RA with bulky groups gave more favorable materials which belonged to the amorphous molecules.[10] Nevertheless, C4-RAs still have some problems regarding their characteristics for the DNQ resist.

We have focused on mono-substituted calix[8]arene (**1**) as the amorphous molecular material, which consists of the corresponding mono-substituted hydroquinone moieties and *m,m*-methylene bridges.[11] The calixarenes **1** were expected to have suitable dissolution characteristics for the DNQ resist because the phenolic hydroxy groups of **1** face out of the ring in the planar model. In this paper, the syntheses and the characterizations of mono-substituted hydroquinone calix[8]arenes **1a** and **1b**, and lithographic evaluations including dissolution studies of DNQ resists based on **1** are described.

Experimental

Materials

2,3,4-Tris[2-diazo-1-oxonaphthalen-4-ylsulfonyloxy]benzophenone {diazonaphthoquinone-4-sulfonate [DNQ(4)]} and 2,3,4-tris[2-diazo-1-oxonaphthalen-5-ylsulfonyloxy]benzo-



mono-substituted hydroquinone calix[8]arene (**1**)

Planar models of mono-substituted hydroquinone calix[8]arene **1**.

phenone {diazonaphthoquinone-5-sulfonate [DNQ(5)]} were kindly donated by Toyo Gosei Kogyo and used without any purification. Solvents were dried and purified in the usual manner, and stored under an atmosphere of argon. Most manipulations were carried out either under dry, oxygen-free argon or nitrogen or under vacuum with Schlenk-type flasks.

Synthesis of 5,11,17,23,29,35,41,47-octakis(benzyloxy)-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene 2

To a hot solution of *p*-benzyloxyphenol (10.00 g, 0.05 mol) in 60 ml of xylene, which was placed in a 300 ml three-necked flask equipped with a Dean–Stark trap, a nitrogen inlet, and a glass cap and heated on an oil bath at 80 °C, was added potassium *tert*-butoxide (0.25 g, 0.0011 mol). After the mixture was stirred at 80 °C for 30 min, paraformaldehyde (2.62 g, 0.082 mol) was added to the mixture, and then the solution turned clear immediately. The oil bath temperature was increased to 150 °C over 1 h and kept at this temperature until a precipitate appeared. Then the bath temperature was increased to 170 °C and the reaction mixture was refluxed, trapping the produced water, for 12 h. The mixture was cooled with an ice bath and the precipitate was collected with a glass filter. The brown powder obtained was added to 200 ml of hot acetone and then the mixture was stirred for 2–3 h. The pale yellow powder was collected, washed with acetone, and dried under reduced pressure at 100 °C. Further purification with hot acetone selectively gave the pure octamer [Yield: 5.98 g (56%)]. ^{1}H-NMR (270 MHz, DMSO-d_6) δ 8.68 (s, OH, 8H), 7.23–7.30 (m, ArH, 40H), 6.61 (s, ArH, 16H), 4.83 (s, CH_2, 16H), 3.78 (s, CH_2, 16H).

Synthesis of 49,50,51,52,53,54,55,56-octakis(acetoxy)-5,11,17,23,29,35,41,47-octakis(benzyloxy)calix[8]arene (3a)

To a mixture of **2** (2.00 g, 9.4 mmol) in 25 ml of acetic anhydride were added a few drops of pyridine and then the mixture was refluxed for 5 h. Excess acetic acid was quenched with cold methanol, and the precipitate was collected with a glass filter and washed with water and methanol. Cyclohexane was slowly added to a saturated solution of the product in toluene previously prepared. A precipitate was collected with a glass filter and dried under reduced pressure at 100 °C. 1.57 g (66%) of compound **3a** was obtained. IR (KBr) ν 1760 (C=O), 1050 and 1210 cm^{-1} (C–O–C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.26 (s, ArH, 40H), 6.53 (s, ArH, 16H), 4.78 (s, CH_2, 16H), 3.55 (s, CH_2, 16H), 1.94 (s, CH_3, 24H).

Synthesis of 5,11,17,23,29,35,41,47-octakis(benzyloxy)-49,50,51,52,53,54,55,56-octakis(*p*-tolylsulfonyloxy) calix[8]arene (3b)

A mixture of **2** (2.12 g, 1.25 mmol) and K_2CO_3 (2.07 g, 15 mmol) in 60 ml of THF was refluxed for 1 h and then toluene-*p*-sulfonyl chloride was added to the mixture. After the mixture was refluxed for 12 h, it was filtered through a filter paper and the filtrate was evaporated. The residue was dissolved in ethyl acetate and the solution was washed with 10% aqueous Na_2CO_3 solution and saturated aqueous NaCl solution. The organic phase was separated and dried over $MgSO_4$ and evaporated after the drying reagent was filtered off. The residue was poured into hexane and a product was collected as a precipitate. In order to remove remaining toluene-*p*-sulfonyl chloride from the product, Soxhlet extraction was carried out with propan-2-ol. 2.18 g (60%) of **3b** was obtained as a yellow powder. IR (KBr) ν 3000–3700 (O–H), 1360 and 1170 cm^{-1} (S=O); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.70 (s, ArH, 16H), 7.09 (s, ArH, 40H), 6.99 (s, ArH, 16H), 6.26 (s, ArH, 16H), 4.38 (s, CH_2, 16H), 3.78 (s, CH_2, 16H), 2.24 (s, CH_3, 24H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 156.9, 145.7, 139.4, 136.4, 135.7, 133.2, 130.0, 128.3, 128.1, 127.8 127.5 and 115.3 (ArC), 69.5 (Ar-CH_2-O), 31.5 (Ar-CH_2-Ar), 21.4 (CH_3); Anal. calc. for $C_{168}H_{144}O_{32}S_8$: C, 68.83; H, 4.95%. Found: C, 68.94; H, 4.93%.

Debenzylation of 3 with a palladium catalyst (synthesis of debenzylated compound 1)

A mixture of **3** (1 mmol) and 0.25 g of 10% Pd/C in THF was stirred at 50 °C under H_2 atmosphere for 17 h. The Pd/C was filtered off and the filtrate was evaporated. The residue was dissolved in 50 ml of ethyl acetate and the solution was washed with water. Then the organic phase was dried over $MgSO_4$ and filtered through a filter paper and the filtrate was concentrated. The concentrated solution was poured into hexane and the precipitated product was collected with a glass filter. A saturated solution of the product in 20 vol% aqueous methanol solution was refluxed for 12 h to give a white powder. Methanol included in the product was removed by co-evaporation with acetone under reduced pressure. Reprecipitation in hexane was finally carried out to give pure **1** as a white fine powder.

49,50,51,52,53,54,55,56-Octakis(acetoxy)-5,11,17,23,29, 35,41,47-octahydroxycalix[8]arene 1a. Yield: 95%; IR (film on NaCl) ν 3000–3700 (O–H), 1759 cm^{-1} (C=O); ^{1}H NMR (270 MHz, DMSO-d_6) δ 9.25 (s, OH, 8H), 6.39 (s, ArH, 16H), 3.35 (s, CH_2, 16H), 1.96 (s, CH_3, 24H); ^{13}C NMR (67.5 MHz, DMSO-d_6) δ 169.4 (C=O), 155.1, 139.7, 133.3, and 115.6 (ArC), 30.7 (Ar-CH_2-Ar), 20.0 (CH_3); Anal. calc. for $C_{72}H_{64}O_{24}\cdot 8H_2O$: C, 60.85; H, 5.39%. Found: C, 61.01; H, 5.40%.

49,50,51,52,53,54,55,56-Octakis(*p*-tolylsulfonyloxy)-5,11, 17,23,29,35,41,47-octahydroxycalix[8]arene 1b. Yield: 82%; IR (KBr) ν 3000–3700 (O–H), 1360 and 1170 cm^{-1} (S=O); ^{1}H NMR (270 MHz, DMSO-d_6) δ 9.27 (s, OH, 8H), 7.68 (s, ArH, 16H), 7.31 (s, ArH, 16H), 6.10 (s, ArH, 16H), 3.59 (s, CH_2, 16H), 2.23 (s, CH_3, 24H); ^{13}C NMR (67.5 MHz, DMSO-d_6) δ 155.8, 146.0, 137.8, 135.2, 132.6, 130.3, 127.7, and 115.7 (ArC), 30.8 (Ar-CH_2-Ar), 20.9 (CH_3); Anal. calc. for $C_{112}H_{96}O_{32}S_8$: C, 60.86; H, 4.38%. Found: C, 60.51; H, 4.43%.

Photosensitivity

Compound **1** was dissolved at 20 wt% in ethyl lactate at room temperature, and to this solution was added DNQ. Films spin-cast at 2000 rpm for 20 s on silicon wafers were prebaked at

100 °C for 60 s and exposed to a filtered super-high pressure mercury lamp (Ushio USH-200DP). Imagewise exposure through a mask was carried out in a contact-printing mode.

Dissolution rate

Silicon wafers coated with 0.9 μm thick resist films, which were prepared by the above procedure, were exposed at 365 nm wavelength to the filtered super-high pressure mercury lamp for the appropriate times. After the wafers were baked at 100 °C for 90 s, they were developed in a 1.5 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature, and rinsed with water. The dissolution rates were based on differences of the thickness of the exposed films before and after development for 60 s. The changes in the film thickness against exposure energy were measured by means of a Dectak^3 system (Vecco Instruments Inc.). Each plot on the characteristic curves was obtained from a new exposure–development (60 s) experiment on individual wafers.

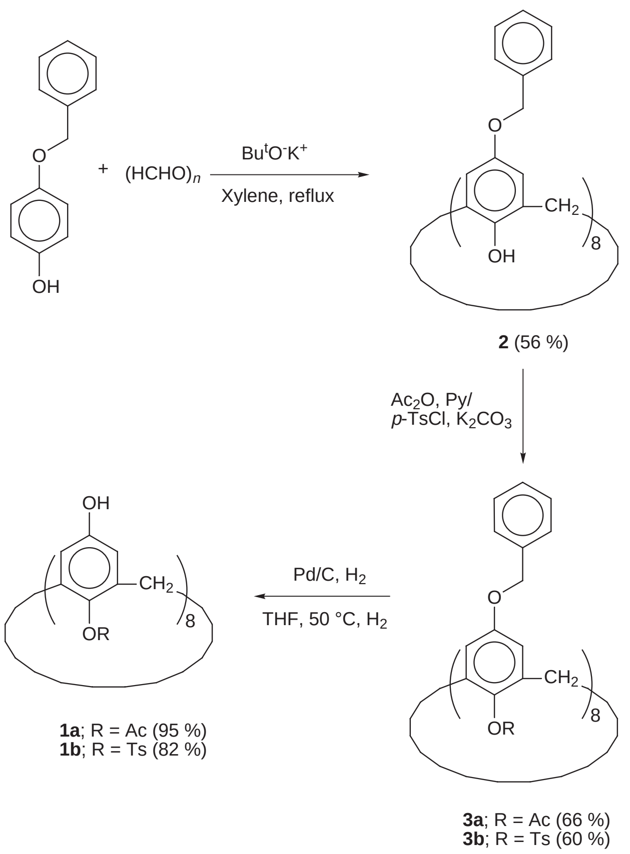
Measurement

Infrared spectra were recorded on a HORIBA FT-210 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL EX 270 spectrometer. UV spectra were obtained on a JASCO V-560 spectrophotometer. Thermal analyses were performed on a Seiko SSS 5200-TG/DTA 220 instrument at a heating rate of 10 °C min^{-1} (TG) and a Seiko SSS 5200-DSC 220 at a heating rate of 20 °C min^{-1} for differential scanning calorimetry (DSC) under nitrogen. Scanning electron micrographs were obtained by a JEOL-5300 microscope.

Results and discussion

Synthesis of mono-substituted hydroquinone calix[8]arenes

Synthesis of mono-substituted hydroquinone calix[8]arenes was carried out as shown in Scheme 1. *p*-(Benzyloxy)-calix[8]arene (**2**) was first prepared by the condensation of *p*-benzyloxyphenol and paraformaldehyde in the presence of a small amount of base. Casnati *et al.* reported that a mixture of six-, seven-, and eight-membered rings was produced by the base-catalyzed condensation and the ratio among the three isomers depended on the bases used in the condensation.[11] We found potassium *tert*-butoxide gave octamer **2** more effectively than sodium hydroxide and potassium hydroxide. Octamer **2** was easily isolated by simple filtration from refluxing acetone and characterized by its ^{1}H NMR spectrum in DMSO-d_6. The acetylation of **2** was performed in refluxing acetic anhydride with a few drops of pyridine and acetylated product **3a** was purified by reprecipitation. The reaction of **2** and toluene-*p*-sulfonyl chloride was carried out in the presence of potassium carbonate in refluxing THF and then excess toluene-*p*-sulfonyl chloride was removed from the mixture of products in a Soxhlet-extraction apparatus with propan-2-ol. Product **3b** after the extraction was pure enough for the next reaction. The structures of **3a** and **3b** were characterized by ^{1}H NMR and IR spectroscopies.



Scheme 1 Synthesis of mono-substituted hydroquinone calix[8]-arene **1**.

The debenzylation of *O*-substituted-*p*-benzyloxyphenol calix[8]arenes with Pd/C under H_2 atmosphere has been reported to be very difficult.[11] However, we successfully obtained debenzylated products, such as mono-acetyl and *p*-tolylsulfonyl hydroquinone calix[8]arenes, **1a** and **1b** by catalytic reaction with Pd/C under H_2. The acetone solution of **1a** was reprecipitated with hexane. Compound **1a** was soluble in highly polar solvents such as acetone and alcohols. On the other hand, **1b** was purified by refluxing in a mixture of methanol and water. The obtained solids were insoluble in methanol, but the solubility of **1b** was recovered by removing the methanol that was included in the calixarene core. The purity of compounds **1a** and **1b** was confirmed by reversed-phase HPLC. In the ^{1}H NMR spectra of **1a** and **1b**, methylene and phenyl protons due to the benzyl groups disappeared in the reactions (Fig. 1). Both ^{1}H NMR spectra of **1a** and **1b** showed a sharp peak around δ 9.2 ppm due to their hydroxy groups. The ^{1}H NMR spectrum of compound **2** exhibited a broad peak at δ 8.7 ppm due to the hydroxy groups on its lower rim. In the case of calix[4]resorcinarene, a sharp peak

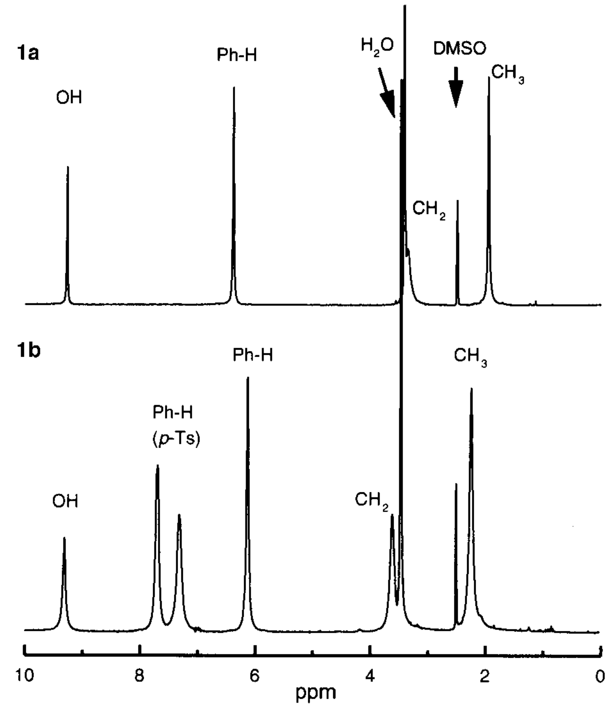


Fig. 1 ^{1}H NMR (270 MHz) spectra of **1a** and **1b** in DMSO-d_6.

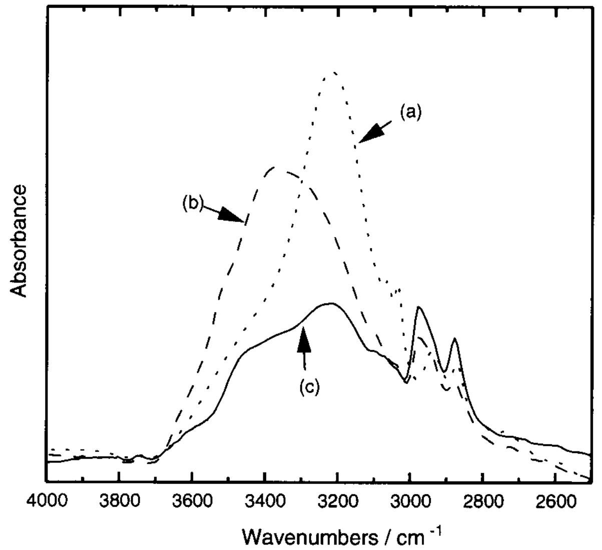


Fig. 2 IR spectra of calixarenes: (a) **2** in a KBr pellet, (b) **1a** and (c) **1b** films cast on a NaCl plate from THF.

was observed at δ 8.6 ppm. In addition, a comparison of the IR spectra of **2**, **1a**, and **1b** is shown in Fig. 2. Compound **2** shows a strong absorption band at 3220 cm^{-1} due to the hydroxy stretching absorption as *p*-*tert*-butyl calix[8]arene and *p*-*tert*-butyl novolac oligomer resin do, indicating that their hydroxy groups readily form intramolecular hydrogen bonds.[12] On the other hand, **1a** exhibits an absorption band at 3360 cm^{-1} due to the intermolecular hydrogen bonds between the hydroxy groups. Two different absorption bands induced by the intramolecular and the intermolecular hydrogen bonds were observed in the IR spectrum of **1b**. These results indicate that simple modification of **2** gives high solubility to the resulting *O*-substituted hydroxyphenol calix[8]arenes **1a** and **1b**. Thus, these compounds are soluble in polar solvents such as alcohols, ethyl acetate, acetone, tetrahydrofuran, 1-acetoxy-2-methoxyethane (PMA) and ethyl lactate (EL), and highly transparent films were easily cast from the solution in PMA or EL.

Thermal properties

The thermal behavior of **1a** and **1b** was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). Compound **1a** shows an initial weight loss below 5% around 200 °C probably due to the vaporization of included solvents and high thermal stability up to 300 °C. On the other hand, **1b** displays a large weight loss around 250 °C. Both DSC curves of **1a** and **1b** showed no endothermic peak due to the melting point being below 200 °C and only **1b** exhibits a glass transition temperature (T_g) at 170 °C on the 2nd heating (Fig. 3). No T_g of **1a**, however, is observed below 200 °C. These results suggest that compound **1b**, having bulky substituents such as toluene-*p*-sulfonate groups, is clearly more amorphous than **1a**.

Lithographic evaluation

The UV spectra of films of compounds **1a** and **1b** (1 µm thick) are shown in Fig. 4. Both films are transparent above 300 nm, indicating that it is possible to use them for i-line (365 nm) lithography. Furthermore, the optical density of the **1a** film is only 0.3 µm^{-1} at 248 nm and it can be used for a wide range of lithography from g-line through KrF eximer laser. On the other hand, **1b** has a strong absorption below 300 nm due to toluene-*p*-sulfonate groups.

Diazonaphthoquinones (DNQs) were chosen as photo-reactive compounds for the new photoresist based on mono-substituted calix[8]arenes **1** because DNQs have been standard photo-reactive compounds for novolac base positive-type photoresists since the 1970s. Calixarenes **1** would be very interesting materials as photoresists if DNQ inhibits their dissolution because DNQ has rarely found a better partner than novolac. We examined whether DNQ acted as a dissolution inhibitor in an aqueous base solution against **1a**. Dissolution inhibition by DNQ was not observed under any conditions because of the low hydrophobicity of the acetate groups. On the other hand, the film of **1b** containing 30 wt% of DNQ showed a dissolution inhibition effect toward a standard alkaline developer, 2.38 wt% aqueous TMAH solution. These results suggest that the hydrophobicity of substituents affects the dissolution of **1**, and the higher hydrophobicity of *p*-tosylate groups is expected to provide **1b** with suitable dissolution properties for the DNQ resist system. After the preliminary experiments, we selected **1b** and 1.5 wt% aqueous TMAH solution as a matrix and a developer, respectively.

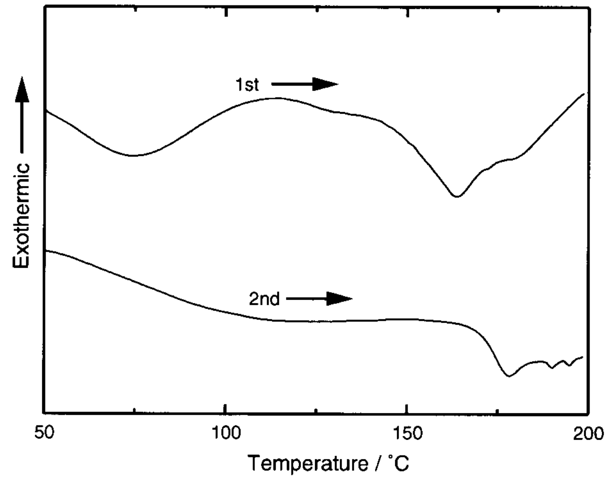


Fig. 3 DSC traces for **1b** at the rate of 20 °C min^{-1} under nitrogen.

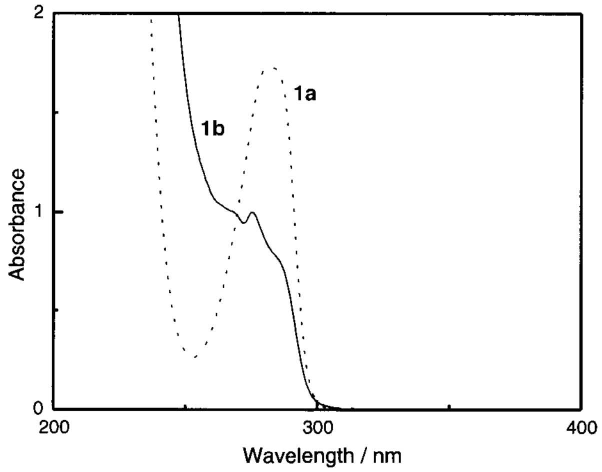
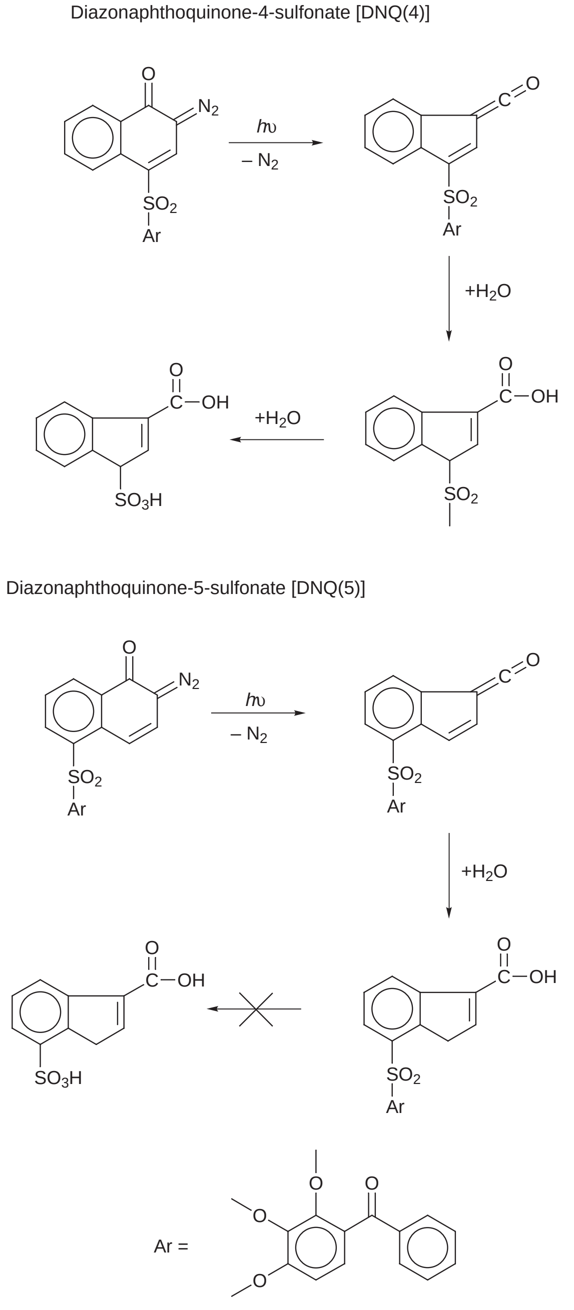


Fig. 4 UV–vis spectra of the **1a** and **1b** films cast on a quartz plate from EL.

2,3,4-Tris[2-diazo-1-oxonaphthalen-4-ylsulfonyloxy]benzophenone [DNQ(4)] and 2,3,4-tris[2-diazo-1-oxonaphthalen-5-ylsulfonyloxy]benzophenone [DNQ(5)] were employed as the photo-reactive compound (Scheme 2). In Fig. 5, the UV–visible spectra of the resist films containing DNQ(4) and DNQ(5) are shown. The typical absorption bands for DNQ(5) are observed at 350 and 400 nm while the absorption bands for DNQ(4) are shifted to 310 and 390 nm. DNQ(5) and DNQ(4) are photochemically transformed to indenecarboxylic acid and 3-sulfoindenecarboxylic acid, respectively.[13] The latter is a stronger acid than the former. Therefore, higher dissolution



Scheme 2 Comparison of the photolysis between DNQ(4) and DNQ(5).

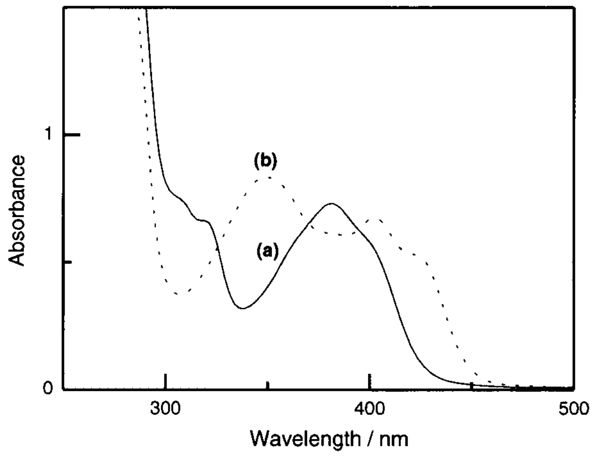


Fig. 5 UV–vis spectra of the resist films containing **1b** with (a) 25 wt% of DNQ(4) and (b) 25 wt% of DNQ(5).

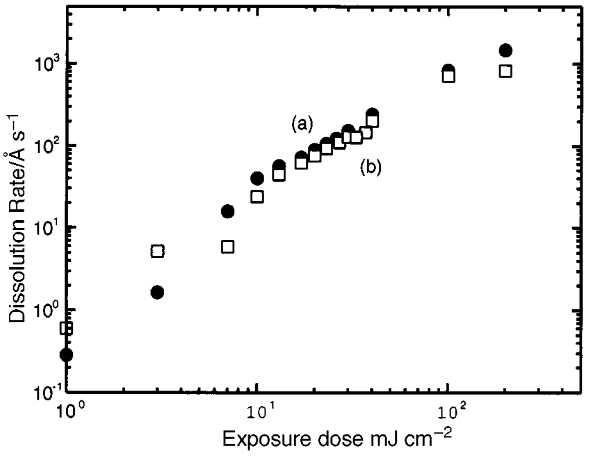


Fig. 6 Photochemical effects on the dissolution rates in 1.5 wt% aqueous TMAH solution of the resist films containing **1b** with (a) 25 wt% of DNQ(4) and (b) 25 wt% of DNQ(5).

acceleration in the resist containing DNQ(4) after UV-irradiation would be expected. We, however, considered both DNQ sulfonates for the new positive-type photoresist with i-line.

The resist was formulated by mixing **1b** and DNQ in ethyl lactate (EL) [4 : 1 : 16 w/w]. The films spin-cast on silicon wafer were prebaked at 100 °C for 90 s. We plotted the correlation between the exposure dose to i-line and the dissolution rate of the exposed part toward 1.5 wt% aqueous TMAH solution (Fig. 6). The dissolution rate of the resist film before UV irradiation (R_0) is reduced to about 10^{-1} Å s^{-1} by the addition of DNQs while that of **1b** film without DNQ is 240 Å s^{-1}. The actual dissolution rates of the resist film containing DNQ(4) and DNQ(5) are 0.28 and 0.60 Å s^{-1}, respectively. These large inhibition effects may be attributed to the interactions between the resist matrix **1b** and DNQs. On the other hand, the dissolution rate of the exposed films (200 mJ cm^{-2})(R_{200}) containing DNQ(4) and DNQ(5) reached 1470 and 820 Å s^{-1}, respectively. These findings indicate that the addition of DNQ(4) is very effective in increasing the dissolution contrast between R_{200} and R_0 by about 5200 times, probably due to strong acid formation. DNQ(5) also demonstrated the high dissolution contrast of over 1000 times.

Thermal treatment after UV exposure, called 'Post Exposure Bake (PEB)' generally improves the resist profile. The effects of the PEB temperature on the dissolution rates of both exposed and unexposed films were investigated, but no large changes were observed up to 120 °C. A higher temperature than 120 °C induces the decomposition of DNQs.

The effect of the DNQ loading on the sensitivity and the contrast was investigated. The film spin-cast on silicon wafer was prebaked at 80 °C for 10 min, exposed to i-line radiation, postbaked at 100 °C for 3 min, and developed in a positive mode with 1.5% aqueous TMAH solution at room temperature. The results are summarized in Table 1. The best sensitivity (D) and contrast (γ) were obtained at a 25% loading of

Table 1 Performance of the resist consisting of **1b** and DNQs

	DNQ(4)		DNQ(5)	
Loading[a] (wt%)	D (mJ cm^{-2})[b]	γ[c]	D (mJ cm^{-2})[b]	γ[c]
20	33	2.1	—	—
25	30	2.8	37	2.5
30	40	2.0	40	2.1

[a] Weight ratio of DNQ against **1b**. [b] Sensitivity estimated with the characteristic curves. [c] Contrast estimated with the characteristic curves.

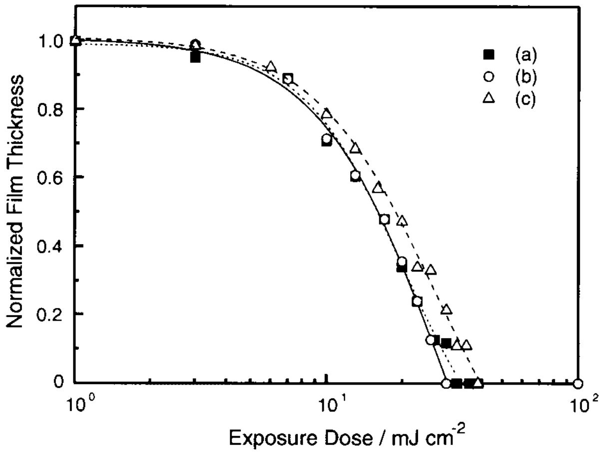


Fig. 7 Characteristic curves of the resist containing **1b**, exposed to i-line: with (a) 20 wt%, (b) 25 wt%, and (c) 30 wt% of DNQ(4).

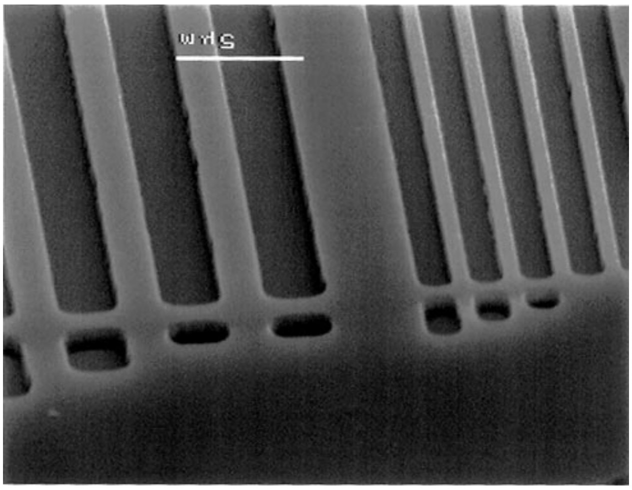


Fig. 8 Scanning electron micrograph of the line and space patterns, indicating 1 μm as a minimum feature size and drawn on the resist film consisting of **1b** and 25 wt% of DNQ(4). PEB at 100 °C for 180 s and development with 1.5 wt% aqueous TMAH solution were applied.

DNQ(4) or (5), they are 30 mJ cm^{-2} and 2.8 for DNQ(4), and 37 mJ cm^{-2} and 2.5 for DNQ(5), respectively. The sensitivity curve for DNQ(4) is also presented in Fig. 7. The typical sensitivity and contrast values of conventional novolac–DNQ(4) resist systems are around 40 mJ cm^{-2} and 3 (γ), respectively. Therefore, the **1b**–DNQ(4) resist system may demonstrate a competitive performance with them.

Fig. 8 presents a scanning electron micrograph of the contact-printed images that were obtained using the resist described above after exposure to 40 mJ cm^{-2} and PEB at 100 °C for 3 min, followed by developing with 1.5% aqueous TMAH solution for 40 s at room temperature. A high resolution positive image featuring 1 μm line and space patterns, which is the limitation of our exposure system, was obtained on the 0.9 μm thick film.

Conclusions

We have successfully designed a new monodisperse compound as a matrix for photoresist, that is, the new positive working photoresist was formulated by mixing *p*-tolylsulfonyl hydroquinone calix[8]arene **1b** and DNQ(4) or (5) as the dissolution inhibitor, and it was found to be an alkaline-developable positive type resist. The new resist consisting of **1b** and 25 wt% loading of DNQ(4) showed a sensitivity of 30 mJ cm^{-2} and contrast of 2.8. Fine images were also available on the resist film by exposure to i-line through a mask. Some calixarenes are potentially transparent around 250 nm wavelength, therefore they are expected to be useful for KrF eximer-laser lithography.

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