

RAPID COMMUNICATION

Photoinduced refractive-index change in 4-*tert*-butylcalix[8]arenes bearing *N*-acyloxyphenylamide chromophores

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Photochemistry has continued to contribute to the development of various types of optoelectronics materials, such as optical fibers, microlenses, optical memories, switching devices, optical waveguides, liquid-crystal-display components and polymer light-emitting diodes.^{1–3} In particular, significant attention has been devoted to the photochemical control of refractive indices of polymer films, owing to their potential use in optical network technology.³ Extensive studies have been conducted on the photoinduced decrease in refractive indices of polymer films,^{4–8} whereas only a few attempts have been made to enhance the refractive index through photochemical transformations.^{9–11} The photo-Fries rearrangement in polymers bearing aromatic ester pendants causes a large increase in refractive indices of these polymer films.^{12–15} The refractive-index changes described above appear to be of sufficient magnitude to utilize these polymers as optical materials. To develop more sophisticated optical materials, it is necessary to precisely control the molecular weights of the above polymers containing covalently bound chromophores, because many polymers exist as a mixture with different chain lengths, thus making it difficult to quantitatively discuss their photoreactivity and optical properties on the basis of those of the corresponding monomer units.

Chemical modification of the phenolic oxygen in 4-*tert*-butylcalixarenes has attracted significant attention owing to the enhanced ability of modified calixarenes to recognize ions, molecules and even biomolecules.¹⁶ In addition to the facile introduction of various functional groups at this reactive oxygen, the film-forming property of the calixarene derivatives with a rigid frame-

work makes them interesting candidates for refractive-index materials. 4-*tert*-Butylcalixarene derivatives have two advantages over polymer systems. One is that their molecular weights are uniform. The other is that they exhibit reactivity very similar to that of the corresponding 4-*tert*-butylphenol structural units.^{16,17} The former advantage makes it possible to quantitatively discuss a correlation between the molecular weight or ring size of 4-*tert*-butylcalix[*n*]arenes and the refractive-index change in these calixarene films. The latter advantage implies that selectivity for a specific reaction in the calixarene supramolecular systems can be estimated from that in their corresponding structural units. Thus, it is possible to establish a relationship between the selectivity of the photo-Fries rearrangement and the magnitude of the photoinduced refractive-index change in 4-*tert*-butylcalixarene films. To this end, we synthesized *O*-(4-acyloxyanilino-carbonylmethyl)-4-*tert*-butylphenols (R = Ph: **1a** and R = Me: **1b**) and *O*-(4-acyloxyanilino-carbonylmethyl)-4-*tert*-butylcalix[8]arenes (R = Ph: **1c** and R = Me: **1d**) and discovered not only a photochemical change in the refractive index of the

calixarene film but also a relationship between the selectivity of the photo-Fries rearrangement and the magnitude of this refractive-index change (Figure 1).

Substituted 4-*tert*-butylcalix[8]arenes **1c** and **1d** were prepared according to the standard procedures shown in Scheme 1. *O*-Alkylation of 4-*tert*-butylcalix[8]arene with ethyl bromoacetate in dry 1-methyl-2-pyrrolidone followed by alkaline hydrolysis of the resulting ester derivative in aqueous ethanol yielded the corresponding carboxylic acid. The reaction of the acid derivative with thionyl chloride resulted in a highly reactive acid chloride, which, in turn, was coupled with 4-benzyloxyaniline in dry *N,N*-dimethylformamide (DMF) to produce the amide conjugate. Catalytic debenzoylation of this conjugate in tetrahydrofuran (THF) followed by the acylation of the deprotected phenolic hydroxyl group formed 4-*tert*-butylcalix[8]arenes **1c** and **1d** substituted with eight 4-acyloxyanilino-carbonyl chromophores. Procedures similar to those given in Scheme 1 were applied to the synthesis of the reference 4-*tert*-butylphenol derivatives **1a** and **1b** using 4-*tert*-butylphenol as a starting material.

Matrix-assisted laser desorption/ionization-time of flight mass spectral analysis of

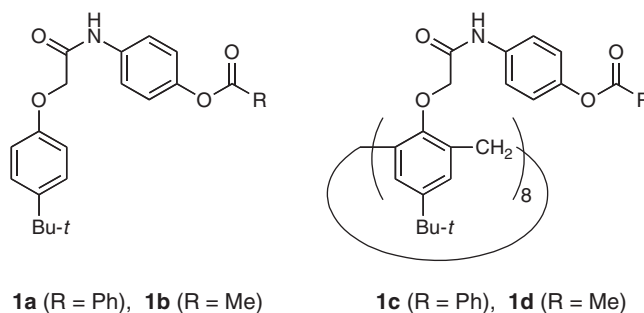
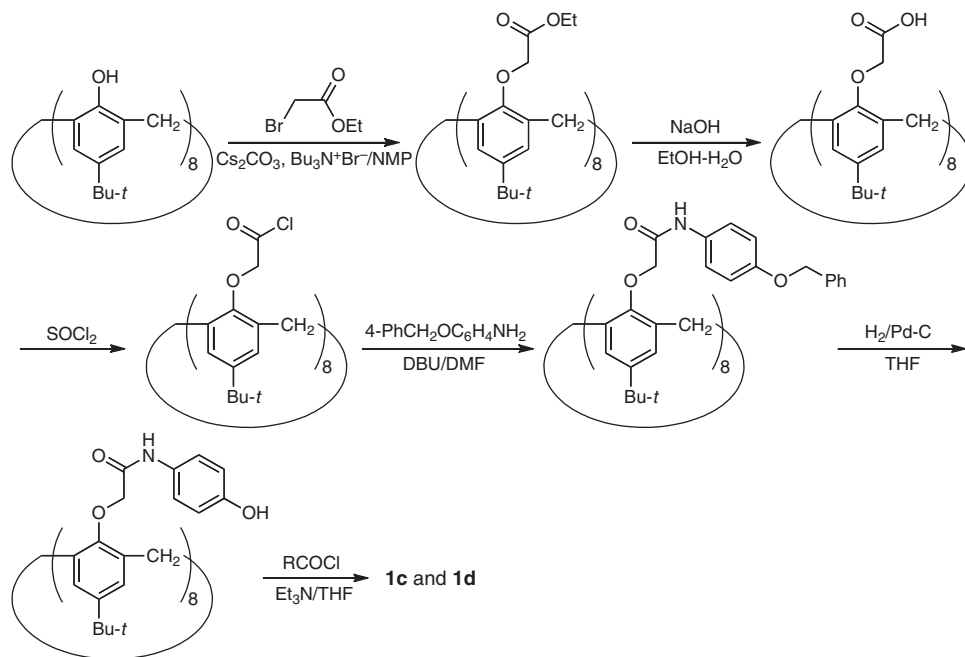


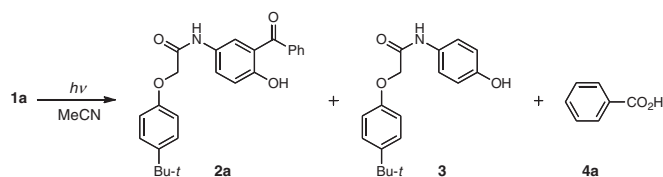
Figure 1 Structures of **1a–d**.



Scheme 1 Synthetic route to the 4-*tert*-butylcalix[8]arene derivatives **1c** and **1d**.

1a–d provided evidence in support of these structures (MALDI TOF mass spectral data for **1a–d**. **1a** (m/z calculated for $C_{25}H_{25}NNaO_4$ $[M + Na]^+$: 426.18. Found: 426.24). **1b** (m/z calculated for $C_{20}H_{23}NNaO_4$ $[M + Na]^+$: 364.16. Found: 364.16). **1c** (m/z calculated for $C_{208}H_{200}N_8NaO_{32}$ $[M + Na]^+$: 3344.52. Found: 3344.85). **1d** (m/z calculated for $C_{168}H_{184}N_8NaO_{32}$ $[M + Na]^+$: 2848.44. Found: 2848.11)). The calix[8]arene **1c** or **1d** film (film thickness $\approx 0.1 \mu\text{m}$) was prepared by spin coating a THF-10 vol% CHCl_3 solution of each derivative onto a silica glass for ultraviolet (UV) spectral analysis or on a silicon wafer for refractive-index analysis. The poly(methyl methacrylate) (PMMA) film containing 30 wt% **1a** or **1b** was prepared in the same way as above, except for the presence of PMMA. The refractive indices of the above films were determined by spectroscopic ellipsometry (He-Ne laser beam, wavelength 632.8 nm) before and after irradiation.^{6–15}

When a nitrogen-saturated MeCN solution of **1a** ($[\mathbf{1a}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ for UV absorption and ^1H NMR spectral measurements; $[\mathbf{1a}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ for product isolation) was irradiated for 60 min with 254-nm UV light from a 95-W low-pressure Hg lamp at room temperature, a new and intense absorption band characteristic of the photo-Fries rearranged product appeared at 365 nm. After completion of the reaction, thin-layer silica-gel chromatography



Scheme 2 Product distribution obtained from the photoinduced reaction of **1a** in acetonitrile at room temperature.

Table 1 Acyl substituent effects on the photoreactivity of the reference compound **1** and the selectivity of the photo-Fries rearranged product **2**

Compound	Irradiation time (min)	Conversion (%)	Composition (%)			Selectivity of 2 (%)
			1	2	3	
1a	0	0	100	0	0	
	10	46	54	37	9	80
	30	74	26	60	14	81
	60	100	0	81	19	81
1b	0	0	100	0	0	
	30	35	65	26	9	75
	60	73	27	55	18	75
	90	92	8	69	23	75

of the reaction mixture allowed us to isolate the photo-Fries rearranged product *O*-(2-benzoyl-4-hydroxyanilino)carbonylmethyl)-4-*tert*-butylphenol (**2a**) and the fragmentation product *O*-(4-hydroxyanilino)carbonylmethyl)-4-*tert*-butylphenol (**3**). The careful ^1H NMR spectral analysis of this reaction

mixture revealed that **3** and benzoic acid (**4a**) were formed in a nearly 1:1 mole ratio (Scheme 2).

Furthermore, the finding that the ^1H NMR spectrum recorded after completion of the reaction can be explained in terms of overlapping of the spectra of **2a**, **3** and **4a**, the

secondary reaction of which was only very minor under the irradiation conditions, enabled us to trace the photo-Fries reaction by means of ^1H NMR spectroscopy. According to the same procedures as those described above, we could isolate the **1b**-derived photo-Fries rearranged product **2b** in addition to **3** but could not detect additional signals for the acetyl group-derived fragmentation product(s) in the ^1H NMR spectrum. An inspection of the composition of **1**–**3** summarized in Table 1 confirmed that the photo-Fries rearrangement of **1** in solution proceeds with high selectivity. Contrary to our expectation, replacing the benzoyl group in **1a** with an acetyl group (**1b**) lowered not only the photoreactivity (conversion) of **1a** but also the selectivity of the Fries-rearranged product **2a** (81 \rightarrow 75%).

The photo-Fries rearrangement occurs by a radical-pair mechanism, in which a photochemically generated radical pair recombines in competition with its diffusional separation to form the rearrangement products.¹⁸ Thus, we expected that the rigid polymer medium would suppress the diffusive motion of paired radicals from the solvent cage to cause a more efficient recombination of these caged radicals; that is, to cause an increase in the composition of the Fries-rearranged product in comparison with the liquid medium. As shown in Figure 2, irradiation of the PMMA film doped with 30 wt% **1a** by 254-nm UV light induced clear changes in the absorption spectrum: the **2a**-derived 365-nm absorption increased with a decrease in the 230-nm absorption.

As the absorbance of **4a** at 270 nm was not negligible, as compared with that of **2a** and **3** at this wavelength, mixtures of **2a** with **3** and **4a** (the mole ratio of which is 1:1) in various proportions were prepared, and the ratio of absorbances at 365 and 270 nm (A_{365}/A_{270}) was estimated for each mixture. A calibration curve was obtained by plotting the fraction of **2a** against the A_{365}/A_{270} ratio for each mixture. The selectivity of the Fries-rearranged product in the PMMA film was determined to be 93% using the calibration curve. Increased selectivity for this product (81 \rightarrow 93%) was consistent with our expectation, thus rendering the glassy film as an excellent medium for enhancing the selectivity of the photo-Fries rearrangement. However, photoinduced acetyl migration in the PMMA film doped with 30 wt% **1b** only slightly increased the selectivity of this rearrangement (75 \rightarrow 77%). The rigid polymer medium might exert its negligible effect on the diffusive motion of the acetyl radical with a less bulkiness than the benzoyl. On the

other hand, we were able to make transparent calix[8]arene thin films by spin coating THF–10 vol% CHCl_3 solutions of **1c** and **1d**. In addition, UV absorption spectral changes very similar to those for the PMMA film were observed when the calixarene films were irradiated under the same conditions. Surface states of the calixarene and PMMA films observed before and after irradiation showed that both the films maintained transparent

and homogeneous states during irradiation. The A_{365}/A_{270} ratio obtained after the 60-min irradiation of the calixarene film prepared from **1c** allowed us to estimate the selectivity of the photo-Fries rearrangement as 95%.

Next, we directed our attention to the refractive-index changes caused by the irradiation of the calixarene films prepared from **1c** and **1d**. Figure 3 shows the refractive-index changes of these films, which are

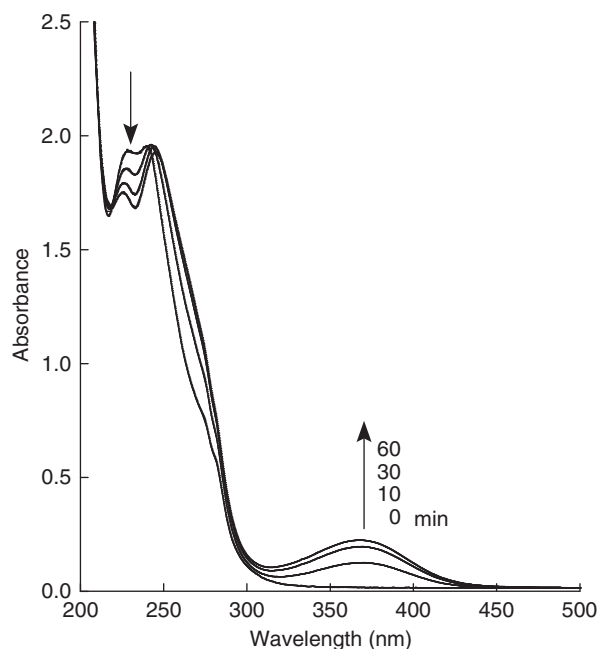


Figure 2 Ultraviolet (UV) absorption spectral changes caused by irradiation of the poly(methyl methacrylate) film doped with **1a** (30 wt%) and prepared on silica glass by 254-nm UV light at room temperature.

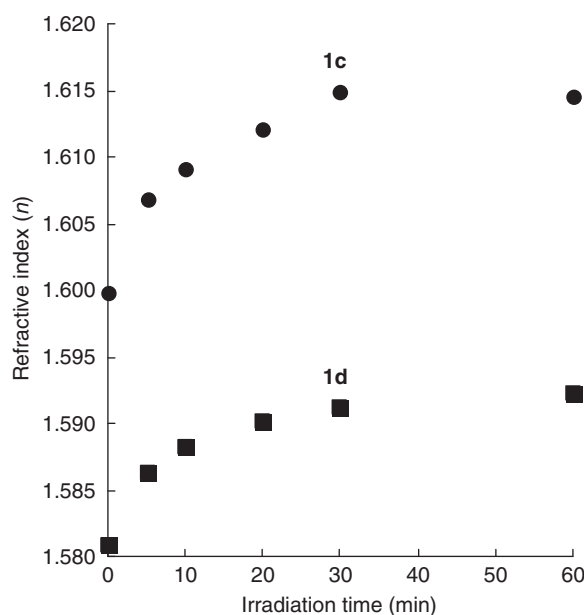


Figure 3 Refractive index of the calix[8]arene films prepared from **1c** and **1d** on Si wafers as a function of irradiation time.

caused by irradiation with 254-nm UV light. The plots depicted in this figure reveal that the refractive index at 632.8 nm increased with irradiation time, and a relatively large refractive-index change of $\Delta n = +0.015$ (film-thickness change = -3%) was achieved after 60-min irradiation of the **1c** film, whereas the **1d** film induced $\Delta n = +0.011$ (film-thickness change = -4%) under the same irradiation conditions. As already described, both the lower photoreactivity of **1b** than that of **1a** and the lower selectivity of **2b** than that of **2a** are considered to be responsible for the smaller refractive-index change in the calixarene **1d** film. A comparison of photochemical behavior in our calixarene film and Griesser group's polymer film revealed that the photoreaction in the former film afforded the photo-Fries rearranged product in a larger yield but induced a smaller increase in the film refractive index. This may be largely due to a difference in the number density of the migratory group.¹⁵

In conclusion, we demonstrated that a 4-*tert*-butylcalix[8]arene derivative bearing eight *N*-(4-acyloxyphenyl)amide chromophores has excellent film-forming ability, and its highly selective photo-Fries rearrangement occurs in the film state. Moreover, we observed a relatively large change in the refractive index of the calixarene **1c** film ($\Delta n = +0.015$) when this film was irradiated for 60 min by 254-nm UV light. It is thus expected that in addition to the high thermal stability of the calixarene derivative **1c**, the irreversibility of the photo-Fries reaction of this derivative that affords thermally and photochemically inert products enables a

precise control of the refractive-index change in the calixarene **1c** film.

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